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Boosting the Performance of Electrocatalytic NO Reduction to NH$_3$ by Decorating WS$_2$ with Single Transition Metal Atoms: A DFT Study

Mamutjan Tursun [1,*], Ayxamgul Abduryim [1] and Chao Wu [2,*]

[1] Xinjiang Key Laboratory of Novel Functional Materials Chemistry, College of Chemistry and Environmental Sciences, Kashi University, Kashi 844000, China; 18709981047@163.com
[2] Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an 710054, China
* Correspondence: mmtj15@stu.xjtu.edu.cn (M.T.); chaowu@xjtu.edu.cn (C.W.)

Abstract: Ammonia (NH$_3$) is a crucial feedstock in chemical manufacturing. The electrocatalytic NO reduction reaction (eNORR) to NH$_3$ represents a promising alternative method for the green production of NH$_3$ and for environmental management. This study presents a comprehensive investigation of eNORR properties of single transition metal atoms deposited on WS$_2$ nanosheets (TM@WS$_2$). Our results indicate that 19 single TM atoms exhibit strong thermal stability. Among these, five specific TM@WS$_2$ catalysts—Ti, Mn, Co, Zr, and Hf—demonstrate remarkable eNORR activity, with limiting potentials of 0, −0.19, −0.26, 0, and −0.15 V, respectively. These catalysts effectively suppress the formation of byproducts (N$_2$O/N$_2$) and the hydrogen evolution reaction (HER), thereby ensuring high NH$_3$ selectivity. Our theoretical study confirms that TM@WS$_2$ catalysts are highly promising for achieving high activity, selectivity, and stability in eNORR, providing valuable insights for future experimental investigations into efficient NH$_3$ production.

Keywords: nitric oxide electrocatalytic reduction; NH$_3$ synthesis; WS$_2$ monolayer; density functional theory

1. Introduction

Ammonia (NH$_3$) serves as a crucial chemical compound not only for the production of fertilizers, pharmaceuticals, and dyes, but also as a significant carrier of carbon-free energy [1–3]. Moreover, given its high hydrogen content (17.6 wt%) and its ability to easily condense into a liquid state, NH$_3$ is considered an ideal medium for hydrogen energy storage [1,4]. As a result, the synthesis of NH$_3$ is of great importance and has garnered widespread attention. Traditionally, the large-scale production of ammonia relies on the Haber–Bosch process, which necessitates extremely high temperatures (400–500 °C) and significant pressures (200–250 bar). However, this widely used process has significant drawbacks, as it depends on fossil fuel combustion and results in the emission of the greenhouse gas CO$_2$ (accounting for approximately 3% of global CO$_2$ emissions annually) [2,5]. The method of electrocatalytic ammonia synthesis has garnered widespread attention and thorough research as a viable alternative [2,6]. This method operates at room temperature and can utilize electric energy derived from solar or wind power [6]. Therefore, electrocatalytic NH$_3$ synthesis is viewed as an environmentally friendly and flexible technique, with nitrogen (N$_2$) or nitrogen oxides, such as nitrate (NO$_3^-$) and nitric oxide (NO) serving as its feedstocks [6–17].

Despite over a decade of research, the electrocatalytic nitrogen reduction reaction (eNRR) has not yet reached practical implementation, mainly attributed to its insufficient

NH$_3$ yield and poor Faradaic efficiency. The challenges arise from the robust nature of the N≡N triple bond, which has a bond energy of 914 kJ/mol and makes nitrogen molecules highly unreactive. Additionally, the eNRR faces issues with poor selectivity, as it often competes unfavorably with the hydrogen evolution reaction (HER) [12]. Consequently, there remains an urgent need and significant opportunity to develop exceptionally efficient and specific electrocatalysts to facilitate efficient NH$_3$ synthesis.

In addition, flue gases from thermal power plants and industrial boilers typically contain high levels of NO$_x$, with NO accounting for approximately 95% of these emissions. The significant presence of NO in flue gases poses a serious threat to both the environment and human health [18,19]. Therefore, electrocatalytic NO reduction (eNORR) offers a dual benefit by not only producing valuable NH$_3$ but also effectively cleaning the flue gases.

To date, numerous types of catalysts have been investigated for the eNORR [20–34]. Noble metal catalysts, in particular, have garnered significant interest due to their intrinsic properties. However, their application is often limited by insufficient activity or prohibitive cost [21,26,27]. In addition to noble metals, transition metal-based composites have also been investigated as potential catalysts for eNORR [20,23–25]. Despite these efforts, the durability and selectivity of these catalysts have not yet reached the desired standards. At present, the primary obstacle in the realm of eNORR is to develop catalysts that simultaneously exhibit high activity, excellent durability, and cost-effectiveness.

Single-atom catalysts (SACs) have emerged as promising candidates for the eNORR due to their exceptional atom utilization efficiency and unique geometric and electronic properties [32–34]. To date, many substrates are used as single-atom catalysts in eNORR, such as graphene [28–31,33], transition metal dichalgonides (TMDs) [32,35–37], metal mxides [38], carbides (including metal and non-metal carbides) [39–41], nitrides (including metal and non-metal nitrides) [42–46], and others [47–51]. However, the inherently high surface energy of single atoms on these substrates tends to drive metal atoms to aggregate into clusters, which, in turn, impedes the formation of highly dispersed single atoms [36–38]. To overcome this challenge, it is crucial to pinpoint the optimal substrates that can firmly immobilize and stabilize the single atoms. Recent research has demonstrated that vacancies in support materials can act as efficient binding sites for individual metal atoms, effectively inhibiting their nucleation and aggregation [22,38–40].

WS$_2$ is an ideal substrate, owing to it is particularly prone to the formation of sulfur vacancies, which provide effective sites for the deposition of single metal atoms [52–54]. Experimental studies have shown that loading Fe, Co, Ni, and Cu atoms on WS$_2$ at concentrations up to 10% does not induce nucleation [53]. Inspired by these findings, we have designed a WS$_2$ nanosheet with a single sulfur vacancy modified by transition metal (TM) atoms, which can serve as highly efficient single-atom catalysts (SACs) for the eNORR.

In this study, we employed DFT calculations to evaluate the electrocatalytic nitric oxide reduction reaction (eNORR) performance of 27 TM single-atom catalysts deposited on WS$_2$ (denoted as TM@WS$_2$, where TM includes atoms from the 3 d to 5 d periods). First, we assessed the thermal stability of these catalysts by calculating their binding energies. Subsequently, we evaluated their practical viability by comparing the binding energies of synthesized TM@WS$_2$ catalysts. After identifying the stable and viable candidates, we examined their ability to adsorb and activate NO. We further explored the eNORR mechanisms leading to NH$_3$ production and evaluated their catalytic performance in competing reactions, such as the formation of N$_2$O or N$_2$ and the hydrogen evolution reaction (HER). Finally, we elucidated the origin of activity for the promising eNORR candidates through detailed electronic structure analysis.

2. Materials and Methods

We conducted spin-polarized periodic density functional theory (DFT) calculations using the Vienna ab initio simulation package (VASP version 5.4.4) [55]. The electron exchange and correlation effects were described using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [56]. The projector augmented wave (PAW) method was applied, and a plane-wave cutoff energy of 450 eV was set [57]. To incorporate van der Waals interactions between adsorbates and substrates, the DFT-D3 correction was employed [58]. A $4 \times 4 \times 1$ supercell was created, and a 15 Å vacuum layer was introduced to reduce interactions between WS_2 nanosheets and their periodic images. The k-point grid of $4 \times 4 \times 1$ was used for Brillouin zone sampling [58]. All atoms were allowed to relax freely without any constraints, and the calculations were converged to an energy tolerance of 10^{-4} eV and a residual force tolerance of 0.02 eV Å^{-1}. The binding energies (E_b) of TM on WS_2 were calculated using the following formula [59,60]:

$$E_b = E_{TM@WS_2} - E_{defective\text{-}WS_2} + \mu_{TM} \tag{1}$$

Here, $E_{TM@WS2}$ signifies the total energy of the transition metal (TM) atoms deposed on WS_2, while $E_{defective\text{-}WS2}$ refers to the total energy of WS_2 with a single sulfur vacancy. μ_{TM} denotes the chemical potential of the TM atoms. The Gibbs free energy (ΔG) for each step of eNORR was determined using the following equation [33,34]:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} \tag{2}$$

In this equation, ΔE denotes the energy difference between the two intermediates involved in each elementary reaction step. This value can be directly obtained from the DFT results. ΔE_{ZPE} and ΔS represent the changes in zero-point energy and entropy, respectively, at room temperature (T = 298.15 K). These values were calculated using vibrational frequencies through the VASPKIT program [61]. The ΔG correction for pH (ΔG_{pH}) was determined by:

$$\Delta G_{pH} = k_B T \times pH \times \ln 10 \tag{3}$$

In this case, the pH was fixed at 0. The influence of the solvent (water) on the ΔG was assessed via implicit solvent model, which is integrated within the VASP computational framework [62].

The limiting potential (U_L) acts as an activity indicator, representing the minimum electrical potential required to make the ΔG of all elementary steps in the reaction exothermic (i.e., to ensure that ΔG decreases for each step). It is calculated using the following equation [33,34]:

$$U_L = -\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \ldots, \Delta G_i)/e \tag{4}$$

In this equation, ΔG_i is the free energy variation corresponding to each specific intermediate step within the overall eNORR process.

3. Results

3.1. Stability of TM@WS$_2$

The specific TM@WS_2 model under investigation is depicted in Figure 1a. In order to assess the stability and experimental viability of the TM@WS_2 catalysts, we first calculated their binding energies (E_b). The E_b values of several synthesized TM@WS_2 catalysts (where TM represents Fe, Co, and Cu) were used as reference values to estimate the stability of other catalysts [53]. Given these values, an E_b of 0.84 eV can be used as a preliminary

benchmark to evaluate the stability of other unsynthesized TM@WS$_2$ catalysts. Figure 1 also shows that, among the 27 TM@WS$_2$ catalysts examined, 11 metal atoms —specifically, V, Cr, Nb, Mo, Tc, Ru, Ta, W, Re, Os, and Ir—exhibit E$_b$ values greater than 0.84 eV, suggesting that they are considered unstable; these have been excluded from further analysis. Conversely, the remaining 16 TM atoms, which possess E$_b$ values below 0.84 eV, are deemed more probable candidates for stable TM@WS$_2$ catalysts.
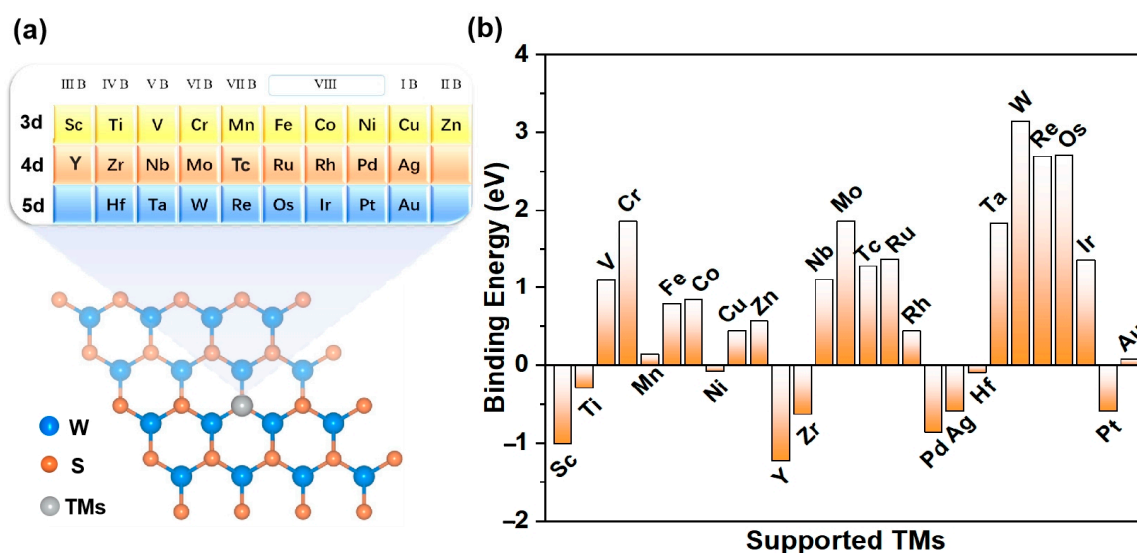

Figure 1. (**a**) The modeled structure of TM@WS$_2$ catalysts; (**b**) E$_b$ values of TM@WS$_2$ catalysts.

In order to conduct a more comprehensive evaluation of the thermodynamic stability of the 16 transition metal (TM) atoms on the WS$_2$ surface, we chose the Zn@WS$_2$ catalyst as a representative case for performing ab initio molecular dynamics (AIMD) simulations. This selection was based on the fact that the binding energy (E$_b$) of Zn@WS$_2$ is 0.56 eV, which is above 0 eV. The AIMD results are presented in Figure S1. Upon reaching a stable state at 500 K, the Zn@WS$_2$ catalyst exhibited no substantial structural distortions or displacements of the Zn atom, thereby confirming its robust thermodynamic stability.

By calculating the electron localization function (ELF), we further reveal the bonding characteristics and stability. The closer the ELF value is to 1, the higher the density of covalent bonds and lone pairs of electrons. As shown in Figure 2, there is a high electron distribution between the metal atoms and sulfur atoms (S), indicating that the TM-S bond is a stable covalent bond. Therefore, the TM@WS$_2$ catalysts possess good thermodynamic stability.
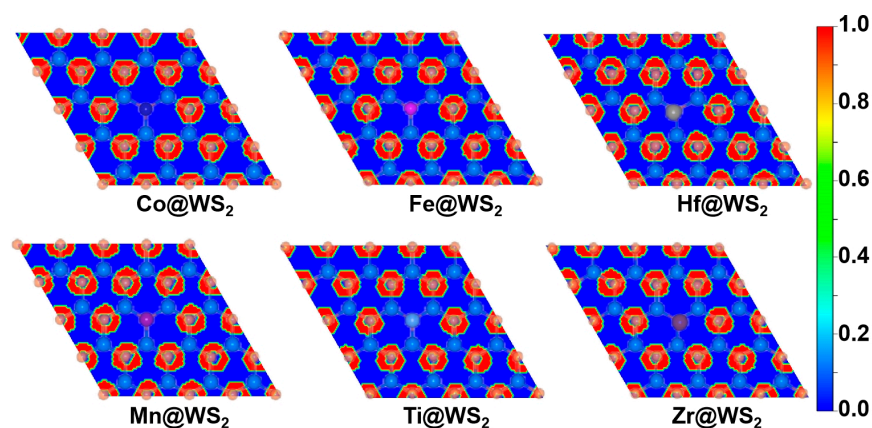

Figure 2. Electron localization function (ELF) plots of TM@WS$_2$ catalysts.

3.2. NO Adsorption

NO adsorption and activation are the first steps in eNORR and play a crucial role in the subsequent reaction [32]. There are three different adsorption configurations of the NO molecule: N-end, O-end, and NO-side (as shown in Figure 3). Among the 16 TM@WS$_2$ catalysts screened, the N-end adsorption configuration exhibited the most negative adsorption energy compared to the other configurations (Table S1), indicating that it is the most stable configuration. Notably, the NO-side configuration was unstable and spontaneously converted to the N-end configuration on several TM@WS$_2$ catalysts, including Co@WS$_2$, Ni@WS$_2$, Cu@WS$_2$, Zn@WS$_2$, Rh@WS$_2$, Pd@WS$_2$, Ag@WS$_2$, Pt@WS$_2$, and Au@WS$_2$. Therefore, our focus is primarily on the N-end configuration.
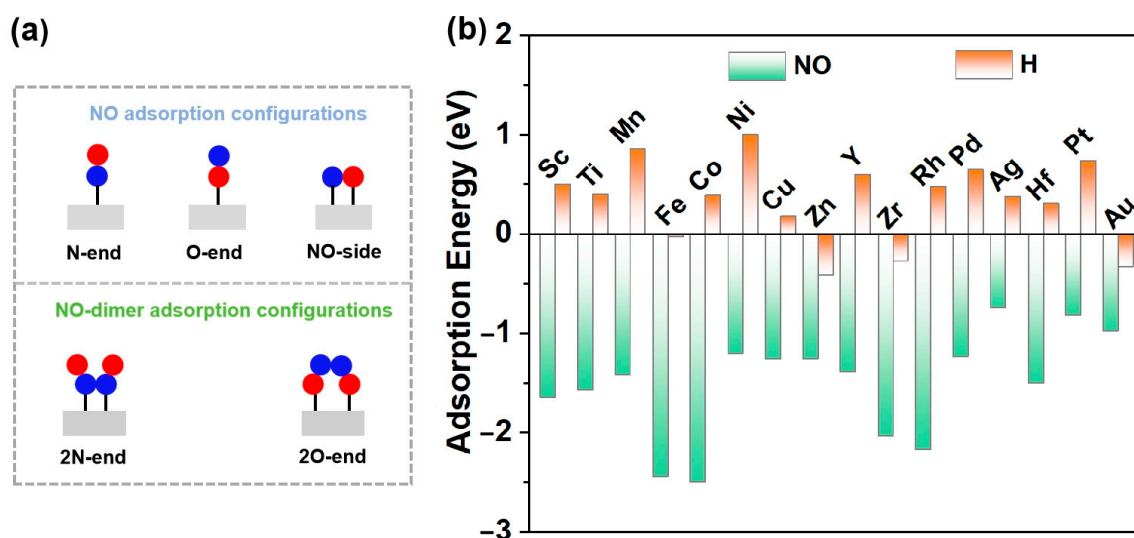

Figure 3. (**a**) Possible NO adsorption configurations both high and low NO concentration; (**b**) NO and H adsorption over 19 TM@WS$_2$ catalysts.

In an aqueous environment, the hydrogen evolution reaction (HER) emerges as a predominant competing process. In the first step, the reactants (here NO and H) are adsorbed on to the catalysts to initiate the reaction. This competition determines whether eNORR or HER is prioritized. Therefore, following a similar approach, we undertook a comparative analysis of the adsorption energies of of H and NO on 16 catalysts. As shown in Figure 3b, NO adsorption is significantly stronger than H adsorption across all 16 catalysts. This indicates that H adsorption is hindered, thereby favoring eNORR over HER.

3.3. eNORR Mechanism and Evaluation of Activity

The eNORR reaction involves multiple reaction pathways (see Figure 4). The selectivity of the eNORR process is significantly influenced by NO concentration. At low NO concentrations, NH$_3$ serves as the final product (as shown in Figure 4a), while at high NO concentrations, N$_2$ and N$_2$O are formed due to dimerization of NO (N$_2$O$_2$). In this scenario, since NH$_3$ is the target product, a series of distinct pathways are followed and each pathway involves five protonation steps to yield NH$_3$. At high NO concentrations, multiple two-pathway branches emerge, with N$_2$ and N$_2$O being formed through dimerization [26].
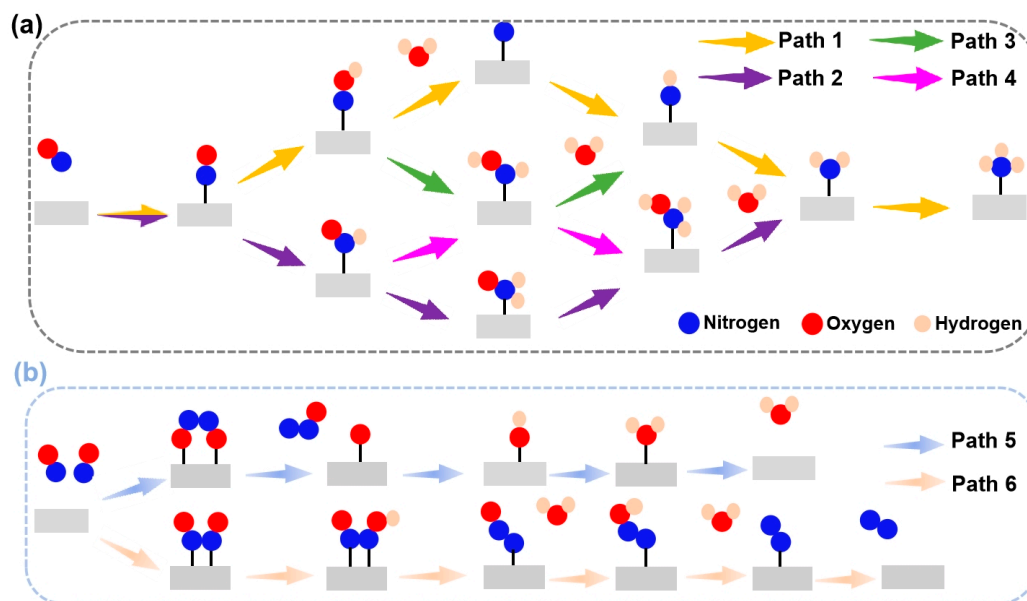
Figure 4. Schematic depiction of the probable reaction pathways for the eNORR. (**a**) Pathways of NO reduction to NH_3; (**b**) Pathways of NO reduction to N_2/N_2O.

The potential and efficiency of the eNORR reaction is typically evaluated based on its potential determination step (PDS), which is marked by the most substantial increase in Gibbs free energy change (ΔG) along the reaction pathway. In this context, processes such as the initial protonation of *NO to form *NOH or *NHO, and the protonation of *NONO to yield *NONOH, are commonly considered as the PDS [63]. To further evaluate the catalytic activity and product selectivity of the 16 catalysts, the ΔG values for the initial hydrogenation steps were calculated, specifically for the pathways from *NO→*NOH (*NO→*NHO) to NH_3 and from *NONO→*NONOH to N_2. As illustrated in Figure 5, for the Ti@WS$_2$, Mn@WS$_2$, Fe@WS$_2$, Co@WS$_2$, Zr@WS$_2$, and Hf@WS$_2$ catalysts, the ΔG values of PDS for the *NO→*NOH or *NO→*NHO steps are lower than those for the *NONO→*NONOH step, indicating that these six catalysts preferentially form NH_3, making them potential candidate catalysts.
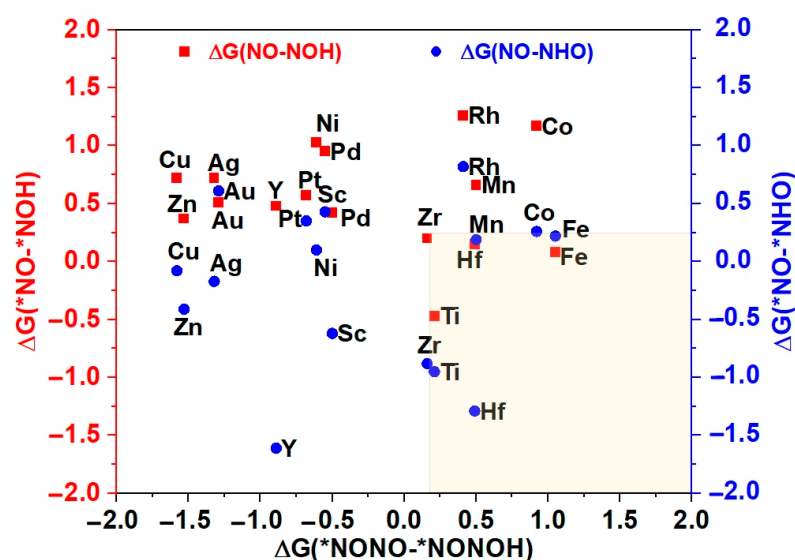

Figure 5. The Gibbs free energy differences of first protonation steps for NH_3 vs. N_2. * represents the adsorption states of reaction species.

We then subsequently evaluated the eNORR activity of Ti@WS$_2$, Mn@WS$_2$, Fe@WS$_2$, Co@WS$_2$, Zr@WS$_2$, and Hf@WS$_2$ catalysts for NH$_3$ synthesis. The eNORR free energy profiles for each reaction pathway of these six catalysts were constructed and are shown in Figure 6a–f. The potential determining step (PDS) for each pathway was identified and labelled, providing a clear indication of the most favorable reaction pathway and associated potential barriers.
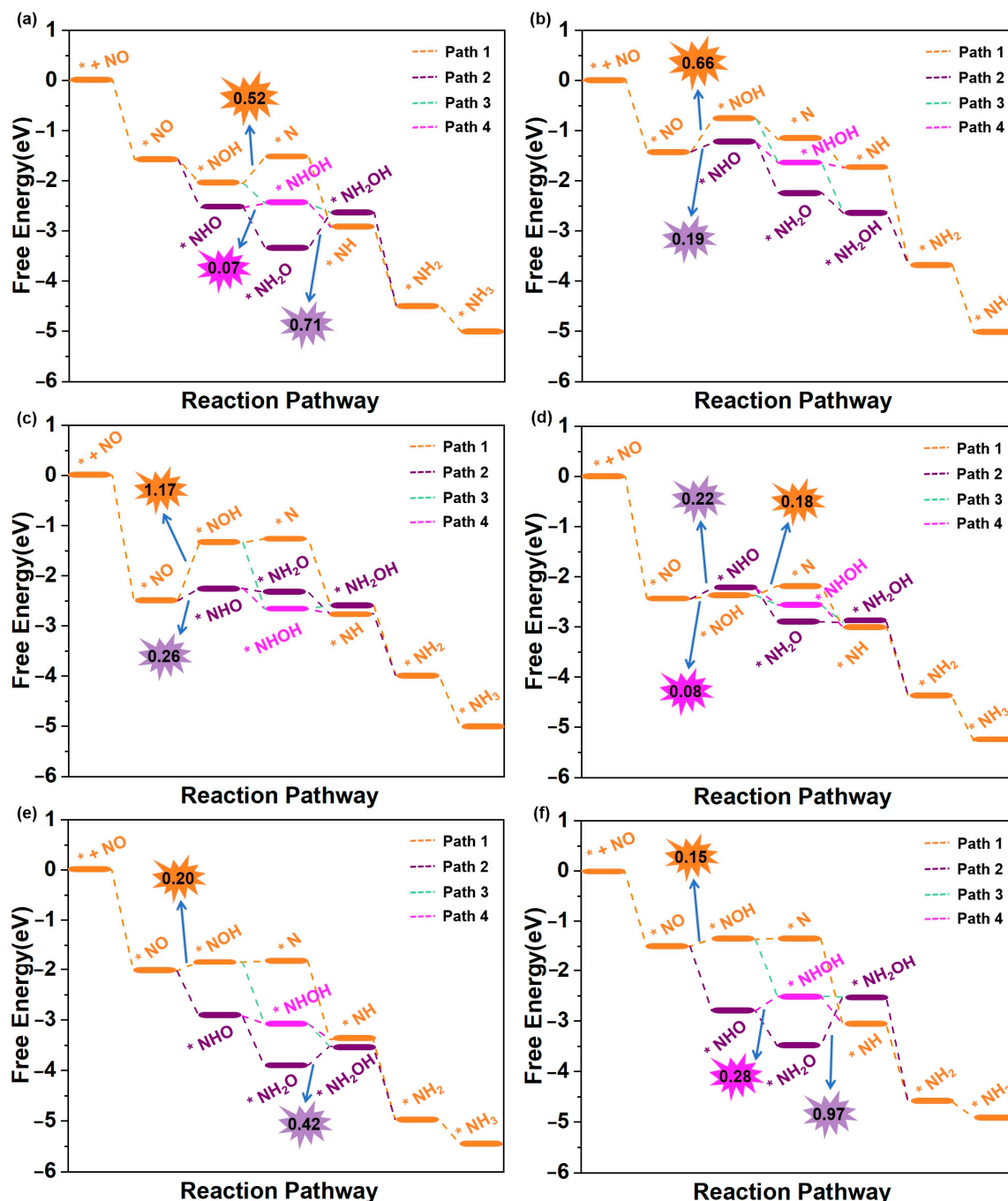

Figure 6. Free energy diagrams of eNORR to NH$_3$ over six TM@WS$_2$ catalysts. (**a**) Ti@WS$_2$; (**b**) Mn@WS$_2$; (**c**) Co@WS$_2$; (**d**) Fe@WS$_2$; (**e**) Zr@WS$_2$; (**f**) Hf@WS$_2$.

The eNORR process is initiated by the adsorption of NO on the catalyst surface, resulting in the formation of the *NO species. Following this, protons from the electrolyte approach and interact with the *NO species, driving the formation of *HNO or *NOH. Subsequently, a series of hydrogenation steps occur, ultimately resulting in the formation of

NH$_3$. As shown in Figure 6a, the most favorable reaction pathway for the Ti@WS$_2$ catalyst is Path3. Along this pathway, all elementary steps are exergonic (ΔG < 0 eV), indicating that the eNORR process occurs spontaneously. Consequently, the U$_L$ of the Ti@WS$_2$ catalyst is 0 V. As shown in Figure 6b,c, for both the Mn@WS$_2$ and Co@WS$_2$ catalysts, Path2 is selected as the most favorable reaction pathway. In this pathway, the eNORR process can occur after overcoming a potential barrier (corresponding to ΔG of *NO$\rightarrow$*NHO) of 0.19 eV for Mn@WS$_2$ and 0.26 eV for Co@WS$_2$. For Fe@WS$_2$ (Figure 6d), Path3 emerges as the most favorable pathway, featuring a minimal energy barrier of 0.08 eV during the transition from *NO to *NHO. For the Zr@WS$_2$ catalyst (Figure 6e), the most favorable reaction pathway is Path4, along which all elementary steps are exergonic, suggesting that the eNORR proceeds spontaneously at 0 V electrolyte potential. For the Hf@WS$_2$ catalyst, as shown in Figure 6f, the most favorable pathway is identified as Path4, with a barrier height of 0.15 eV. In particular, in an acidic environment, the transformation of NH$_3$ into NH$_4^+$ proceeds rapidly, primarily because this process releases a significant amount of energy [22,26,35]. As a result, the desorption of NH$_3$ is not taken into account when evaluating the performance of all six catalysts.

In summary, the limiting potentials (U$_L$) of the Ti@WS$_2$, Mn@WS$_2$, Fe@WS$_2$, Co@WS$_2$, Zr@WS$_2$, and Hf@WS$_2$ catalysts are 0, -0.19, -0.26, -0.08, 0, and -0.15 V, respectively. These values are either equivalent to or significantly lower than those of reported for other single-atom catalysts. For ease of comparison, we have compiled the limiting potentials from our study and those reported in the literature in Table S2.

In order to further elucidate the effects of TM atoms modification, the eNORR activity of WS$_2$ with single sulfur vacancies was investigated. As demonstrated in Figure S2, the most favorable reaction pathway is Path4, which involves a relatively low potential barrier of 0.96 eV for the *NHO$\rightarrow$*NHOH step, corresponding to U$_L$ of -0.96 V. In comparison, TM depositing on sulfur vacancy site significantly enhances the catalytic activity of WS$_2$. Specifically, the U$_L$ values for the TM@WS$_2$ catalysts exhibit a notable increase from -0.96 V for WS$_2$ to 0 V for Ti@WS$_2$, -0.19 V for Mn@WS$_2$, -0.26 V for Fe@WS$_2$, -0.08 V for Co@WS$_2$, 0 V for Zr@WS$_2$, and -0.15 V for Hf@WS$_2$. These observations demonstrate that TM atoms modification substantially improves the eNORR activity of WS$_2$.

During the eNORR process, N$_2$O and N$_2$ can be produced as by-products due to the formation of the NO dimer (N$_2$O$_2$), as shown in Figure 3a. Therefore, we investigated the NO-to-N$_2$O and NO-to-N$_2$ pathways (Path5 and Path6 in Figure 4b) on the above six catalysts from the 2N-end (*N$_2$O$_2$) and 2O-end (*O$_2$N$_2$) configurations of N$_2$O$_2$, respectively. Figure 7a–f illustrate the energy diagrams for the formation of N$_2$O and N$_2$ on Ti@WS$_2$, Mn@WS$_2$, Fe@WS$_2$, Co@WS$_2$, Zr@WS$_2$, and Hf@WS$_2$ catalysts; during the NO-to-N$_2$O process, starting from *O$_2$N$_2$ configurations, it is evident that all of these six catalysts face potential barriers (in the process of *OH$\rightarrow$* + H$_2$O step) of 0.67, 0.33, 0.81, 0.55, 1.24, and 0.93 eV, respectively. This indicates that the conversion of *OH to *+H$_2$O is a rather challenging step for these catalysts. For the N$_2$ formation process, over Ti@WS$_2$, Mn@WS$_2$, Fe@WS$_2$, Co@WS$_2$, Zr@WS$_2$, and Hf@WS$_2$ catalysts, the first hydrogenation of first step, namely the *N$_2$O$_2$-*N$_2$O$_2$H step, is the PDS step, and corresponding potential barriers are 0.21, 0.50, 1.04, 0.92, 0.16, and 0.49 eV, respectively. Based on the above results, the energy barriers of N$_2$O and N$_2$ formation are higher than those of NH$_3$ formation. Consequently, although under conditions of high NO concentration, the formation of N$_2$O and N$_2$ can be effectively suppressed on these six catalysts. Hence, these catalysts demonstrate high selectivity for NH$_3$ production.
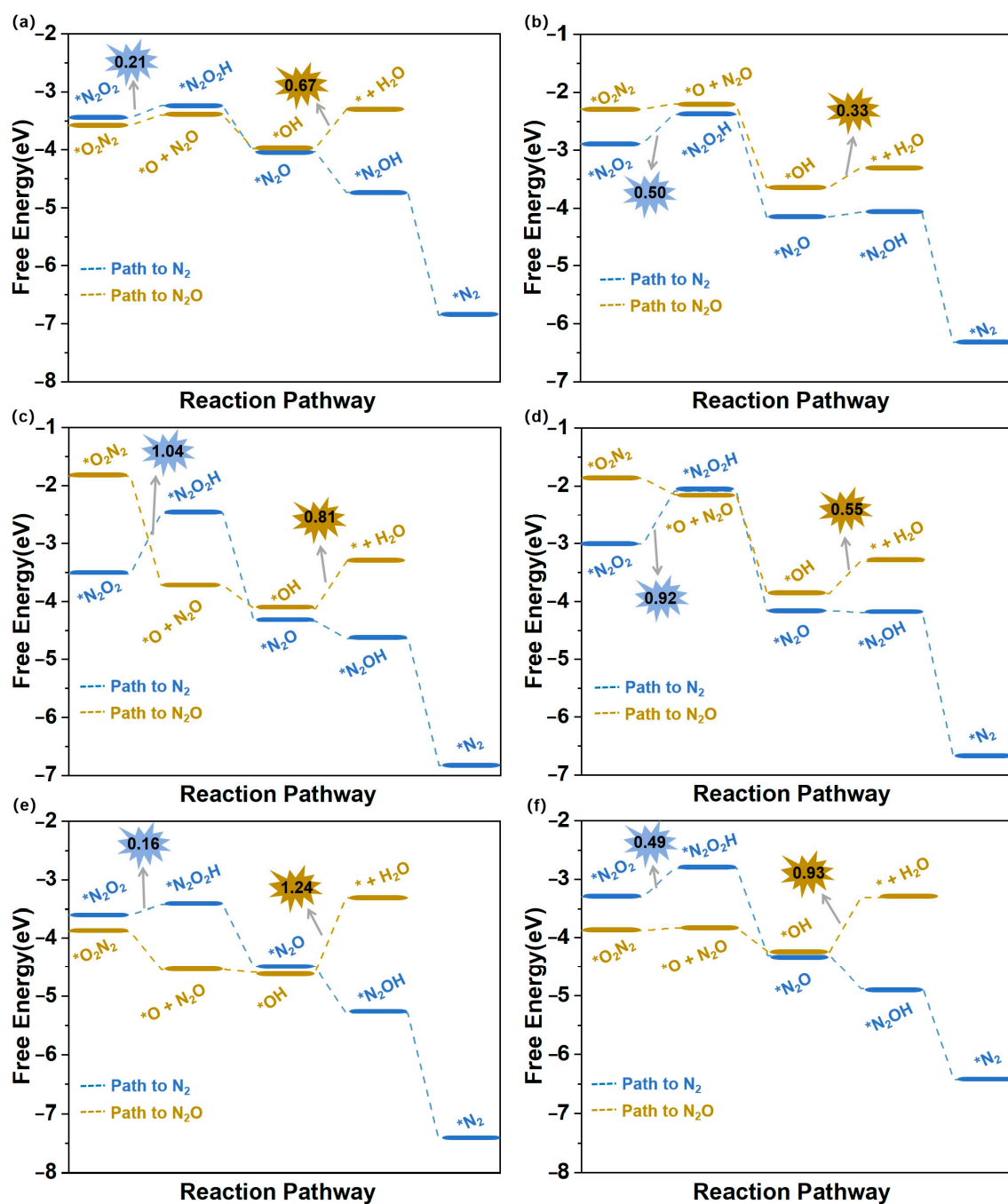
Figure 7. Free energy diagrams of eNORR to N_2O/N_2 over six TM@WS$_2$ catalysts. (**a**) Ti@WS$_2$; (**b**) Mn@WS$_2$; (**c**) Fe@WS$_2$; (**d**) Co@WS$_2$; (**e**) Zr@WS$_2$; (**f**) Hf@WS$_2$.

3.4. Selectivity Analysis

To more effectively elucidate the product selectivity of NH$_3$ and N_2O/N_2, as well as the HER, for the Ti, Mn, Fe, Co, Zr, and Hf@WS$_2$ catalysts, we have constructed a graph depicting the differences in the limiting potentials between NO reduction to NH$_3$ and N_2O/N_2, as well as the HER. As shown in Figure 8a,b, the Ti, Mn, Fe, Co, Zr, and Hf@WS$_2$ catalysts exhibit a pronounced preference for NH$_3$ production over N_2O and N_2. Meanwhile, as depicted in Figure 8c, with the exception of the Fe@WS$_2$ catalyst, the remaining five catalysts—Ti, Mn, Co, Zr, and Hf@WS$_2$—maintain a pronounced selectivity for the eNORR over the HER, thereby highlighting their exceptional selectivity for NH$_3$ production.
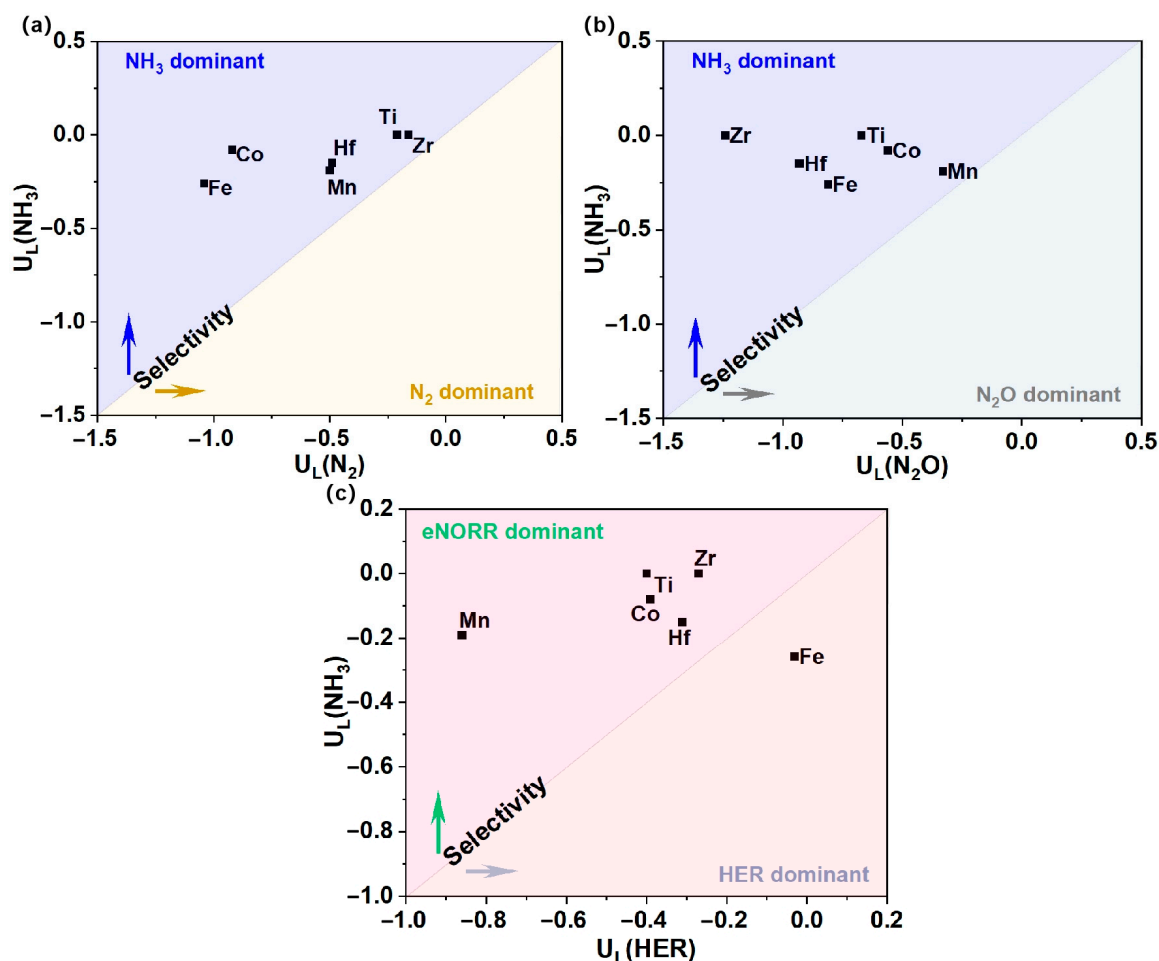
Figure 8. Selectivity for NH_3 production vs. N_2O/N_2 and HER on TM@WS$_2$ catalysts. (**a**) $U_L(NH_3)$ vs. $U_L(N_2)$; (**b**) $U_L(NH_3)$ vs. $U_L(N_2O)$; (**c**) $U_L(NH_3)$ vs. $U_L(HER)$.

3.5. Pourbaix Diagram Analysis

Since eNORR typically occurs under solution conditions, hydroxyl groups (*OH), oxygen groups (*O), or water molecules (*H$_2$O) present in the solution may adsorb onto the active sites, thereby reducing the activity of catalysts. The Pourbaix diagram, which provides detailed information about the catalyst surface under different pH values and applied voltages [64,65], is a valuable tool for evaluating the electrochemical stability of catalysts. Thus, we employed the Pourbaix diagram to evaluate the electrochemical stability of the TM@WS$_2$ catalysts. As shown in the Figure 9, the minimum redox potentials (U_R) required to eliminate *OH/*O on the surfaces of the Mn@WS$_2$, Hf@WS$_2$, Zr@WS$_2$, Co@WS$_2$, and Ti@WS$_2$ catalysts are 0.36 V, 0.59 V, 0.85 V, 0.28 V, and 0.77 V, respectively. When the value of U_R is greater than U_L, the electrocatalysts exhibit significant oxidation resistance, preventing the adsorption of *OH/*O on the catalyst surface. This, in turn, facilitates the adsorption of NO molecules on the active sites, thereby promoting the subsequent eNORR process. Notably, for the Mn@WS$_2$, Hf@WS$_2$, Zr@WS$_2$, Co@WS$_2$, and Ti@WS$_2$ catalysts, the value of U_R is greater than the corresponding U_L. This indicates that these catalysts possess both stability and high selectivity for eNORR. Therefore, they can serve as stable and promising candidates for eNORR applications.
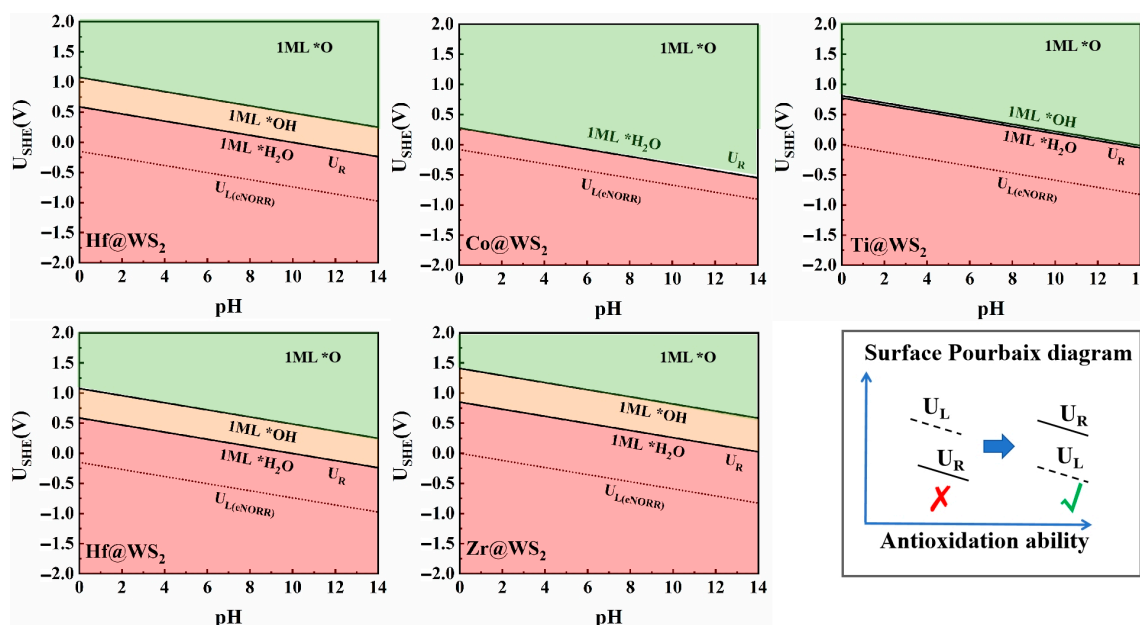
Figure 9. Surface Pourbaix diagrams of TM@WS$_2$ catalysts.

3.6. Revealing the Origin of Activity

The initial stages of the eNORR process are highly contingent upon the adsorption and activation of NO, as these steps serve as the cornerstone for the entire reaction mechanism. To elucidate the origin of eNORR activity, we performed detailed electronic structure analyses to illustrate the activation of *NO. As depicted in Figure 10a, the analysis of electron density difference maps for five TM@WS$_2$ catalysts reveals substantial charge redistribution occurring between the adsorbed *NO species and the catalyst substrates, primarily characterized by the accumulation of electrons on the *NO. The Bader charge analysis provides additional validation for this observation, demonstrating that the quantity of electrons transferred from the TM@WS$_2$ catalysts to the *NO species varies among different transition metals: 0.50 for Ti, 0.43 for Mn, 0.25 for Co, 0.55 for Zr, and 0.55 for Hf.

A detailed analysis was conducted on the partial density of states (PDOS) for the five catalyst candidates. As shown in Figure 10b, there is a clear overlap between the p orbital of the *NO species and the d orbitals of the Ti, Mn, Co, Zr, and Hf atoms. This overlap indicates a strong interaction between the d orbitals of these metal atoms and the p orbital of *NO, which ultimately promotes the activation (weakening) of the N-O bond in the NO molecule.

The analysis of the crystal orbital Hamiltonian population (COHP) and the integrated crystal orbital Hamiltonian population (ICOHP) further supports the above findings. These metrics have been established as effective indicators for characterizing the level of NO activation [25,60]. The quantitative determination of ICOHP values is achieved by integrating the energy up to the Fermi level. Typically, a more negative ICOHP value signifies a stronger binding interaction.

As demonstrated in Figure 11, upon NO adsorption, the COHP of the adsorbed *NO exhibits a greater number of antibonding states compared to that of the isolated NO molecule. Additionally, the ICOHP (N-O) values for the N-O bond of *NO adsorbed on Ti, Mn, Co, Zr, and Hf@WS$_2$ catalysts are −8.59, −8.66, −8.73, −8.07, and −7.97, respectively. It is evident that this is less pronounced in negativity compared to that of the isolated NO molecule (−9.66), indicating a substantial weakening of the N-O bond upon adsorption.
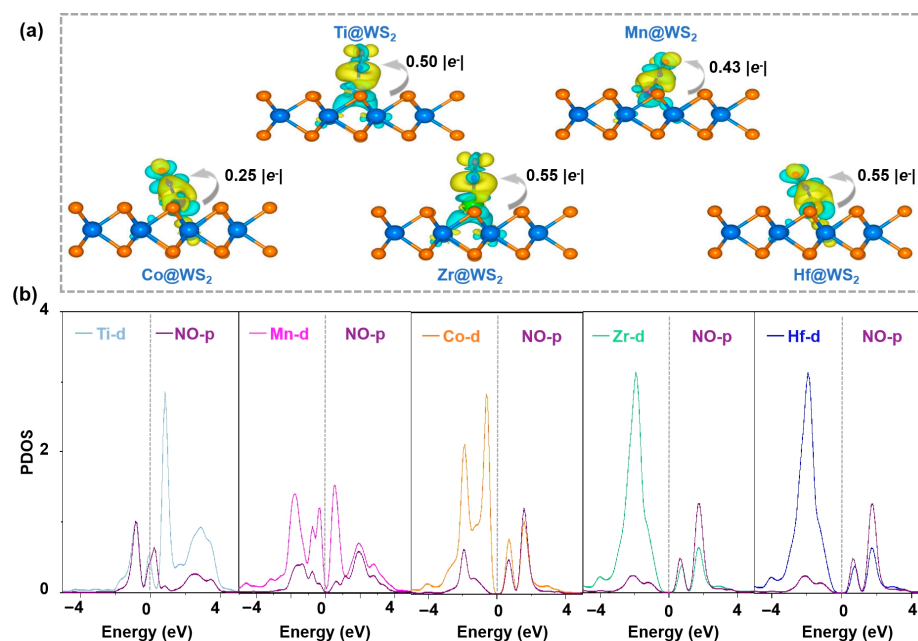
Figure 10. (**a**) The charge density difference maps of five TM@WS$_2$ catalysts. In these visualizations, the isosurface threshold is 0.003 e/Å^3, yellow regions signify areas of charge accumulation, while cyan regions indicate charge depletion; (**b**) partial density of states (PDOS) of NO adsorbed on five TM@WS$_2$ catalysts.
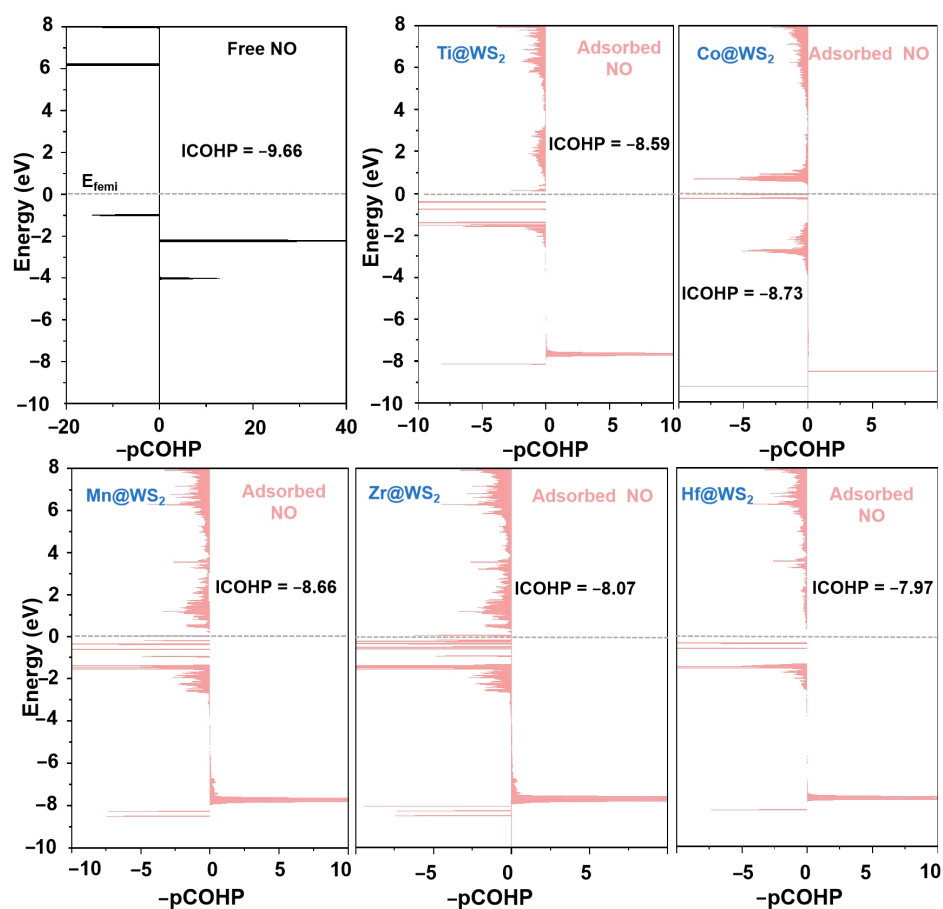

Figure 11. Projected COHP (-pCOHP) analysis of the N-O bond in free NO molecule (dark) versus that in the *NO species (light red) on five TM@WS$_2$ catalysts.

4. Conclusions

In summary, a range of single-atom catalysts comprising 27 transition metal (TM) atoms deposited on single sulfur vacancy sites of WS_2 nanosheets have been successfully designed and their performance in eNORR evaluated using DFT calculations. The results indicate that 19 TM atoms exhibit potential stability. In terms of eNORR activity for NH_3 production, the five $TM@WS_2$ catalysts—specifically $Ti@WS_2$, $Mn@WS_2$, $Co@WS_2$, $Zr@WS_2$, and $Hf@WS_2$—show remarkable potential, with their U_L's being 0.00, −0.19, −0.26, 0.00, and −0.15 V, respectively. Moreover, by comparing the differences in the limiting potentials for NO reduction to NH_3 and N_2O/N_2, as well as the HER, we reveal their exceptional selectivity for NH_3 production.

This study is significant for both environmental and energy applications, as it provides a sustainable route for ammonia synthesis and reduces NO emissions through electro-catalytic NO reduction. The identified $TM@WS_2$ catalysts, with high activity, selectivity, and stability, are promising for experimental validation. However, limitations exist due to the idealized models and approximations used in DFT calculations, which may not fully reflect real-world complexities such as impurities and solvent conditions. Therefore, close collaboration between theoretical and experimental researchers is essential to validate and refine these predictions.

Overall, this work highlights the potential of $TM@WS_2$ catalysts for efficient NO removal and sustainable NH_3 synthesis, emphasizing the need for further experimental research to realize their practical application.

Abbreviations

The following abbreviations are used in this manuscript:

eNORR	Electrocatalytic nitric oxide reduction
TM	Transition metal
HER	Hydrogen evolution reaction
eNO$_3$RR	Electrocatalytic nitrate reduction
eNRR	Electrocatalytic N$_2$ reduction reaction
SACs	Single-atom catalysts
E$_b$	Binding energies

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