

Understanding the Intrinsic Mechanism of High-Performance Electrocatalytic Nitrogen Fixation by Heterogenization of Homonuclear Dual Atom Catalyst

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Abstract

A heteronuclear dual transition metal atom catalyst is a promising strategy to solve and relieve the increasing energy and environment crisis. However, the role of each atom still does not efficiently differentiate due to the high activity but low detectivity of each transition metal in the synergistic catalytic process when considering the influence of heteronuclear induced atomic difference for each transition metal atom, thus seriously hindering intrinsic mechanism finding. Herein, we proposed coordinate environment vary induced heterogenization of homonuclear dual transition metal, which inherits the advantage of heteronuclear transition metal atom catalyst but also controls the variable of the two atoms to explore the underlying mechanism. Based on this proposal, employing density functional theory study and machine learning, 23 kinds of homonuclear transition metals are doping in four asymmetric C₃N for heterogenization to evaluate the underlying catalytic mechanism. Our results demonstrate that five catalysts exhibit excellent catalytic performance with a low limiting potential of -0.28 to -0.48 V. In the meantime, a new mechanism, ‘capture-charge distribution-recapture-charge redistribution’, is developed for both side-on and end-on configuration. More importantly, the pronate site of the first hydrogenation is identified based on this mechanism. Our work not only initially makes a deep understanding of the transition dual metal-based heteronuclear catalyst indirectly but also broadens the development of complicated homonuclear dual atom catalysts in the future.

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Abstract: A heteronuclear dual transition metal atom catalyst is a promising strategy to solve and relieve the increasing energy and environment crisis. However, the role of each atom still does not efficiently differentiate due to the high activity but low detectivity of each transition metal in the synergistic catalytic process when considering the influence of heteronuclear induced atomic difference for each transition metal atom, thus seriously hindering intrinsic mechanism finding. Herein, we proposed coordinate environment vary induced heterogenization of homonuclear dual transition metal, which inherits the advantage of heteronuclear transition metal atom catalyst but also controls the variable of the two atoms to explore the underlying mechanism. Based on this proposal, employing density functional theory study and machine learning, 23 kinds of homonuclear transition metals are doping in four asymmetric C_3N for heterogenization to evaluate the underlying catalytic mechanism. Our results demonstrate that five catalysts exhibit excellent catalytic performance with a low limiting potential of -0.28 to -0.48 V. In the meantime, a new mechanism, 'capture-charge distribution-recapture-charge redistribution', is developed for both side-on and end-on configuration. More importantly, the pronate site of the first hydrogenation is identified based on this mechanism. Our work not only initially makes a deep understanding of the transition dual metal-based heteronuclear catalyst indirectly but also broadens the development of complicated homonuclear dual atom catalysts in the future.

1. Introduction

Ammonia (NH_3) plays an essential role in human society for fertilizer, industry chemistry, dyes, hydrogen carriers, etc.^{1, 2} Currently, the primary industrial method to produce ammonia is the century-wide Haber-Bosch process^{3, 4}, where the massive energy is required to break the triple bond of nitrogen (N_2), leading to nearly 2% energy cost annually. Meanwhile, this process releases 1% CO_2 of the whole emission every year, accelerating the greenhouse effect and climate warming^{5, 6}. As an alternative strategy, electrocatalytic nitrogen reduction reaction (eNRR) for NH_3 synthesis has attracted more attention for its multichannel energy input and CO_2 -free emission^{7, 8}.

Nowadays, various electrocatalysts have been investigated for eNRR, including bulk catalysts, two-dimensional catalysts, atomic cluster catalysts, single-atom catalysts, dual-atom catalysts, MOF-based catalysts, and three-atom cluster catalysts. For example, the PdCu nanoparticle⁹, MXenes¹⁰, Fe_3 cluster¹¹, W/g-CN¹², $Mo@C_9N_4$ ¹³, $NiCo@GDY$ ¹⁴ and so on^{15, 16, 17, 18}. Among them, dual atom catalyst (DAC) shows excellent electrocatalytic performance for eNRR since the synergistic catalytic process among two active sites^{19, 20}. Detailly, the DAC can be divided into two categories, the homonuclear^{21, 22, 23} and heteronuclear ones^{24, 25}. For the homonuclear DAC, the two active sites show the same properties, while the same characters of the dimers make the activity of DAC very limited²⁶. Compared to homonuclear DAC, heteronuclear DAC with various properties in both electronic and structural characters, leading the active sites not only play different role in catalytic process, but also break the scaling relationship for eNRR, which effectively enable highly activity and selectivity during the eNRR process^{19, 27}. For example, He et al, demonstrated that B site and Si site take different roles in electrocatalytic eNRR process and put forward 'capture-backdonation-recapture' mechanism for metal-free dual atom-based catalyst¹⁹. Hu et al. verified that the scaling relationship is broken through adding additional atom in M/C_3N system, leading to significantly decreased in limiting potential in M_1M_2/C_3N system²⁸. Nevertheless, for the widely studied transitional metal (TM) based heteronuclear dual atom catalyst, the underlying mechanism is still unclear. On one hand, the roles of each TM atoms could not sensitively detect and efficiently differentiate during the eNRR process due to high activity and low distinction of them. On the other hand, heteronuclear induced atomic diversity could enlarge this dilemma and pollute the intrinsic electronic influence during the

underlying electronic mechanism finding process, thus leading people could not make deep understanding to the intrinsic electronic determined mechanism finding exactly. Therefore, how to remove the heteronuclear atomic influence and enhance the intrinsic properties' sensitivity for investigating the underlying mechanism is extremely urgent for TM-based dual atom catalyst.

To solve this dilemma, an efficient strategy is to enlarge the intrinsic properties' variety to minimize the diversity of two TM atoms. For example, turning dual heteronuclear TM atoms into single active atoms and spontaneously removes this influence, while this strategy violates the purpose of DAC's investigation, such as the synergistic effect among two active sites. It should be noted that maintaining dual TM atoms homogeneity^{29, 30} could remove the atomic diversity effect as well, but it makes the intrinsic properties can't be detected efficiently at the same time due to the same intrinsic properties they owned. Comparatively, it is impossible to answer how to remove the heteronuclear induced atomic diversity for heteronuclear by uniting their atomic size properties. However, it is easy to make the intrinsic properties different when atomic properties remain the same for homonuclear dual TM atom catalysts. Therefore, changing the strategy to keep structural properties the same but make the intrinsic properties vary could be an efficient method for sensitively detecting and differentiating the roles of each TM atom in the catalytic process. In fact, this phenomenon is noticed in some experiments and is also initially investigated for organic synthesis³¹ and CO₂RR³². Meantime, the complicated coordinating environment of the substrate (especially for the porous materials) further guarantees the feasibility of this proposal^{33, 34}. However, a general and systematic investigation of the intrinsic mechanism is rare, especially since this strategy can remove the atomic diversity effect. Hence, by considering the different configuration properties as proved in the experiment, it is evident to study the same atomic properties but intrinsic properties' variety homonuclear DAC and dig out the intrinsic mechanisms for dual TM atoms catalyst.

Combining the advantage of homonuclear DAC's atomic similarity and the configuration difference induced heteronuclear-like DAC, as well as the high sensitivity of N₂ molecule, we designed 23 kinds of dual transition metals doping on four asymmetric defective C₃N (total of 92 systems) to investigate the homonuclear induced atomic size-constant DAC for electrocatalytic NRR by density functional theory. After ascertaining the stability of the doped systems, the homonuclear twain TM atom catalyst systems exhibit differential intrinsic properties identified by analyzing the intrinsic properties like Bader charge analysis, magnetic analysis, and d-band center analysis, demonstrating the feasibility of our proposal. Then, a novel and extended 'capture-charge distribution-recapture-charge redistribution' mechanism was developed by performing the N₂ capture, activation, and hydrogenation and analyzing the capture capacity charge distribution as well as intrinsic electronic properties combined with machine learning. Finally, a total 5 candidates are selected as high active, high selective, and high stable electrocatalysts for NRR. Our work not only makes a deep understanding of the catalytic behavior of NRR but also develops a new method for designing heteronuclear-like catalysts.

2. Computational Methods

All the spin-polarized calculations are performed by Vienna Ab Initio Simulation Package (VASP) on the framework of density functional theory (DFT) study³⁵, where the interaction between ions and electrons is described by Projector-augmented wave (PAW) method³⁶, and cutoff energy of 500 eV is used to certain the basis sets. Geometric optimization is carried out by the Perdew-Burke-Ernzerhof (PBE) functional with the generalized gradient approximation (GGA)³⁷. To avoid the interlayer interaction induced by the periodic boundary condition, a 20 Å vacuum layer is applied in the z-direction. The DFT-D3 method³⁸ is implemented to describe the Van der Waals dispersion. The 3×3×1 Γ -center k-mesh is used for structural relaxation, while a 5×5×1 k-mesh is used for electronic properties calculation. The energy and force convergence criteria are set to 10⁻⁵ eV and -0.02 eV/Å, respectively. The Bader analysis³⁹ is employed to explore the charge transfer quantitatively. The projected Crystal Orbital Hamilton Population (COHP)⁴⁰ is used to analyze the N-N triple and TM-N bonds' bonding nature for the adsorbed systems by implementing LOBSTER code⁴¹. To test the thermostability of the selected eNRR candidates, ab Initio molecular dynamics simulations (AIMD)⁴² are performed for 9 ps with a time step of 1.5 fs. Since the eNRR usually occurs under the aqueous condition,

the solvent effect is considered using the VASPsol model⁴³. The VASPKIT code⁴⁴ developed by Wang et al. is employed for pre- and post-data extraction.

For the eNRR process, the Gibbs free energy of each hydrogenation step is calculated using the computational hydrogen electrode model proposed by Nørskov et al.⁴⁵. The eNRR to ammonia catalytic reaction contains six proton-coupled electron transfer processes, for each process, the Gibbs free energy change can be obtained as:

$$\Delta G = \Delta E + \Delta ZPE - \Delta TS + \Delta G_U + \Delta G_{pH} \quad (1)$$

where ΔE , ΔZPE , T , and S are the total energy changes obtained from DFT calculation, zero-point energy, temperature, and entropy, respectively. G_U is the electrode potential, and G_{pH} is the effect of the pH.

3. Results and Discussions

3.1 Atomic diversity free homonuclear DAC heterogenization and the Stabilities of homonuclear DAC systems

Since both heteronuclear TM atoms exhibit high activity in the eNRR process, it is hard to detect which active site is more sensitive for N_2 capture and activation, especially when considering both heteronuclear induced atomic diversity and intrinsic properties' variety in the same system, which may seriously impede the underlying electronic mechanism finding. In fact, heteronuclear induced atomic difference may contribute more to the eNRR process when the intrinsic properties keep high activity and low distinction, especially for the radius variety of each TM atom. Hence, the atomic diversity should be minimal to get more sensitive detection to differentiate intrinsic electronic influences. However, it is hard to remove the impact of this effect in heteronuclear TM DAC. For example, the physical radius of TM atoms varies from 1.24 to 1.60 Å, as summarized in our previous work⁴⁶, which could deteriorate when considering the Van der Waals radius (1.40 to 2.09 Å)⁴⁷. After constructing heteronuclear DAC (see in **Figure 1(a)**), the dual TM atoms present a 'large and small size' active site, where the N_2 molecule from the solution is seriously affected by the atomic diversity, thus insufficient for intrinsic mechanism finding. The best strategy to minimize this effect is to keep the dual TM atoms far away from each other to form a single atom active site and follow the famous 'donation/back-donation' mechanism⁴⁸. Or enlarge the intrinsic properties to ignore the existing effect, e.g., metal-free dual atom following the 'capture-backdonation-recapture' mechanism³⁶.

Nevertheless, those methods are unsuitable for investigating the dual TM atoms systems. It is worth noting that localizing atomic size to the same structural properties could be a better strategy to remove the undesired effect, such as homonuclear DAC, while the intrinsic properties remain constant at the same time, leading the N_2 molecule to show no sensitivity to each TM atom. Besides, according to our recent studies, the captured N_2 molecule keeps its equilibrium state and impedes the hydrogenation process in B-B, C-C metal-free homonuclear DAC⁴⁹. Hence, the unfunctionalized homonuclear DAC is also not suitable for mechanism finding. To solve this dilemma, we constructed homonuclear dual TM atoms coordinating with various coordinate environments to differentiate the intrinsic properties. In this system, the heteronuclear induced atomic difference effect is entirely removed, and the intrinsic properties are varied with each TM atom simultaneously. More importantly, a single-element catalyst could form the homonuclear DAC with various intrinsic properties when considering the complicated loading environment. Meantime, it is essential to select an ideal substrate for homonuclear TM loading. Based on previous studies of the coordination effect atomic catalyst, the C_3N monolayer is an ideal candidate substrate for homonuclear TM atoms doping^{28, 50}. Advantageously, several possible defective sites such as monocarbide defect, mononitride defect, dicarbide defect, and diatomic defect consisting of a C and N atom can be formed on C_3N (**Figure S1**) with defect formation energy of 4.61, 4.82, 4.83, and 6.71 eV⁵¹, respectively, which is lower than the wide-studied monovacancy and divacancy in graphene (8.09 and 8.20 eV), indicating that the easier synthesis of the defective sites in C_3N nanosheet⁵². Furthermore, when considering various doping sites (**Figure 1(b)**), the bond length between two TM atoms could be well-tuned, which is vital for subsequent analysis. For the C_3N monolayer, after complete optimization, the obtained lattice constant is 4.86 Å, consistent with the previous reports^{28, 51, 53}, demonstrating the precision of this study. Then, a $3 \times 3 \times 1$ supercell of the C_3N is adopted

for further investigation, and four candidate sites (C_2N-C_3 , C_3-CN_2 , C_4-C_3 , and $C_2N-C_2N_2$) are filtrated finally since the asymmetric vacant geometry and none-dangling bonds of them, which provide diverse sites for TM embedding (**Figure 1(b)**). Finally, 23 kinds of homonuclear dual TM atoms from Ti to Au (except for Tc) are used to dope in site₁, site₂, site₃, and site₄ within 92 systems. To ascertain the stability of the homonuclear TM atoms doped systems ($TM_2@site_x$, $x = 1, 2, 3, 4$), the formation energy (E_{form}) of the $TM_2@site_x$ ($x = 1, 2, 3, 4$) is systematically investigated initially, which is defined as:

$$E_{form} = (E_{TM_2-C_3N} - E_V - 2E_{TM})/2 \quad (2)$$

where $E_{TM_2-C_3N}$, E_V , E_{TM} is the total energy of the $TM_2@site_x$ ($x = 1, 2, 3, 4$) system and defective system, as well as the TM atoms in their bulk phase, respectively. When the $E_{form} < 0$ eV, the doped systems can be considered thermodynamic stability. As depicted in **Figure 1(c)** and **Table S1**, most of the considered systems show negative E_{form} , indicating their thermodynamic stability. In contrast, the systems that own positive E_{form} would be excluded for further exploration, including Zr, Nb in Site₂ and Ti, Cu, Zr, Nb, Hf in Site₃ since their unstable configuration and the easy aggregation in defective C_3N substrate. Apart from the formation energy of the doped system, the dissolution potential (U_{diss}) is further investigated to test the electrochemical stability of the rest systems, and it can be defined as follows⁵⁴:

$$U_{diss} = U_{diss-bulk} - E_{form}/(n_e e) \quad (3)$$

in which $U_{diss-bulk}$, n_e represents the dissolution potential of the bulk metal as well as the number of transferred electrons during the dissolution process. It can be regarded as electrochemical stability of the $TM_2@site_x$ ($x = 1, 2, 3, 4$) when $U_{diss} > 0$. As demonstrated in **Figure 1(d)**, all the doped systems show electrochemical stability except for Ti, V, Zr, Nb, Hf, Ta in Site₁, Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta in Site₂, Ti, V, Mn, Zr, Nb, Hf, Ta in Site₃ and Ti, Zr, Nb, Hf, Ta in Site₄. Notably, most of the former TM atom anchored systems exhibit electrochemically instability, while the latter TM atoms doped system shows high stability in an electrochemical view. This phenomenon mainly originates from the high activity and high dissolution potential in their bulk phase of the TM atom, thus leading the doped systems to prefer to dissolve in the solution. Eventually, a total of 72 candidates are selected for the following investigations.

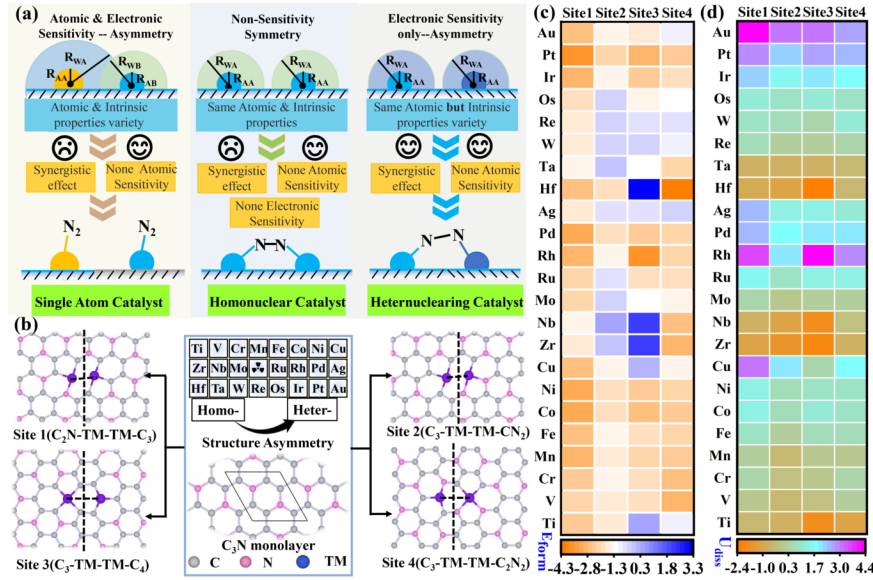


Figure 1 . (a) Schematic diagram of the atomic diversity and atomic diversity free homonuclear DAC transformation. (b) The selected asymmetric structure of defective C_3N monolayer and the transitional metal candidates for homonuclear dual atoms doping, the gray, plum, and blue ball representative of the C, N, and TM, respectively.

N, and TM atom. (c) The formation energy of homonuclear dual TM atoms anchoring on defective C₃N substrate. (c) Dissolution potential of the TM₂@site_x (x = 1, 2, 3, 4).

After ensuring the stability of the TM-doped defective C₃N systems, we next focus on evaluating the configuration-induced intrinsic properties' variety of the atomic property-constant homonuclear DAC. We first investigated the structural properties of the doped TM's configuration environment, for which the changes of coordinate environment can effectively tune the intrinsic properties for the homonuclear system, as confirmed by various electrocatalytic reactions for single atom catalyst^{55, 56}. Quantitatively, bond length values of each adjacent decorated atom could directly reflect the bonding nature between the TM atom and the coordinate C and N atom, which indirectly affects the intrinsic properties' variety of the doped homonuclear TM atoms. As shown in **Figure S2** and **Table S2-S5**, we list the bond length values of each TM-C and TM-N in the inline filled diagram for site₁, site₂, site₃, and site₄. The bond length between dual TM atoms varies, demonstrating the differentiation of each TM atom, especially for the bond difference in site₃ and site₄, which can significantly impact the intrinsic properties of the active sites.

Next, to prove the coordination-induced intrinsic properties' variety, the charge transfer between TM atoms and the substrate is quantitatively investigated initially since the charge transfer plays an essential role in the electrocatalytic field, as confirmed in recent research for eNRR^{49, 57, 58}. Nearly all the doped homonuclear TM atoms lost electrons since the average negative charges transfer (see in **Figure 2** (a), (b)), which is suitable for charges transferred from the N₂ molecule during the capture process. Differentially, it was proved that the quantity of charge transfer for each TM atom shows observable variety for nearly whole systems in TM₂@site_x (x = 1, 2, 3, 4), especially for Fe, Cu, W, Re, Os, Ir in site₁, Ni, Cu, Re, Ir, Pt, Au in site₂, Cr, Co, Pd, W, Os, Pt in site₃ and Co, Ni, Cu, Os, Pt in site₄. However, the negligible charge transfer differentiation of Mo, Ru, Pt in site₁, Pd, W, Os in site₂, Ni, Ag in site₃ and Fe, Ru in site₄ suggested the inefficient modulation of the homonuclear DAC heteronuclear, and other factors should be considered for further investigation. The spin moment of the doped TM atoms could be an excellent descriptor to explain the catalytic behavior in electrocatalytic fields, which has been systematically studied by some scholars^{59, 60, 61, 62, 63, 64, 65, 66, 67}. So, we then compared the spin moment differences of the doped systems. It was worth noting that nearly half of the selected candidates show zero spin moment, so those systems are excluded for spin moment differentiating in this part. The rest systems, including Cr, Mn, Fe, Co, Mo, Ru, Re, Os in site₁, Fe, Co, Ru, Os in site₂, Fe, Co, Mo, Pd, W, Re, Pt in site₃, V, Cr, Mn, Fe, Co, Ru, W, Re, Os, Ir, Au in site₄, are investigated for further studying. As depicted in **Figure S3**, among them, Cr₂@site₁, Fe₂@site₁, Fe₂@site₂, Fe₂@site₃, and Mn₂@site₄ show huge different spin moments of 6.10μ_B (TM1: -3.11μ_B; TM2: 3.00μ_B), 1.86μ_B, 1.90μ_B, 1.38μ_B, 3.08μ_B, revealing the fully heteronuclear of them, for the negligible charge difference of Mo, Ru, Pt in site₁, Pd, W, Os in site₂, Ni, Ag in site₃ and Fe, Ru in site₄. Parts of them show observable spin moment differences, such as Mo₂@site₁ (0.52μ_B), Ru₂@site₁ (0.15μ_B), Fe₂@site₄ (0.29μ_B) and Ru₂@site₄ (0.40μ_B). Those results proved that the intrinsic properties' varieties of atomic property-constant homonuclear dual TM atoms are further differentiating.

Nevertheless, the d-band center of the TM atoms is also investigated further since the d-band center is highly related to the adsorption energy of the reactant molecule and their corresponding intermediates^{47, 68}, as depicted in **Figure S3**(b) and (c), the d-band center difference varies from 0.01 to 1.70, indicating the complete differentiation of them. Among them, the indistinctive-liked charge transfer difference and zero spin moment of Pt₂@site₁, Pd₂@site₂, W₂@site₂, Os₂@site₂, Ni₂@site₃, Ag₂@site₃ exhibit d-band center difference of 0.07eV, 0.28 eV, 0.30 eV, 0.09 eV, 1.24 eV, 0.25 eV, respectively, suggest the observable intrinsic properties' variety of the homonuclear dual TM atoms. Therefore, the doped homonuclear dual TM atoms would exhibit different properties from the geometric variety to electronic property difference since the mirror broke off the coordinate environment, which realizes heteronuclear-like homonuclear DAC on the fundament of atomic properties keeps constant.

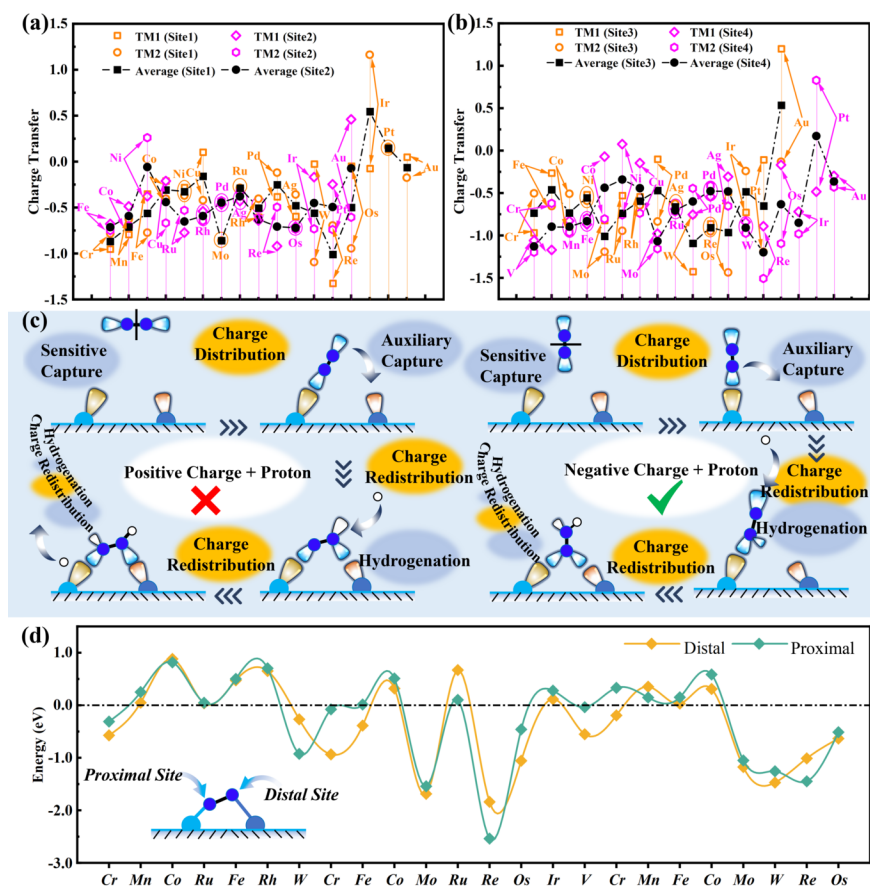


Figure 2 . (a)-(b) Values of charge transfer between TM1 and TM2 on TM₂@site₁, TM₂@site₂, TM₃@site₃, and TM₄@site₄ systems as well as the average charge transfer between them, respectively. (c) Schematic diagram of the N₂ sensitive capture, activation, and hydrogenation under the 'capture-charge distribution-recapture-charge redistribution' mechanism. (d) Gibbs free energy changes of the first hydrogenation for side on configuration in distal and proximal N₂ side, the sky blue, cornflower-blue, and blue ball represent TM1, TM2, and, N atom, respectively.

3.2 N₂ adsorption, activation, selective hydrogenation behavior, and the underlying 'capture-charge distribution' mechanism.

Now, we obtained the structural properties that keep constant induced high detectivity but intrinsic properties largely various homonuclear DAC induced high sensitivity system, and it is essential to investigate how the N₂ adsorption, activation, and hydrogenation behavior under the intrinsic-properties-only determined system. For the N₂ capture process, we divided it into two capture pathways, as depicted in **Figure 2** (c); for the N₂ molecule that parallels the plan, each side of the N₂ molecule exhibits the same sensitivity to the active site, while the higher active TM site tends to capture the free N₂ molecule successively, resulting N₂ molecule tilts to interact with a stronger side of the TM site. Once the N₂ molecule is captured by the adsorption stronger one with end-on configuration, charges quickly transfer between the N₂ molecule and the active site, following the 'donation-backdonation' mechanism. Subsequently, the rest of the active site continues to capture the distal N atom until forming a side-on configuration since its high activity as well. During this process, the charges redistribute again, and an asymmetric charge distribution forms. For the vertical configuration N₂ molecule capture process, things get simpler than the parallel one but still follow three capture steps: the proximal N atom is captured by the higher active TM site. It forms the end-on con-

figuration first, while the charge distribution also follows the 'donation-backdonation' mechanism. However, the distal N atom may not act with the rest of the active site since the N atom is located above the substrate. To relieve the activity of the rest active site, a weak interaction between the captured proximal N atom and the uncaptured TM active site further enlarges the charge asymmetric redistribution in the N_2 molecule and accelerates the hydrogen process. The dynamic 'capture-charge distribution-recapture-charge redistribution' mechanism occurred in both parallel and vertical N_2 capture processes corresponding to side-on and end-on configurations.

Meanwhile, charge redistribution asymmetry tends to enlarge gradually under the synergistic effect of atomic diversity-free induced high detective, but sensitive intrinsic properties vary in homonuclear DAC systems. For the hydrogenation process, estimating which side tends to hydrogenate priorly for the side on configuration is controversial. Conventionally, it is necessary to calculate and compare the Gibbs free energy changes of both first hydrogenation sites and select the optimal one. At the same time, this strategy may be imperfect due to the lack of charge distribution analysis. For example, the interaction between proton and distributed charges is vital for the hydrogenation process but lacks consideration in structural optimization. In other words, selecting a desirable side for a proton attack is subjective. It could also get energy and force minimum to obtain optimal hydrogenated configuration due to restarted charge self-consistent calculation. In contrast, the final results may be inaccurate once the selected site is occupied by positive charges (see **Figure S4**).

Thanks to a mass of data collected in our study and the reasonable 'capture-charge distribution-recapture-charge redistribution' mechanism, several typical charge distribution pictures are shown to select the correct hydrogenate site. As can be seen in **Figure S5** (a), after the stronger active TM site sensitively captures the N_2 molecule, charges from the N_2 molecule donate to the TM site and then back donate to the N_2 molecule, where the adsorbed N atom act as charges carrier and packaged by positive charges, thus avoid proton's attack, and among all N_2 captured systems, Cr, Fe, Co, Ru, Re, Os in site₁; Fe, Pd, Os, Ir in site₂; Co, Cu in site₃; Mn, Co, W, and Re in site₄ belong to this type of N_2 capture (See in **Figure S6**). For the second adsorption type, which could be regarded as the rest TM active, tends to attract the distal N atom (see in **Figure S5** (b)), positive charges still distribute around the bonded N atom, thus avoiding proton's attack, where Mn, W in site₁; Co, Ni, Rh, W, Re in site₂; Cr, Ni, Mo, Pd, Ir, Pt in site₃; V, Ni, Cu, Ru, Rh, Pd, Os, Pt in site₄ show this type of N_2 capture configuration (**Figure S6**). After bonding with the second TM site under the 'capture-charge distribution-recapture-charge redistribution' mechanism, it is clearly shown that the initial bonded N atom still acts as a charge transporter enveloped by positive charges (**Figure S5** (c), (d)). And systems such as Co, Cr, Mn, Ir in site₁; Fe, W, Ir in site₂; Cr, Fe, Co, Mo, Ru, Rh, W, Os, Re, Ir, Pt, Au in site₃; V, Cr, Mn, Fe, Co, Mo, W, Re, Os in site₄ exhibit this kind of N_2 capture configuration. Noticeably, an unexpected N_2 captured configuration with negative charges contained in both sides of the N_2 molecule may be observed in our homonuclear dual TM atom catalyst system, which can be explained by the little variety-tuning for the homonuclear DAC and the weak adsorption energy of N_2 , thus are not considered in our researches, as plotted in **Figure S5** (e).

In total, the bonded proximal N acts as a charge transporter enveloped by positive charge in both side-on and end-on, as considered in our study, demonstrating that the proton can't attack the proximal N atoms, thus certain the proton prefers to attack the distal N atom in both side on and end on configurations. Nevertheless, the Gibbs free energy changes of both N_2 molecule sides attacked by proton are comparatively calculated, although the charge distribution is not considered. As depicted in **Figure 2** (d), nearly all the captured N_2 systems with side-on configuration exhibit lower Gibbs free energy changes for the distal site than the proximal one, reasonably meet the results of the charge distribution analysis while may mislead the correct hydrogenate site for $W_2@site_2$, $Re_2@site_3$, $Mn_2@site_4$, and $Re_2@site_4$. However, it disclosed fantastic information when concentrating on their structural properties. Taking $Mn_2@site_1$ as an example (**Figure S4** (a)), the bond lengths between TM-N are 1.87 Å and 1.99 Å, respectively, and can be elongated to 1.94 and 2.08 Å after hydrogenation, where the elongated values increased by 0.07 and 0.09 Å, respectively. That's to say, it is hard to hydrogenate the proximal N site hydrogenation while easily hydrogenating the distal one, meeting the 'capture-charge distribution-recapture-charge redistribution' mechanism and further confirmed by the rest of the systems' structural properties summarized in **Table S6**.

3.3 High throughput screening strategy and full reaction pathways for selected homonuclear systems

Based on the conclusion discussed above, we then use a three-step screening to filtrate high catalytic candidates for eNRR from the stable TM anchored systems: (1) we first screen out the adsorption energy of N_2 molecule on $TM_2@site_x$ ($x = 1, 2, 3, 4$) by calculating the Gibbs free energy change of the adsorbent (ΔG_{*N_2}), where $\Delta G_{*N_2} < 0$ means that the N_2 molecule can spontaneously adsorb on the active site; (2) Based on the results from the first screening and the priority of the first hydrogenation site as discussed former, the Gibbs free energy changes of the first hydrogenation ($\Delta G_{*N_2-*N_2H}$) process is smaller than 0.50 eV could be the new screening strategy for following selection. (3) After ensuring the candidates from the second filtration, we further screen out the catalyst with the Gibbs free energy changes of the last hydrogenation process ($\Delta G_{*NH_2-*NH_3}$) on the $TM_2@site_x$ ($x = 1, 2, 3, 4$) less than 0.50 eV. Meanwhile, we also implemented state-of-the-art machine learning to predict certain descriptors for explaining the screen relationship using a gradient-boosted regression (GBR) algorithm. It should be worth noting that the intrinsic properties, such as d-band center, charge transfer, spin moment, etc., are not considered, which can advantageously minimize the intrinsic properties' impact and reprove the influence of the atomic structural effect. The details of the machine learning strategies are noted in **Support Information Note 2**.

For the eNRR process, the spontaneous adsorption of the N_2 molecule on $TM_2@site_x$ ($x = 1, 2, 3, 4$) is the fundamental step for the later activation. As plotted in **Figure 3(a)** and **Table S7**, among all the adsorbed systems, most of them show negative ΔG_{N_2} (-2.71 eV to -0.02 eV), demonstrating the efficient capture of the N_2 molecule. On the contrary, the rest systems, such as Pd, Ag, W(side-on), Pt and Au in site₁, Co(side-on), Ni(side-on), Cu, Pd, Ag, Os(side-on), Pt in site₂, Pd(side-on), Ag(end-on), Pt(side-on) and Au(end-on) in site₃ as well as Ag(end-on) and Au(side-on) in site₄ show positive ΔG_{N_2} of 0.01 to 0.91 eV, would be excluded for further exploration. For the machine learning prediction part, end-on and side-on configurations are predicted with nine input factors. The machine learning results are plotted in **Figure 3** (d, e). For end-on configuration, the outermost electron number of TM atoms (N_e), as well as the average bond length between TM atoms and neighboring coordinated atoms (r_a), has the most proportion in the bar chart with feature importance of 41%, 16.3% to predict ΔG_{*N_2} . The high coefficient of 0.97/0.91 and a low RMSE of 0.09/0.16 (**Figure S7**) demonstrate that the built GBR model is reliable. The N_e could be a good descriptor for end-on N_2 adsorption. The main reason may originate from the most active electron of them. For the side-on configuration part, ΔG_{*N_2} also successfully predicted by the machine learning method within a high coefficient of 0.99/0.97 and low RMSE of 0.08/0.13 (**Figure S7**), further revealing the GBR model's reliability. At the same time, d-electron count (ϑ_d) and TM bond length (r_{TM}) become the main features with proportions of 47.9% and 21.7%, respectively.

According to recent studies^{69, 70}, the limiting potential steps of the eNRR are highly related to the first protonation step ($*N_2 - *N_2H$) and the last protonation step ($*NH_2 - *NH_3$) among the six protonation steps. Thus, the $\Delta G_{*N_2-*N_2H}$ and $\Delta G_{*NH_2-*NH_3}$ are comprehensively calculated in the second and third screening, and the built machine learning model is also carried out for descriptors finding. As depicted in **Figure 3(b)**, we first screen potential candidates and then employ the GBR model to predict descriptors. For the screening process, there are 15 kinds of N_2 - $TM_2@site_x$ ($x = 1, 2, 3, 4$) configurations with $\Delta G_{*N_2-*N_2H}$ less than 0.50 eV, including Cr (end-on), Ru(side-on) in site₁, Co(end-on), W(side-on) in site₂, Cr(end-on/side-on), Mo(end-on/side-on), W(side-on), Os(side-on) in site₃, and V(side-on), Cr(side-on), Ni(end-on), Mo(side-on), W(end-on/side-on), Re(end-on/side-on) in site₄, so those systems are selected for the last filtration. Meanwhile, machine learning predicts that r_{TM} , as well as the radius of the TM atom (r_d), are good factors that affect the first catalytic step, with the features of 49.2% and 31.2%, along with a high coefficient of 0.98/0.91 and low RMSE of 0.21 and 0.44, respectively (**Figure S7**). Successively, the values of $\Delta G_{*NH_2-*NH_3}$ are further investigated to make deep filtration, as concluded in **Figure 3(c)**, 10 kinds of candidates are selected eventually for the $\Delta G_{*NH_2-*NH_3}$ is less than 0.50 eV, including Mn and Ru in site₂, Co, W in site₂, Os in site₃, V, Cr, Ni, W, Re in site₄, as for the rest systems whose $\Delta G_{*NH_2-*NH_3}$ more than 0.50 eV are eliminated for further exploration. Therefore, after a series of screenings, Mn and Ru in site₂, Co, W in site₂, Os in site₃, and V, Cr, Ni, W, Re in site₄ have high activity and may be promising

candidates for full eNRR reaction. Besides, though there are few data after the second screening (15 kinds of screened systems), machine learning is also carried out to search for excellent descriptors, as depicted in **Figure 3(g)**, the coefficient also reaches up to 0.96/0.95 for the $\Delta G^{*NH_2 \rightarrow *NH_3}$ with low RMSE of 0.18/0.12. Simultaneously, r_{TM} as well as r_a between TM and the neighbor modified atoms, are the major contributors (42.7%, 37.3%), proving they are good descriptors for the last hydrogenation step.

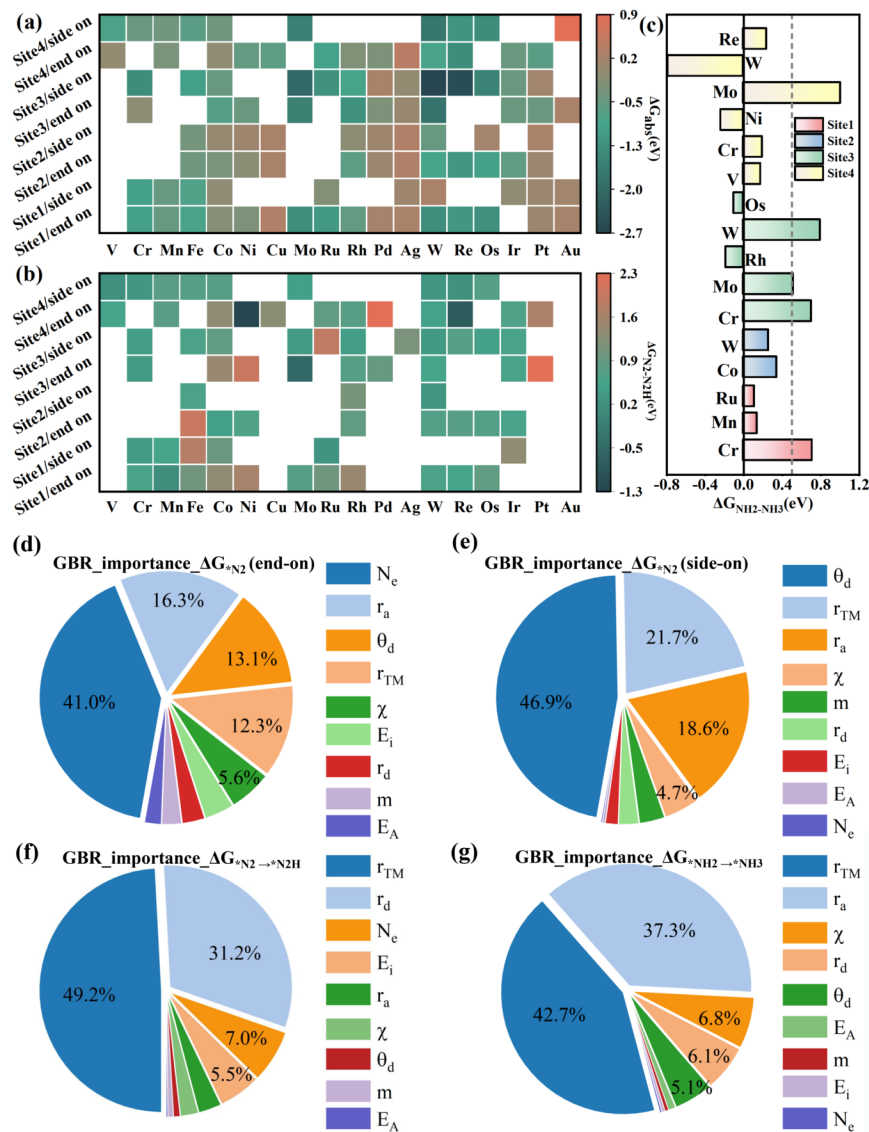


Figure 3. (a) Gibbs free energy changes for the N_2 adsorbed ($*N_2 - *N_2H$), (b) Gibbs free energy changes for the first protonate step ($*N_2 - *N_2H$), (c) Gibbs free energy changes for the last protonate step ($*NH_2 - *NH_3$), (d)-(g) Features importance of the GBR model precited for Gibbs free energy changes of ΔG^{*N_2} (end on), ΔG^{*N_2} (side on), $\Delta G^{*N_2 \rightarrow *N_2H}$, and $\Delta G^{*NH_2 \rightarrow *NH_3}$, respectively, where N_e , r_a , θ_d , r_{TM} , χ , E_i , r_d , m , E_A are the outmost electron number, the average bond length between TM atom and the coordinated C and N atom, d electron count, bond length between TM atoms, electronegativity, first ionization energy, radius of TM atoms, mass of TM atoms, electron affinity, the values of the parameters are summed in **Table S8** and **Table S9**.

In brief, several potential candidates are selected to show excellent electrocatalytic performance due to their proper N_2 capture energy small Gibbs free energy changes of the first and last hydrogenate steps. It is worth noting that the relatively unimportant structural properties, such as r_{TM} , r_a , and r_d , play the predominant role in the N_2 capture hydrogenation process even though the structural variety is entirely removed. In fact, those factors do not contradict the proposed atomic diversity effect since the objects of r_d are the same. Hypothetically, we think the distance between TM atoms may play an essential role during the hydrogenation process since both r_a and r_d are highly related to the r_{TM} , which should be further investigated.

To accurately obtain certain steps determining the NRR process, the whole Gibbs free energy changes are systematically investigated for the selected homonuclear systems. The complete reaction contains six proton-couple electron transfer steps ($N_2 + 3H_2 - 2NH_3$), making several possible intermediates ($*N_2H$, $*N_2H_2$, $*N_2H_3$, $*N_2H_4$, $*N$, $*NH$, $*NH_2$, $*NH_3$) existed under the electrocatalytic process. The difference in the N_2 configurations leads to various reaction pathways for the eNRR. To obtain detail information of the NRR on $TM_2@site_x$ ($x = 1, 2, 3, 4$), the traditional distal, alternative, and enzymatic reaction pathways are selected for limiting potential searching. Besides, we expand a new reaction pathway for the end-on configuration systems for the confirmed 'capture-charge distribution-recapture-charge redistribution' mechanism and name it Distal-1, as depicted in **Figure 4 (a)**. For the distal and alternative mechanisms, we do not have much discussion on them since a single TM atom participated predominately in the electrocatalytic NRR process, which does not efficiently reflect the synergistic effect for DAC. Among the screened systems, $Ni_2@site_4$ and $Re_2@site_4$ follow the distal and alternative reaction pathway, and the limiting potentials are -2.69 V/-2.31 V and -0.61 V/-1.47 V, respectively. For the highlighted distal-1 and enzymatic reaction pathway, the synergistic effect between dual TM atoms varies with each other. But both reaction pathways enlarge the charge distribution asymmetry under the 'capture-charge distribution-recapture-charge redistribution' mechanism, thus accelerating the hydrogenation process. Among the rest systems, $Mn_2@site_1$ and $Co_2@site_2$ follow the Distal-1 reaction pathway, while $Ru_2@site_1$, $W_2@site_2$, $Os_2@site_3$, $V_2@site_4$, $Cr_2@site_4$, and $W_2@site_4$ go through the enzymatic reaction pathway. Briefly, $Co_2@site_2$, $V_2@site_4$, and $Cr_2@site_4$ are selected as examples for analysis. For the $Co_2@site_2$ system, Gibbs free energy change is -0.32 eV after N_2 capture, within N-N bond length elongated to 1.15 Å; continuously, the $*N_2$ to $*N_2H$ need an energy input of 0.44 eV, within the N-N bond increase to 1.25 Å and the second TM atom participated to bond with the proximal N atom. Then, the distal N atom keeps being attacked by the second proton-electron pair to form $*N_2H_2$ with an energy input of 0.08 eV, and the N-N bond expands into 1.33 Å, demonstrating the further activation of the N_2 molecule. After the third proton hydrogenation, the first NH_3 is formed and desorbed away from the adsorbed system, leaving a bald N atom adsorbed on the active site, and the energy change of this process is -0.87 eV. Subsequently, the proton-electron pair continues to attack the isolate N atom until the second NH_3 form, within energy changes of -0.30 eV, -0.70 eV, and +0.35 eV for $*N - *NH$, $*NH - *NH_2$, and $*NH_2 - *NH_3$, respectively. Therefore, among the six electron-participated intermediates, the maximum values of the input energy are 0.44 eV during the first protonation process; thus, the $*N_2$ to $*N_2H$ is the potential determining step for the $Mn_2@site_1$ system via end-on configuration, and the limiting potential is -0.44 V, as depicted in **Figure 4(b)** and **Figure S8**.

For the enzymatic mechanism under the cooperation effect between two TM atoms in atomic diversity free DAC, as depicted in **Figure 4(a)**, the $H^+ + e^-$ pair initially protonates the distal-like adsorbed N atom as confirmed former, then the second $H^+ + e^-$ pair points out to protonate the other N atom. Gradually, the additional $H^+ + e^-$ pairs from the solution continue to hydrogenate the protonated N atoms until all the NH_3 desorption. As shown in **Figure 4** for $V_2@site_4$ and $Cr_2@site_4$ systems, N_2 is spontaneously captured by the active site with side-on configuration within adsorption energy changes of -0.83 eV and -0.49 eV. Meantime, the N-N bonds increase to 1.22 Å and 1.21 Å, respectively. Then the initially activated N_2 is attacked by the first $H^+ + e^-$ pair, forming $*N-*NH$ species, where the Gibbs free energy climbs to -0.55 eV and -0.19 eV, and the N-N bonds increase to 1.33 Å and 1.30 Å. The second $H^+ + e^-$ pair successfully turns to hydrogenate the other side N atom, generating $*NH-*NH$ with the Gibbs free energy changes of 0.91 eV and 0.23 eV.

Consequently, the third and fourth $H^+ + e^-$ pair continue to attack the formed $*NH-*NH$ to generate $*NH-$

$^*\text{NH}_2$ and $^*\text{NH}_2\text{-}^*\text{NH}_2$, causing the breakdown of the N-N triple bond. At the same time, the changes of Gibbs free energy are 0.18 eV and -0.58 eV, meaning that a 0.18 eV energy input is enough for the N-N bond breaking for $\text{V}_2@\text{site}_4$. Excitingly, the N-N broken energy of the $\text{Cr}_2@\text{site}_4$ system is -0.58 eV, suggesting the N-N bond's spontaneous breaking. Finally, for the fifth and sixth protonation, the $\text{H}^+ + \text{e}^-$ pair keeps attacking both isolated $^*\text{NH}_2$, causing the formation of $^*\text{NH}_3$. For this process, the Gibbs free energy climb step by step for both $\text{V}_2@\text{site}_4$ and $\text{Cr}_2@\text{site}_4$ systems, where the energy inputs are 0.19 eV and 0.05 eV for fifth step and 0.18 eV and 0.19 eV for sixth step, respectively. For the desorption of $^*\text{NH}_3$, the energy changes of this process usually do not conclude for limiting potential finding since any $\text{H}^+ + \text{e}^-$ pair is participating. Therefore, among the six $\text{H}^+ + \text{e}^-$ pair protonation processes, the max Gibbs free energy changes of $\text{V}_2@\text{site}_4$ and $\text{Cr}_2@\text{site}_4$ systems are 0.28 eV and 0.29 eV for Gibbs energy changes of $^*\text{N}\text{-}^*\text{N}$ - $^*\text{N}\text{-}^*\text{NH}$ in both $\text{V}_2@\text{site}_4$ and $\text{Cr}_2@\text{site}_4$ systems, thus the limiting potential of them are -0.28 V and 0.29 V vs CHE (Computational Hydrogen Electrode⁷¹), respectively. Similarly, the Gibbs free energy is -0.36 V, -0.25V, and -0.48 V for the rest of $\text{Ru}_2@\text{site}_1$, $\text{W}_2@\text{site}_2$, and $\text{Os}_2@\text{site}_3$ systems, respectively.

It is noted that for all the selected candidates, the $\text{Mn}_2@\text{site}_1$ and $\text{Co}_2@\text{site}_2$ exhibit end-on configuration while $\text{Ru}_2@\text{site}_1$, $\text{W}_2@\text{site}_2$, $\text{Os}_2@\text{site}_3$, $\text{V}_2@\text{site}_4$, and $\text{Cr}_2@\text{site}_4$ show side-on configuration. But for the hydrogenation process, especially for the $^*\text{N}_2$ to $^*\text{N}_2\text{H}$, $^*\text{N}_2\text{H}$ to $^*\text{N}_2\text{H}_2$, $^*\text{N}\text{-}^*\text{N}$ to $^*\text{N}\text{-}^*\text{NH}$, $^*\text{N}\text{-}^*\text{NH}$ to $^*\text{NH}\text{-}^*\text{NH}$, $^*\text{NH}\text{-}^*\text{NH}$ to $^*\text{NH}\text{-}^*\text{NH}_2$, $^*\text{NH}\text{-}^*\text{NH}_2$ to $^*\text{NH}_2\text{-}^*\text{NH}_2$, $^*\text{N}_2\text{H}_2$ to $^*\text{N}$, $^*\text{N}$ to $^*\text{NH}$, and $^*\text{NH}$ to $^*\text{NH}_2$ steps, nearly all of them adsorbed on both TM active sites (see in **Figure S9**), thus lower the activation energy during the protonation process. For the $\text{Ni}_2@\text{site}_4$, $\text{W}_2@\text{site}_4$, and $\text{Re}_2@\text{site}_4$ systems, the isolated active site participated in the initial N-N activation and hydrogenation process reaction steps. In contrast, the second TM site does not participate in it significantly, thus leading to their hard hydrogenation of them. Hence, dual TM atoms must take part in the eNRR process to enhance the cooperation effect between dual atoms. At the same time, the adsorption behavior, activation behavior, and desorption behavior are significantly changed since the heteronuclear of dual TM exhibits differential properties in heteronuclear DAC, thus breaking the limitation of homonuclear DAC.

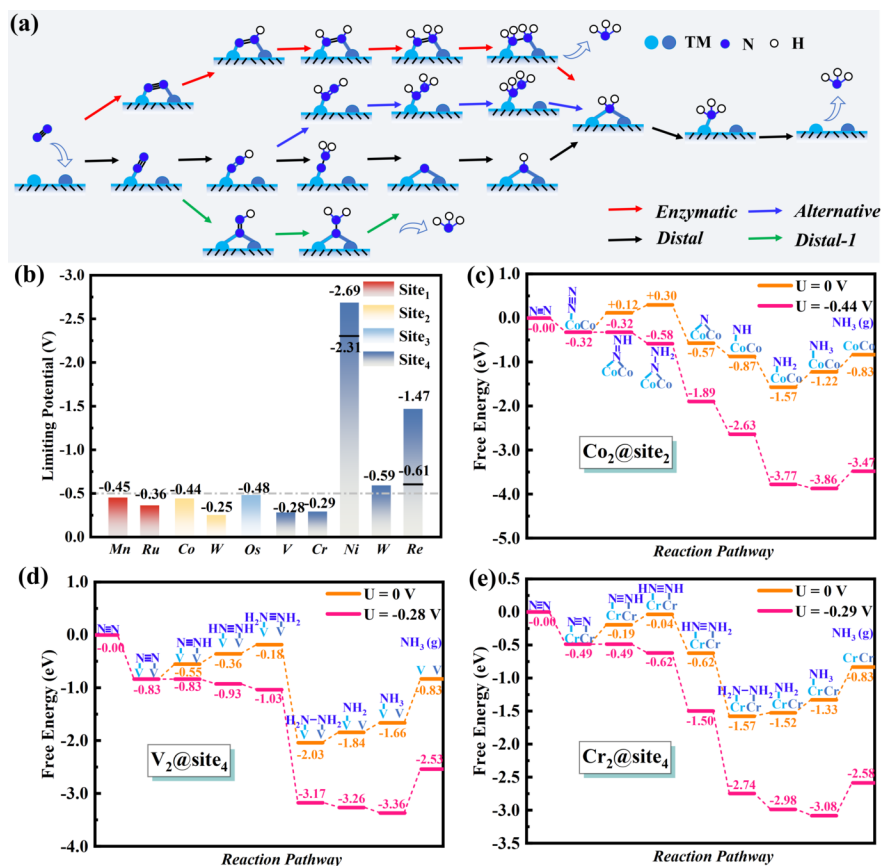


Figure 4 . (a) Limiting potential of the selected candidates (Mn₂@site₁, Ru₂@site₁, Co₂@site₂, W₂@site₂, Os₂@site₃, V₂@site₄, Cr₂@site₄, Ni₂@site₄, W₂@site₄, and Re₂@site₄, respectively. (b)-(e) Gibbs free energy changes diagrams for Co₂@site₂, V₂@site₄, and Cr₂@site₄, respectively.

3.4 Origin of high catalytic activity on TM₂@site_x (x = 1, 2, 3, 4)

The intrinsic electronic properties of the atomic diversity free dual TM atom catalyst, including charge density difference, Bader analysis, projected density of state (pDOS), and COHP, are systematically investigated for the dual TM atom cooperative eNRR process. We primarily focus on charge distribution for the selected candidates. Typically, the charge density difference of end-on and side-on configurations of the screened seven systems is presented by Mn₂@site₁ and V₂@site₄. The charge density difference of the representative Mn₂@site₁ and V₂@site₄ meets the results analyzed previously, guaranteeing the accuracy of our analysis. Quantitatively, charges back to the captured N₂ from the substrate are insured, as shown in **Figure 5** (b), meeting the analyzed 'backdonation' process. Next, the pDOS of the N₂adsorbed systems and the COHP of the N₂ molecule are explored to determine adsorption and activation behavior. As plotted in **Figure 5** (b)-(g), the pDOS of the d orbital for each TM atom (colored dark and blue) are shown for comparison; meantime, the orbital of adsorbed N₂ is also considered for analyzing the hybridization between d orbital of TM atom and the orbital of N₂. As it can be seen, for all the selected systems, TM₁ and TM₂ exhibit observable variety d orbital of the pDOS, further revealing the intrinsic properties' variety induced by coordinate environment change. Besides, the electron orbital of N₂ is highly hybridized with the d orbital of dual TM atoms. For the Mn₂@site₁ system, the Mn₁ atom is the main contributor near the Fermi level, where the d orbital of Mn₁ acts with the 3σ of the N₂ molecule; the primary reason is that N₂ adsorbed on the Mn₁ site, which is suitable for charge transfer. For the deep occupied orbital, the d orbital of Mn₁ and Mn₂ significantly contribute to N₂ activation gradually. In contrast, the d orbital of Mn₂ becomes a

deeper occupied state since it is far from the Fermi level. Those results demonstrated that both Mn atoms gain electrons in the $\text{Mn}_2@\text{site}_1$ system, and the d orbital of Mn_2 gains more electrons from the substrate. Meantime, both Mn atoms take up the unoccupied state above the Fermi level, indicating that both Mn atoms lose electrons as well, which meet the analyzed "donate-back donate"¹⁹ mechanism. In addition, the d orbital electron of the Mn_1 atom overlaps with N_2 more than Mn_2 atoms, where the main reason is that the N_2 molecule bonds with Mn_1 , but it can't be ignored that the Mn_2 offers an extra force to attract the N_2 molecule, thus explain why both Mn atom bond with N_2 in the hydrogenation process.

To better explore the activation of the N_2 molecule, COHP analysis is employed to illustrate the bond nature of adsorbed N_2 ; the injected electrons from the $\text{Mn}_2@\text{site}_1$ lower the occupied 3σ orbital of N_2 , leading the antibonding state occurred near the Fermi energy, thus weakening the N-N triple bond, and further confirmed by integrated COHP (-ICOHP) (-ICOHP = -18.40). Similarly, For the $\text{Co}_2@\text{site}_2$ via end-on configuration, the interaction between N_2 and Co atoms are weaker than $\text{Mn}_2@\text{site}_1$ systems, which mainly originate from fewer electron transfer among them and the little activation of N-N molecule, as confirmed by the Bader analysis (nearly 0.36 |e|) and ICOHP (-20.80). Still, both Co atoms contribute to the activation of N_2 than the Mn atom, which can be seen from the pDOS hybridization. For the side-on configuration, including $\text{Ru}_2@\text{site}_1$, $\text{W}_2@\text{site}_2$, $\text{Os}_2@\text{site}_3$, $\text{V}_2@\text{site}_4$, and $\text{Cr}_2@\text{site}_4$ system, the interaction between N_2 and TM active sites is more significant than the end-on configuration. Quantitatively, the side-on configuration's charge transfer between N_2 and substrate range from 0.66 |e| to 0.96 |e| is larger than that of the end-on configuration (range from 0.36 |e| to 0.44 |e|), as shown in **figure 5(b)**. What's more, the orbital hybridization between N_2 and TM atoms is not limited to the 3σ orbital of N_2 but expands to 2π and $2\sigma^*$ orbitals of N_2 since the co-adsorption of N_2 for both TM atoms. This led to the full activation of the N_2 molecule, and it is also observed in COHP analysis, where the ICOHP values increased to -18.15, -16.18, -19.08, -10.99, and -17.99 for $\text{Ru}_2@\text{site}_1$, $\text{W}_2@\text{site}_2$, $\text{Os}_2@\text{site}_3$, $\text{V}_2@\text{site}_4$, and $\text{Cr}_2@\text{site}_4$, respectively. The main reason is the cooperation of the two TM atoms, which offer an intrinsic force to pull the triple bond of N-N. Still, the cooperation effect is also observed in the hydrogenation process for the end-on configuration, thus lowering the Gibbs free energy barriers under the protonation process. Therefore, for both side-on and end-on configurations, though the side-on configuration takes more advantages than the end-on ones for the N_2 activation and the $^*\text{N}_2$ to $^*\text{N}_2\text{H}$ hydrogenation, the cooperation during the protonated species is also an important factor for whole eNRR, which should be comprehensively studied in the future investigations. Hence, we explore the intermediate species to illustrate the intrinsic mechanism further. As an excellent descriptor in the eNRR field, the charge transformation has been widely employed to dig out intrinsic mechanical properties for the intermediate steps^{72, 73}.

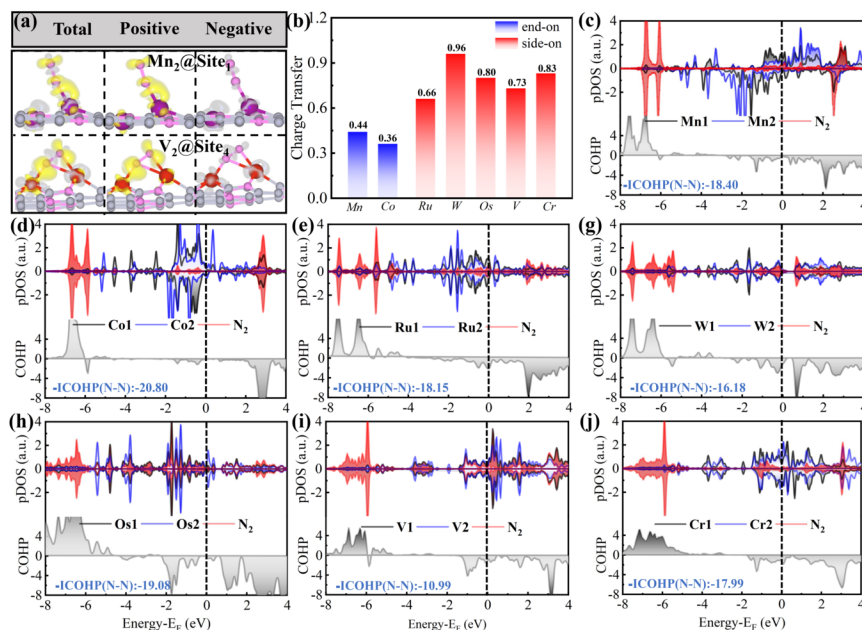


Figure 5 . (a) Charge density difference of the represented N₂ captured Mn₂@site₁ and V₂@site₄ systems, the yellow and green area stand for the charge depletion and accumulation, the isosurface value is 0.05 Å³; the dark magenta and red ball represent the Mn and V atoms. (b) the values of charges transfer between the adsorbed N₂ molecule and the substrate for the Mn₂@site₁, Co₂@site₂, Ru₂@site₁, W₂@site₂, Os₂@site₃, V₂@site₄, and Cr₂@site₄; (c)-(j) pDOS and COHP of N-N bond for the selected N₂ adsorbed TM₂@site_x (x = 1, 2, 3, 4) systems, including Mn₁@site₁, Co₂@site₁, Ru₂@site₂, W₂@site₂, Os₂@site₃, V₂@site₄, and Cr₂@site₄, respectively.

Generally, several moieties, such as the adsorbed species, active dual TM sites, neighboring atoms bonded to the TM site, and the substrate without TM and TM-bonded atoms, are common in most eNRR studies. But in our systems, the TM sites are divided into the fundamental moiety of intermediate species (moiety 1) and the substrate without TM and TM-bonded atoms (moiety 6). Four new moieties are implemented in our systems, including moiety 2, moiety 3, moiety 4, and moiety 5. As depicted in **Figure 6(a)**, to ensure the various roles of TM1 and TM2 and the adjacent atoms affected by each TM atom. For the Mn₂@site₁ system, all the intermediate species gain electrons from the substrate except for the last species (*NH₃). Meanwhile, both TM atoms lose electrons after adsorbing the N₂ molecule except for the TM2 atom in *N₂ intermediate, leading to electrons transfer into the adsorbed species, similar to most studies in the eNRR field. However, we note that moiety 4 and moiety 5 gain electrons, where the extra electrons may come from the substrate or the TM atoms, but considering the substrate gains electrons in 3 to 7 protonation process, moiety 4 and moiety 5 gain electrons from the TM atoms in 3 to 7 protonation steps reasonably. In contrast, the 1 to 3 steps remain uncertain. Besides, it is notable that each TM atom and its adjacent atoms show differential charge transfer for the whole hydrogenate steps, mainly from the fully heteronuclear of two homonuclear TM atoms. For a similar end-on configuration Co₂@site₂ system, the charge distribution changes significantly; moiety 1 obtains electrons for the first six proton steps and loses electrons for the last step. For Moiety 4 and 5, slight charge transformation in moiety 4 while huge electron transferred into moiety 5, demonstrate each TM atom act in various roles. Meanwhile, all moiety 2, moiety 3, and moiety 6 as donors donate electrons to moiety 1, moiety 4, and moiety 5, causing the TM atom to act as the electron donor and carriers among the eNRR process for the Co₂@site₂ system. Charge transformation between various moieties becomes more complex for the side-on configuration N₂ adsorbed systems. Taking V₂@site₄ and Cr₂@site₄ as examples, both moiety 2 and moiety 3 lose electrons for the whole interaction. Meanwhile, moiety 6 loses electron less than TM1 and TM2 slightly. In contrast, moiety 4 and moiety 5 obtain most of the electrons compared with

moiety 1, suggesting that TM-bonded atoms obtain electrons from both TM atoms and moiety 6, while the electron transfer into moiety1 only originates from the TM atoms. Therefore, both TM atoms act as two roles during the electrocatalytic process; that is, both the TM atoms lose electron and donated them to the adjacent atoms (either adsorbed species or TM-bonded atom in the substrate), which is inversed to most of the eNRR studies, where the TM atoms act as charge carrier among most studies. The primary origin may be due to the additional TM atom participating in the eNRR process and offering more electrons. Those may explain why heteronuclear DAC is more effective than homonuclear DAC for the eNRR.

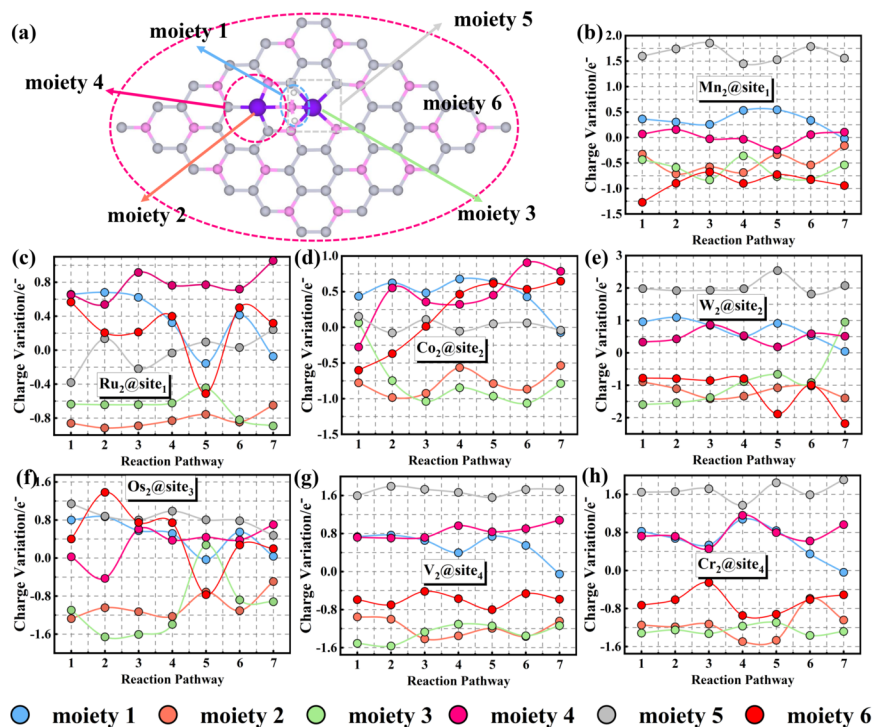


Figure 6. (a) Definition of six moieties for the adsorbed $*N_xH_y$ on various $TM_2@site_x$ ($x = 1, 2, 3, 4$) systems. (b)-(h) charge variation of the six moieties for $Mn_2@site_1$, $Ru_2@site_1$, $Co_2@site_2$, $W_2@site_2$, $Os_2@site_3$, $V_2@site_4$, and $Cr_2@site_4$, respectively.

3.6 Selectivity and thermostability of filtrated $TM_2@site_x$ ($x = 1, 2, 3, 4$) systems

For eNRR performance in many studies, the competitive hydrogen evolution reaction (HER) is the major hamper for ammonia yield. Thus, it is necessary to compare N_2 and H atom adsorption strength. As depicted in **Figure 7**, for all the selected systems, the Gibbs free energy of $*N_2$ is smaller than the corresponding $*H$ (mean the ΔG_{*N_2} is more negative) and can be regarded as efficient adsorption of N_2 , thus inhibiting the competitive HER. Therefore, the $Ru_2@site_1$, $W_2@site_2$, and $W_2@site_4$ may not be suitable for the eNRR of the HER competition. Therefore, they are excluded from eNRR exploration. Among the rest systems with high activity eNRR performance, high stability is required for $Mn_2@site_1$, $Co_2@site_2$, $Os_2@site_3$, $V_2@site_4$, and $Cr_2@site_4$ systems. Herein, the AIMD simulation is performed at 300 K for 9 ps within a step of 1.5 fs are employed. As shown in **Figure 7** (b)-(f), after simulation, the structures of the selected systems are well maintained, meaning that the systems chosen could keep their geometry under 300 K. At the same time, the changes in temperature and energy are slightly, further revealing the thermostability of the selected systems. Thus, the $Mn_2@site_1$, $Co_2@site_2$, $Os_2@site_3$, $V_2@site_4$, and $Cr_2@site_4$ would keep stable during the eNRR process.

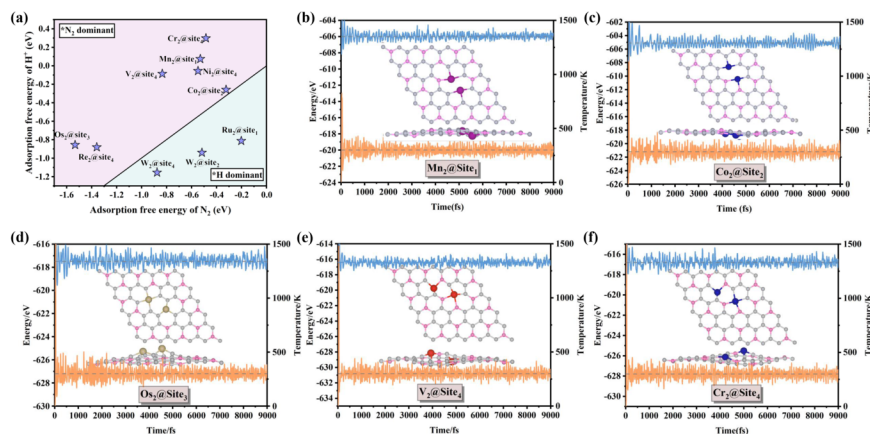


Figure 7 . (a) The selectivity of eNRR and HER for ten kinds of selected candidates. (b)-(f) AIMD simulations for Mn₂@site₁, Co₂@site₂, Os₂@site₃, V₂@site₄, and Cr₂@site₄ lasting for 9000 fs, the insert figures are the after-simulated structures of Mn₂@site₁, Co₂@site₂, Os₂@site₃, V₂@site₄, and Cr₂@site₄, respectively.

4. Conclusion

In conclusion, for the proposed 'atomic diversity free but intrinsic properties variety' homonuclear TM catalyst, we verified that the 'capture-charge distribution-recapture-charge redistribution' mechanism could occur in dual TM catalyst for both end on and side on N₂ configuration under the synergistic effect of dual TM sites as well. After ensuring the stability of TM-anchored defective C₃N systems, the heteronuclear of homonuclear DAC behavior is revealed by comparing the bond length (TM atom bonded with an adjacent atom), charge transfer, magnetic moment, d band center of TM1 and TM2. Subsequently, we highlighted the advantages of heteronuclear DAC. We made high throughput screenings to filtrate initial candidates for eNRR, and the corresponding screenings are the adsorption Gibbs free energy of N₂ ($\Delta G^*_{N_2} < 0$ eV), the first ($\Delta G^*_{N_2} - \Delta G^*_{N_2H} < 0.50$ eV) and last pronation steps ($\Delta G^*_{NH_2} - \Delta G^*_{NH_3} < 0.50$ eV). Meanwhile, machine learning is implemented to verify the impact of the atomic diversity effect. However, it is entirely removed, and it is suggested the r_{TM} may take an essential role in the NRR process, which should be further studied in the future.

Consequently, seven candidates, Mn₂@site₁, Ru₂@site₁, Co₂@site₂, W₂@site₂, Os₂@site₃, V₂@site₄, and Cr₂@site₄ are selected for fully eNRR calculation, and their corresponding limiting potentials are -0.45 V, -0.36 V, -0.44 V, -0.25 V, -0.48 V, -0.28 V, and -0.29 *vs* CHE, respectively. To evaluate the intrinsic mechanism, the electronic properties, including pDOS, Bader analysis, charge density difference, and COHP, are implemented for the intrinsic properties only determined systems; it was found that each TM atom exhibits different roles in the eNRR process, which lower the energy barriers for each intermediate since the synergistic effect between two TM active sites under the proposed 'capture-charge distribution-recapture-charge redistribution' mechanism. Finally, the selectivity and thermostability are systematically investigated by comparing the adsorption Gibbs free energy of *N₂ and *H, as well as the AIMD simulations, and five candidates, Mn₂@site₁, Co₂@site₂, Os₂@site₃, V₂@site₄, and Cr₂@site₄ are filtrate eventually. This study proves that the homonuclear DAC can be functionalized as a heteronuclear DAC and develops a new method for simplifying the complicated secondary experimental heteronuclear DAC synthesis procedure.

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