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Theoretical exploration of the nitrogen fixation mechanism of two-dimensional dual-metal $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ electrocatalysts†

Jinxin Sun,^{‡a} Peng Xia,^{‡a} Yuxing Lin,^{‡a} Yunfan Zhang,^a Anjie Chen,^a Li Shi,^b Yongjun Liu,^a Xianghong Niu,^{‡c} Ailei He^{*a} and Xiuyun Zhang^{‡*a}

The electrochemical nitrogen reduction reaction (eNRR) to NH_3 has become an alternative to traditional NH_3 production techniques, while developing NRR catalysts with high activity and high selectivity is of great importance. In this study, we systematically investigated the potentiality of dual transition metal (TM) atom anchored electrocatalysts, $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ ($\text{TM}_1, \text{TM}_2 = 3(4)\text{d}$ TM atoms), for the NRR through the first principles high-throughput screening method. A total of 78 $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ candidates were designed to evaluate their stability, catalytic activity, and selectivity for the NRR. Four $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ candidates ($\text{TM}_1\text{TM}_2 = \text{NiRu}, \text{FeNi}, \text{TiNi},$ and NiZr) with an end-on N_2 adsorption configuration, and two candidates ($\text{TM}_1\text{TM}_2 = \text{TiNi}$ and TiFe) with a side-on adsorption configuration, were screened out with the advantage of suppressing the hydrogen evolution reaction (HER) and exhibiting high NRR activity. Moreover, the catalysts with end-on and side-on N_2 adsorption configurations were determined to favor distal and consecutive reaction pathways, respectively, with favorable limiting potentials of only -0.33 V to -0.53 V. Detailed analysis showed that the N_2 adsorption and activation are primarily ascribed to the strong back-donation interactions between the d-electrons of TM atoms and the anti-orbitals of an N_2 molecule. Our findings pave a way for the rational design and rapid screening of highly active C_9N_4 -based catalysts for the NRR.

New concepts

Inspired by the synergistic effect of multi-active centers in dual-atom catalysts (DACs) or few-atom catalysts (FACs), we proposed to explore the nitrogen reduction reaction (NRR) performance of $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ ($\text{TM} = 3(4)\text{d}$ transition metal atoms) electrocatalysts by a high-throughput screening method. Compared with many SACs and DACs, the screened dual-metal atom $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ candidates are found to display ultra-high stabilities, high NRR activity, and ability to effectively suppress the hydrogen evolution reaction (HER). The superior activity of these $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$ s can primarily be ascribed to the strong back-donation interactions between the d-electrons of TM atoms and the anti-orbitals of a N_2 molecule and other nitrogen intermediates. This study paves a way for the rational design and rapid screening of highly active C_9N_4 -based catalysts for the NRR.

1. Introduction

Currently, the electrochemical nitrogen reduction reaction (eNRR) to ammonia (NH_3) is attracting more attention due to its mild conditions with attractive features of low cost and sustainable development,^{1–3} and is regarded as one promising way to break the barrier of industrial NH_3 synthesis under harsh conditions. During the eNRR, the use of suitable catalysts is crucial, because the inertness of N_2 leads to the difficulty of its adsorption and activation, leading to a low reaction efficiency.^{4–6} In addition, the N_2 reduction process is seriously suppressed by the accompanying hydrogen evolution reaction (HER).^{7–9} Therefore, designing or fabricating NRR catalysts with high activity and high selectivity is one great challenge for researchers.

To date, various electrocatalysts for the NRR have been developed and explored by experimental and theoretical researchers.^{10–13} Among them, the single-metal atom catalysts (SACs) or few-metal atom catalysts (FACs), in which single or few metal atoms are well adsorbed on suitable substrates, are becoming one promising type of candidates for the eNRR and other electrochemical reactions due to their advantage of precisely controlling the rate-determining or other reaction steps.^{14–17} For example, Zeng *et al.* synthesized a N-doped carbon monolayer with Ru atoms anchored, which

^a College of Physics Science and Technology, Yangzhou University, Yangzhou 225002, China. E-mail: heailei@yzu.edu.cn, xyzhang@yzu.edu.cn

^b State Key Laboratory of Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), School of Materials Science and Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210023, China

^c New Energy Technology Engineering Laboratory of Jiangsu Province & School of Science, Nanjing University of Posts and Telecommunications, Nanjing, 210023, China. E-mail: xhniu@njupt.edu.cn

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‡ Jinxin Sun, Peng Xia, and Yuxing Lin contributed equally to this work.

achieved a record-high faradaic efficiency (FE) of 29.6% and a yield rate of $120.9 \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{mag}_{\text{cat}}^{-1}$.¹⁸ Li *et al.* reported that the SAC of Mo atoms atomically distributed graphdiyne and has a high FE of over 21% and a yield rate of $145.4 \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{mag}_{\text{cat}}^{-1}$.¹⁹ However, the key challenge in designing outstanding SACs or FACs is the choice of supporting substrates, which play an important role in anchoring and transferring charges to metal atoms. Interestingly, various 2D materials, *e.g.*, graphene,²⁰ transition metal dichalcogenides (TMDs),^{21,22} hexagonal BN,²³ *etc.*, have been widely used as supports for SACs or FACs. Particularly, B or N atom doped 2D materials are confirmed to be good at binding and enhancing the catalytic activity of metal atoms.^{24–26} Through density functional theory calculations, Le *et al.* revealed that SACs obtained by Mo anchoring on N-doped graphene can achieve 100% selectivity for N_2 fixation.²⁷ Similarly, Zhao *et al.* found that “CrN₃” doped graphene possesses excellent catalytic performance for N_2 reduction.²⁸ Interestingly, Jiao *et al.* revealed that the NRR activity of the Fe atom in Fe–N–C SACs can be greatly improved by coordinating with a B dopant,²⁹ in which the limiting potential (U_L) of the NRR on Fe–B₂N₂ is -0.65 V. Besides, Ou *et al.* found a highly active NRR catalyst by embedding isolated Mo atoms on N-doped black phosphorous,³⁰ with U_L of -0.56 V.

In addition to SACs, the FACs possessing two or more active metal centers^{31,32} were also revealed to be potential NRR catalysts due to their synergistic effects in adjusting the adsorption configuration of NRR reactive species and reducing the energy barrier in the reaction process. For example, Luo *et al.* reported that the FeMo dual atomic cluster embedded on N-doped carbon shows an FE of 41.7% at 0.2 V for the NRR, much smaller than those of its SAC counterparts (FeN₄ and MoN₄).³³ Deng *et al.* systematically studied the NRR reactivity of homo dual atomic catalysts formed by 20 transition metal (TM) elements supported by N-doped graphene and screened out Ru₂N₆@G as an excellent catalyst.³⁴ Zheng *et al.* theoretically designed hetero dual-metal Fe/M–N–C catalysts and revealed the synergistic effect of Fe/M dual-metal active sites by theoretical calculations.³⁵ Very recently, Zheng *et al.* systematically investigated the catalytic performance of various triple-TM clusters anchored on nitrogen-doped graphene for the NRR and confirmed that Co₃–N₄@G possesses the highest activity with a limiting potential of -0.41 V through the enzymatic mechanism.³⁶ Moreover, Li and co-workers revealed that Ru₃–N₄@G with three Ru trimer clusters anchored on N-doped carbon (Ru₃–N₄) have better 2-amino-benzaldehyde catalytic activity than the SAC counterpart of RuN₄.³⁷

Furthermore, many pristine 2D C_xN_y systems, such as g-C₃N₄, g-C₂N, and g-CN, have received extensive attention in many catalysis fields due to their large surface area, high stability, rich coordination environments, *etc.*^{16,38,39} As a member of the C_xN_y family, C₉N₄ possesses semimetallic properties, high thermodynamic stability, and numerous nanopores favorable for TM loading.⁴⁰ For example, Zhou *et al.* theoretically designed Ni@C₉N₄ bifunctional electrocatalysts for efficient water splitting.⁴¹ Chen *et al.* screened TM@C₉N₄ (TM = 3d,

4d, and 5d TM atoms) candidates for potential NRR catalysts by high-throughput computation, and found that the optimal catalyst W@C₉N₄ favors the distal mechanism with a confinement potential of -0.24 V.⁴² However, the work of anchoring homo-/hetero-nuclear transition metal atoms on C₉N₄ to obtain excellent NRR catalysts has not been addressed.

In this work, we systematically explored the NRR performance of bimetal catalysts, TM₁TM₂@C₉N₄ (TM₁TM₂ = 3d, 4d TM atoms), by first principles high-throughput calculations. A total of 78 TM₁TM₂@C₉N₄ candidates, including 12 homo dual TM based systems and 66 hetero dual TM based systems, are considered. After the six-step screening, we obtained five high activity TM₁TM₂@C₉N₄ catalysts with high stability and high selectivity.

2. Computational methods and modeling

All the calculations were carried out using the projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP).^{43,44} The exchange–correlation interaction was treated using the generalized gradient approximation (GGA) parameterized by Perdew,⁴⁵ Burke and Ernzerhof (PBE).^{46,47} A vacuum space of 18 Å was inserted in the z-direction of the $2 \times 2 \times 1$ C₉N₄ supercell to eliminate the interaction between adjacent periodic units. $3 \times 3 \times 1$ Monkhorst–Pack *k*-point meshes were applied to sample the first Brillouin zone, while denser *k*-points of $7 \times 7 \times 1$ were applied for electronic structure calculations. In structural relaxation, the total energy and the force on each relaxed atom were converged to 10^{-5} eV and 0.01 eV Å⁻¹. Spin polarization is considered, and the energy cutoff for the plane-wave basis set was 450 eV. *Ab initio* molecular dynamics (AIMD) simulations were applied to identify the thermodynamic stability of TM₁TM₂@C₉N₄ candidates.⁴⁸ In the electrochemical process of the NRR, six proton and electron transfer steps, *e.g.*, $\text{N}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_3$, are evolved. To efficiently evaluate the NRR activity of all the TM₁TM₂@C₉N₄ candidates, the reaction free energy (ΔG) for each fundamental step was calculated according to the computational hydrogen electrode (CHE) model.^{49,50} In this framework, the chemical potential of the proton–electron pair ($\text{H}^+ + \text{e}^-$) can be referenced to one half of that of H₂ under standard reaction conditions, and the change in the reaction free energy for each step can be evaluated as:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + eU + \Delta G_{\text{pH}} \quad (1)$$

where ΔE , ΔZPE , T , and ΔS are the reaction energy, zero-point energy, temperature (298.15 K), and entropy change, respectively. eU is the free energy contribution related to the applied potential U . ΔG_{pH} is the free energy correction of pH, which is the free energy correction related to H⁺ concentration and can be calculated using $\Delta G_{\text{pH}} = k_{\text{B}}T \times \text{pH} \times \ln 10$, and the pH value is assumed to be 0.

3. Results and discussion

3.1. Structures and stability of $\text{TM}_1\text{TM}_2@C_9N_4$

First, we investigated the structures and stabilities of these $\text{TM}_1\text{TM}_2@C_9N_4$ catalysts. As shown in Fig. 1a and b, the selected substrate is a 2×2 C_9N_4 supercell containing 72 carbon atoms and 32 nitrogen atoms. Here, eight of the 3d TM atoms (*e.g.*, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) and four of the 4d TM atoms (*e.g.*, Zr, Mo, Tc, and Ru) were taken into consideration. As a result, 78 dual-metal $\text{TM}_1\text{TM}_2@C_9N_4$ catalysts were constructed, including 12 homonuclear and 66 heteronuclear systems. Besides, three types of anchoring sites (S_1 , S_2 , and S_3) were tested: (i) S_1 configuration, two TM atoms sit in a horizontal line with each atom binding to three adjacent N atoms (see Fig. 1a), (ii) S_2 configuration, the TM-TM bond of the S_1 configuration was anticlockwise rotated by 30 degree (see Fig. 1b),

in which each TM atom only bonds with two nearest N atoms, and (iii) S_3 configuration, two TM atoms from the systems are no longer coordinated equally, and bind with two and three adjacent N atoms, respectively (see Fig. 1c). All the optimized structures are shown in Fig. S1–S4 in the ESI.† Clearly, no significant structural deformation is found for all the studied $\text{TM}_1\text{TM}_2@C_9N_4$ systems. For $\text{TM}_1\text{TM}_2@C_9N_4$ anchored with homonuclear dual-metal atoms ($\text{TM}_1 = \text{TM}_2$, see Fig. S1, ESI†), the S_1 configuration is favored for those with smaller diameters, *e.g.*, Fe, Co, and Ni, and the S_2 configuration is preferred for the candidates having larger diameters, *e.g.*, Ti–Mn, Cu, Zr, and Ru. Similarly, for $\text{TM}_1\text{TM}_2@C_9N_4$ combined with hetero TM atoms ($\text{TM}_1 \neq \text{TM}_2$), the S_1 configuration is observed for those with close to TM diameters (see Fig. S2, ESI†), and the S_2 one is found for those with larger TM diameters (see Fig. S3, ESI†). And for the systems with large diameter differences for two TM atoms, taking

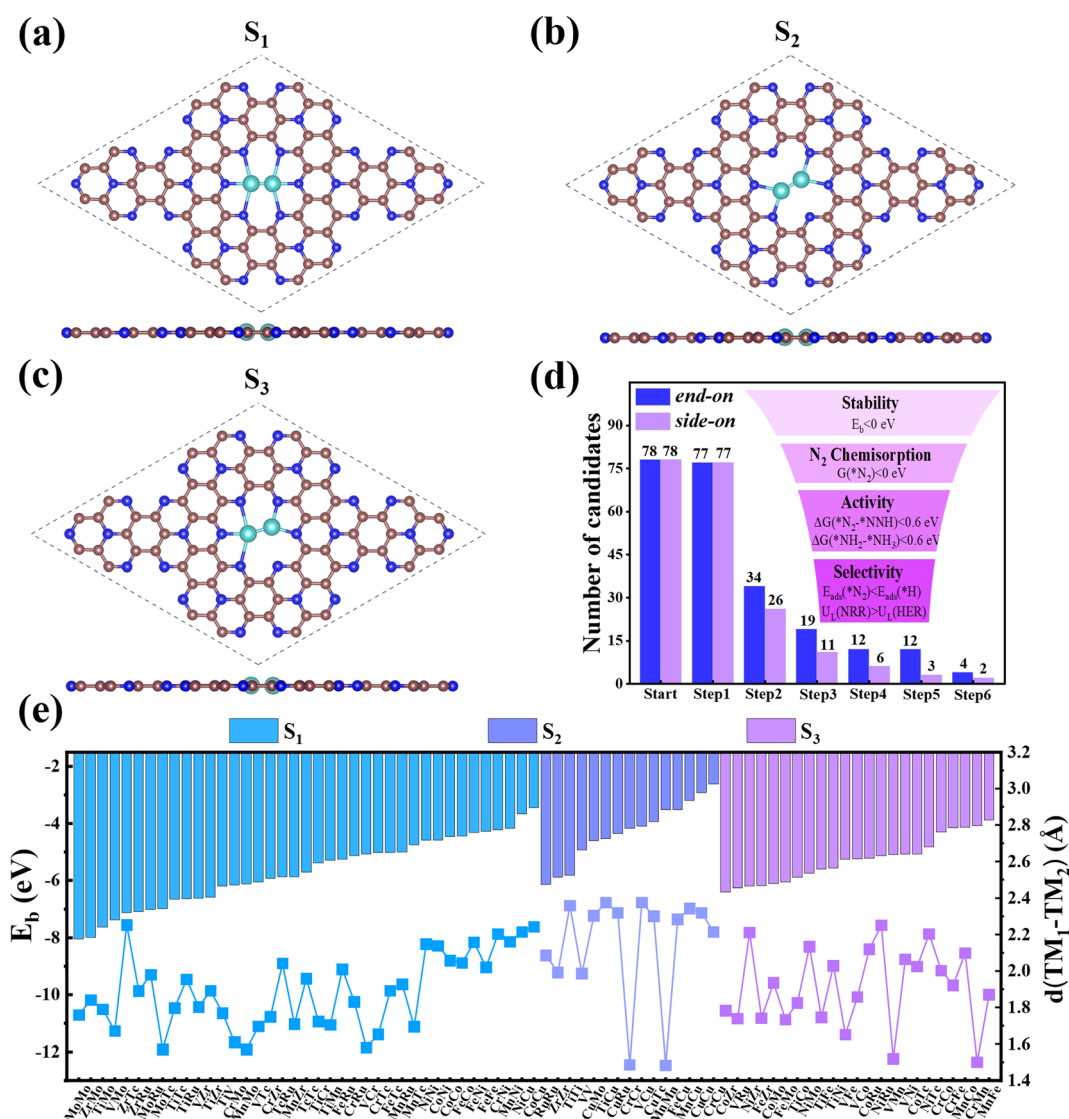


Fig. 1 Top and side views of (a) S_1 -, (b) S_2 - and (c) S_3 -configuration $\text{TM}_1\text{TM}_2@C_9N_4$. (d) Schematic illustration of the screening results by the "six-step" strategy. (e) Binding energies of dual TM atoms (TM_1 and TM_2) (E_b) and TM_1 - TM_2 bond length ($d_{\text{TM}_1\text{-TM}_2}$) of the 78 $\text{TM}_1\text{TM}_2@C_9N_4$ catalysts. The brown, navy blue and light blue balls represent C, N, and TM atoms, respectively.

CuTM@C₉N₄s (TM = Ti, V, Cr, Mn, Fe, Ru, Mo, and Tc) as an example, the Cu atom with a large atomic diameter favors the S₂ bonding style, while the other TM atoms with smaller diameters favor the S₃ bonding style. As the Cu atom sits out of the CuZr@C₉N₄ plane, it is unsuitable to form a dual catalytic center site for nitrogen adsorption. The TM₁-TM₂ bond lengths ($d_{\text{TM}_1\text{-TM}_2}$) of the remaining systems are around 1.484–2.376 Å, which are smaller than those in their metal bulk (see Fig. 1e). Among which, Mn₂@C₉N₄ has the shortest $d_{\text{TM}_1\text{-TM}_2}$ (= 1.484 Å), while TiCu@C₉N₄ has the longest $d_{\text{TM}_1\text{-TM}_2}$ (= 2.376 Å).

To explore the stability of these TM₁TM₂@C₉N₄ systems, we calculated their binding energies (E_b) per TM atom using the following equation:

$$E_b = \frac{E_{\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4} - E_{\text{C}_9\text{N}_4} - E_{\text{TM}_1} - E_{\text{TM}_2}}{2} \quad (2)$$

where $E_{\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4}$ and $E_{\text{C}_9\text{N}_4}$ are the energies of the TM₁TM₂@C₉N₄ monolayer and the C₉N₄ monolayer. E_{TM_1} and E_{TM_2} represent the energies of the isolated TM atoms. As Fig. 1e illustrates, the binding energies of all the studied TM₁TM₂@C₉N₄ systems are in the range from –8.64 eV to –2.62 eV, close to those of the TM@C₉N₄ monolayer and other carbon-based substrates doped with single or double TM atoms. The negative binding energies ($E_b < 0$) indicate the strong interaction of TM atoms on the C₉N₄ substrate, which is also the first step of screening criteria for suitable NRR catalysts. Such E_b is in line with the structural characters, as shown in Fig. 1c, and the candidates with smaller $d_{\text{TM}_1\text{-TM}_2}$ are found to have more prominent binding energies, and *vice versa*.

3.2. N₂ adsorption and activation of TM₁TM₂@C₉N₄

Then, we systematically explored the adsorption of N₂, which is the prerequisite for the subsequent hydrogenation process in the NRR. Generally, two forms of N₂ adsorption on catalysts, end-on and side-on configurations, are considered. In the two dual-metal atom doped systems, we investigated six possible adsorption ways, including two end-on adsorption configurations (E-1 and E-2, see Fig. 2a and b) and four side-on adsorption configurations (S-1, S-2, S-3, and S-4, see Fig. 2c–f). For the E-1 configuration, the end N atom from N₂ sits atop one TM atom (see Fig. 2a), while for the E-2 configuration, the end N atom from N₂ resides on the bridge site of two TM atoms (see Fig. 2b). As for S configurations, the N₂ plane is parallel with the C₉N₄ substrate. Of these, the S-1 and S-4 configurations have structures with the N≡N bond perpendicular to the TM–TM bond (see Fig. 2c and f), while for S-2 and S-3 configurations, the N≡N bond is found to be parallel to the TM–TM bond (see Fig. 2d and e).

In order to ensure the effective adsorption of N₂, the Gibbs free energy of N₂, $\Delta G(*\text{N}_2) < 0$ eV, is set as the second screening criterion, and the catalysts that could effectively adsorb N₂ in two adsorption configurations are selected. The $\Delta G(*\text{N}_2)$ values of 77 TM₁TM₂@C₉N₄ with end-on and side-on bonding characters are described in Fig. 2g and h, respectively. It is observed that $\Delta G(*\text{N}_2)$ values on 34 TM₁TM₂@C₉N₄ with end-on adsorption for N₂ are negative, ranging from –0.001 to –0.91 eV. Besides, 26 candidates with side-on adsorption for N₂ are confirmed to have

negative $\Delta G(*\text{N}_2)$, around –0.03 to –1.60 eV. Among which, 17 systems display negative $\Delta G(*\text{N}_2)$ in both adsorption configurations, ranging from –0.03 to –0.85 eV. Except TiNi@C₉N₄, TiCu@C₉N₄, and FeNi@C₉N₄, the $\Delta G(*\text{N}_2)$ values of all the other TM₁TM₂@C₉N₄ candidates with end-on adsorption patterns are more negative than those of side-on configurations, indicating that they are more energetically favorable. It is noted that most candidates containing Cr or Mn atoms (20 systems) are not conducive to the adsorption of N₂; exceptions are found for CrNi@C₉N₄, CrCu@C₉N₄, and MnCu@C₉N₄ candidates with side-on adsorption configurations. The inertness of these candidates can be ascribed to the stable half occupied electronic structures of Cr(3d⁵4s¹) or Mn(3d⁵4s²). As for the systems containing 4d TM (= Zr, Mo, Tc, and Ru) atoms, end on adsorption of N₂ is favored, with an exception of TiZr@C₉N₄.

The N≡N bond lengths ($d_{\text{N}\equiv\text{N}}$) of the adsorbed N₂ molecule on these TM₁TM₂@C₉N₄ candidates are summarized in Fig. 2g and h. Compared with the free N₂ molecule (1.12 Å), the N≡N bond lengths for *N₂ were elongated, indicating the effective activation of the N₂ molecule. For the end-on adsorbed systems, the $d_{\text{N}\equiv\text{N}}$ values (= 1.147Å–1.160 Å) of the E-2 adsorption configurations are longer than those of the E-1 ones ($d_{\text{N}\equiv\text{N}} = 1.120$ –1.148 Å) (see Fig. 2g). However, for the side-on adsorbed systems, the $d_{\text{N}\equiv\text{N}}$ of *N₂ is much longer, around 1.162–1.279 Å, indicating that the N₂ molecule is more pronouncedly activated. Moreover, the $d_{\text{N}\equiv\text{N}}$ of the systems with the S-1 adsorption configuration (1.221–1.299 Å) is longer than those of the other three adsorption configurations (S-2: 1.167–1.247 Å, S-3: 1.162–1.187 Å, and S-4: 1.169–1.204 Å).

To explain the origin of the activation of N₂ on these TM₁TM₂@C₉N₄ substrates, the relationships of the N≡N bond length ($d_{\text{N}\equiv\text{N}}$) and the charge transfer from the TM₁TM₂@C₉N₄ substrate to *N₂ (ΔQ) are summarized in Fig. 2g and h. Clearly, the $d_{\text{N}\equiv\text{N}}$ is linearly related to ΔQ from TM₁TM₂@C₉N₄ to *N₂; that is, the more the charge transfer, the longer the N≡N bond length. Compared with the systems with end-on configurations ($\Delta Q = 0.096$ –0.489 *e*), more charge transfer is found for the ones with side-on configurations, *e.g.*, $\Delta Q = 0.327$ –1.071 *e* (see Fig. 2g and h). Accordingly, $d_{\text{N}\equiv\text{N}}$ values of the *N₂ in the side-on adsorption systems are longer than those of the end-on ones as discussed above. Also, the significant difference between $d_{\text{N}\equiv\text{N}}$ and ΔQ indicates that TM₁TM₂@C₉N₄ systems with side-on configurations for N₂ are easier to obtain electrons and activate the N≡N triple bond. Moreover, the systems with the E-2 adsorption configuration have more charge transfer ($\Delta Q = 0.333$ –0.489 *e*) than those of the E-1 adsorption configuration ($\Delta Q = 0.096$ –0.399 *e*), indicating that the E-2 adsorption configuration is easier to activate N₂ than the E-1 ones. The different activation behaviors can be attributed to the direct interaction between the N atoms of the E-2 adsorption configuration and the two TM atoms. As shown in Fig. 2j, the ΔQ of the S-1 adsorption configurations ($\Delta Q = 0.626$ –1.071 *e*) is higher than those of the S-3 ($\Delta Q = 0.327$ –0.496 *e*) and S-4 ($\Delta Q = 0.359$ –0.569 *e*) ones, indicating that the S-1 adsorption configuration is more likely to activate N₂, which can be attributed to the direct interaction of both N atoms with TM atoms in the S-1

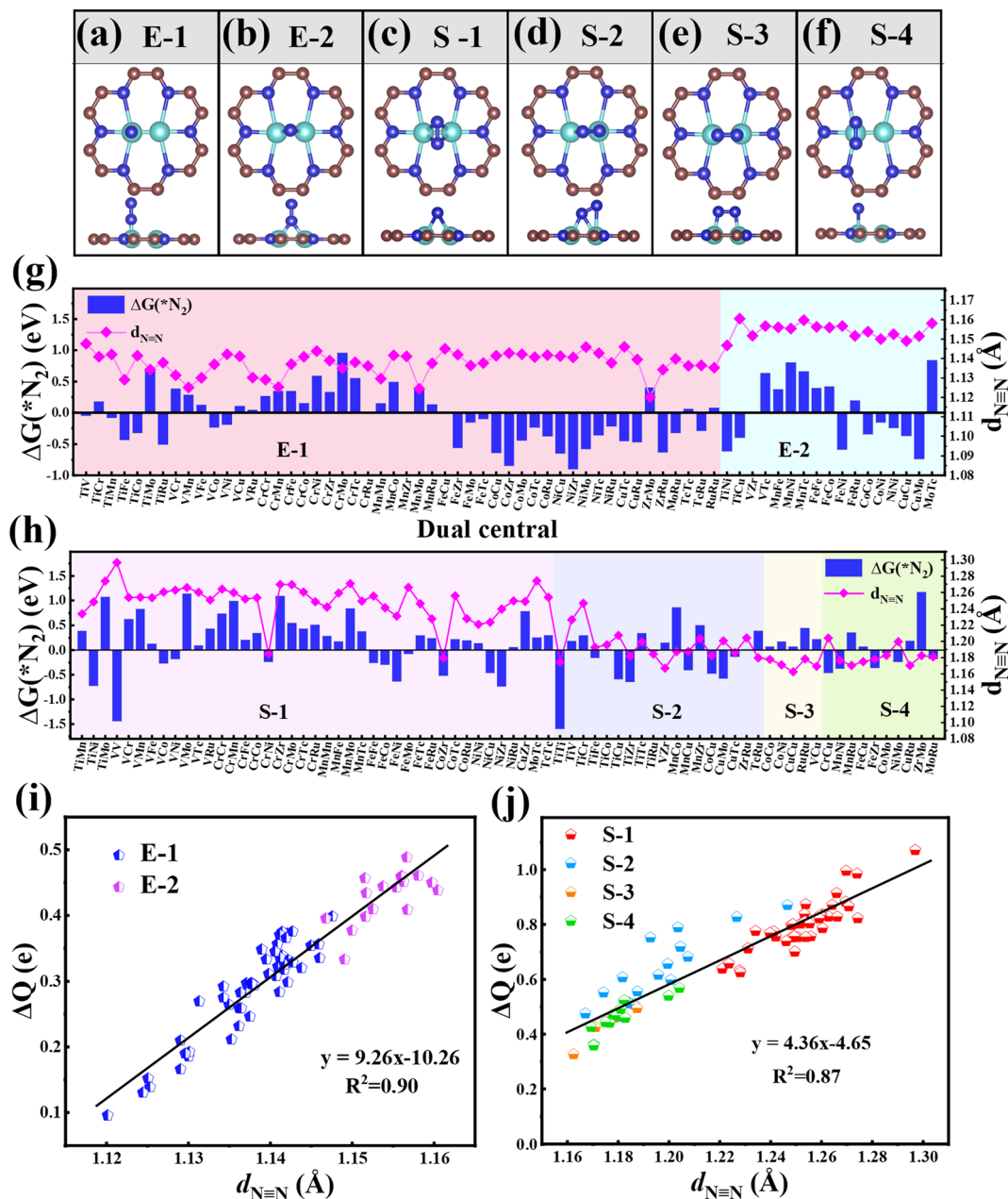


Fig. 2 The considered adsorption configurations of (a and b) end-on (E-1, E-2) and (c–f) side-on (S-1, S-2, S-3, and S-4) for N_2 on the $TM_1TM_2@C_9N_4$ substrate. Gibbs free energy change $G(*N_2)$ values and $N\equiv N$ bond lengths of $*N_2$ ($d_{N\equiv N}$) adsorbed on 77 $TM_1TM_2@C_9N_4$ catalysts with (g) end-on and (h) side-on adsorption configurations. Relationships between charge transfer (ΔQ) and $d_{N\equiv N}$ adsorbed on 77 $TM_1TM_2@C_9N_4$ catalysts through (i) end-on and (j) side-on adsorption configurations.

adsorption configuration. In contrast, the ΔQ of the S-2 adsorption configuration is moderate due to the direct interaction of one N with two TM atoms and the other N with only one TM atom. Based on the above analysis, we considered 34 $TM_1TM_2@C_9N_4$ candidates with the end-on configuration and 26 candidates with the side-on configuration having $\Delta G(*N_2) < 0$ eV in the following section (see Fig. 1d).

3.3. The NRR process of $TM_1TM_2@C_9N_4$

As the catalytic efficiency of the NRR is usually limited by the first and last protonation steps,^{39,42} the free energy change of

the first and last hydrogenation steps is set to be less than 0.60 eV, that is $\Delta G_{*N_2 \rightarrow *NNH} < 0.60$ eV, $\Delta G_{*NH_2 \rightarrow *NH_3} < 0.60$ eV, as the third and fourth step screening criteria.⁵² Fig. 3a and b plot the Gibbs free energy changes of the first ($\Delta G_{*N_2 \rightarrow *NNH}$) and last ($\Delta G_{*NH_2 \rightarrow *NH_3}$) protonation steps of the candidates with end-on and side-on N_2 adsorption configurations. As shown in Fig. 3a, 15 candidates with the end-on adsorption configuration like $CoRu@C_9N_4$, $CuTc@C_9N_4$, etc. are eliminated due to their larger protonation energy of $\Delta G_{*N_2 \rightarrow *NNH} > 0.6$ eV, leaving the remaining 19 candidates for potential catalysts. Next, 7 candidates, like $VZr@C_9N_4$, $TiV@C_9N_4$, etc., are further

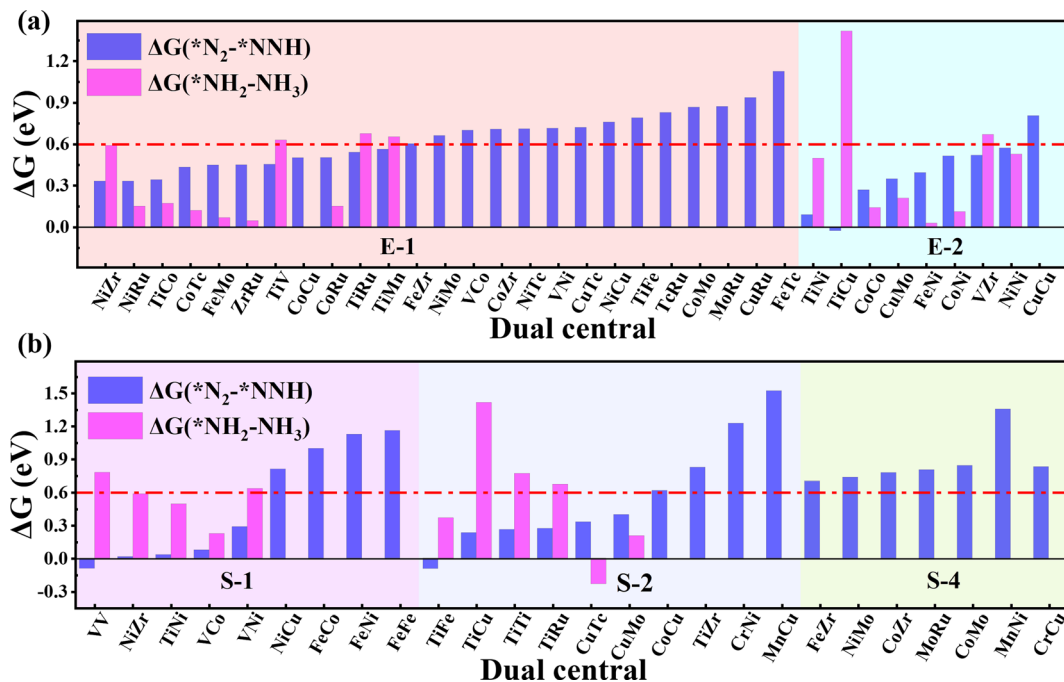


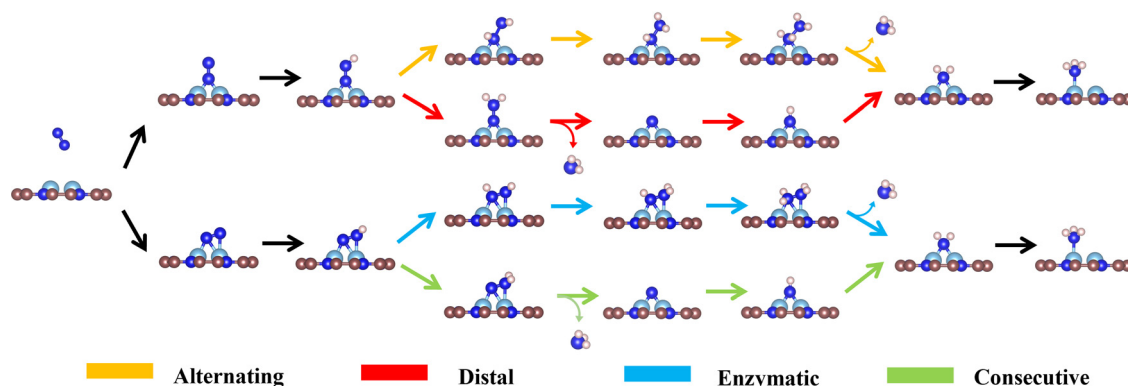
Fig. 3 Gibbs free energy change of $*N_2 + H^+ + e^- \rightarrow *NNH$ ($\Delta G(*N_2-*NNH)$) and $*NH_2 + H^+ + e^- \rightarrow *NH_3$ ($\Delta G(*NH_2-*NH_3)$) adsorbed on 34 and 26 $TM_1TM_2@C_9N_4$ catalysts through (a) end-on and (b) side-on configurations.

rejected due to their higher protonation energies in the last step with $\Delta G_{*NH_2 \rightarrow *NH_3} > 0.6$ eV. For the side-on adsorption configurations, respective 15 candidates and 5 candidates are rejected due to the higher energies for the first and last protonation steps (see Fig. 3b). As a result, 18 $TM_1TM_2@C_9N_4$ candidates with 12 end-on and 6 side-on adsorption configurations are reserved based on the third and fourth step screening criteria (see Fig. 1d).

To carefully examine the potential-determining step (PDS) of each catalyst, we further do a full reaction path search for the remaining 18 $TM_1TM_2@C_9N_4$ candidates. For 12 end-on adsorption configurations, 8 $TM_1TM_2@C_9N_4$ candidates ($TM_1TM_2 = NiRu, TiCo, CoTc, FeMo, CoRu, NiTc, NiZr,$ and $CoCo$) with E-1 N_2 adsorption configurations and 4 $TM_1TM_2@C_9N_4$ candidates ($TM_1TM_2 = FeNi, TiNi, CoNi,$ and $NiNi$) with E-2 N_2 adsorption configurations are determined. As for 6 side-on adsorption

candidates, respective 3 $TM_1TM_2@C_9N_4$ candidates ($TM_1TM_2 = VCo, TiNi,$ and $NiZr$) with S-1 adsorption configurations and 3 S-2 candidates ($TM_1TM_2 = CuTc, TiFe,$ and $CuMo$) are determined. As shown in Scheme 1, various NRR reaction pathways of different N_2 adsorption configurations are discussed. For the candidates with the end-on adsorption configuration, distal and alternating paths are considered, respectively. And for the systems with the side-on adsorption configuration, consecutive and enzymatic paths are considered. For the alternating and enzymatic paths, proton-electron pairs are added alternately to the two N atoms, while for the distal and consecutive paths, the proton-electron pairs continuously attack the same one of two N atoms until the first NH_3 is released.

The limiting potential (U_L), the lowest negative voltage endows a spontaneous hydrogenation reaction, can also be used to reveal the activity of NRR electrocatalysts. The U_L of



Scheme 1 Schematic diagram of possible reaction pathways for the NRR on $TM_1TM_2@C_9N_4$.

the NRR can be calculated using the following equation:

$$U_L = -\frac{\Delta G}{e} \quad (3)$$

where ΔG refers to the free energy difference of the PDS under various reaction pathways. Fig. 4a illustrates the U_L s of the 18 remaining $\text{TM}_1\text{TM}_2@C_9N_4$ candidates.

Our results show that all the studied candidates are more active than the Ru(0001) stepped surface with smaller U_L s (< -1.0 V).³⁸ Particularly, four candidates $\text{Co}_2@C_9N_4$ ($U_L = -0.27$ V), $\text{NiRu}@C_9N_4$ ($U_L = -0.33$ V), $\text{TiCo}@C_9N_4$ ($U_L = -0.34$ V), and $\text{FeNi}@C_9N_4$ ($U_L = -0.35$ V) are determined to be potentially excellent catalysts with

high activity. The relationship between the catalyst activity and intrinsic properties is important for understanding the origin of catalytic activity and guiding the rational design of catalysts. According to the Sabatier principle,⁵¹ moderate binding between the catalyst surface and reaction intermediates will provide an optimal catalyst. Fig. 4b shows the volcano curve between U_L s and adsorption energy for the N_2 molecule ($\Delta E_{\text{ads}}(*\text{N}_2)$) of the potentially highly active catalysts with the end-on configuration of N_2 . Among all the candidate catalysts, $\text{Co}_2@C_9N_4$ is the closest to the top of the volcano plot, which has a moderate ($\Delta E_{\text{ads}}(*\text{N}_2) = -0.81$ eV) N_2 adsorption binding and the highest catalytic activity. If the adsorption strength of N_2 is too strong or too weak,

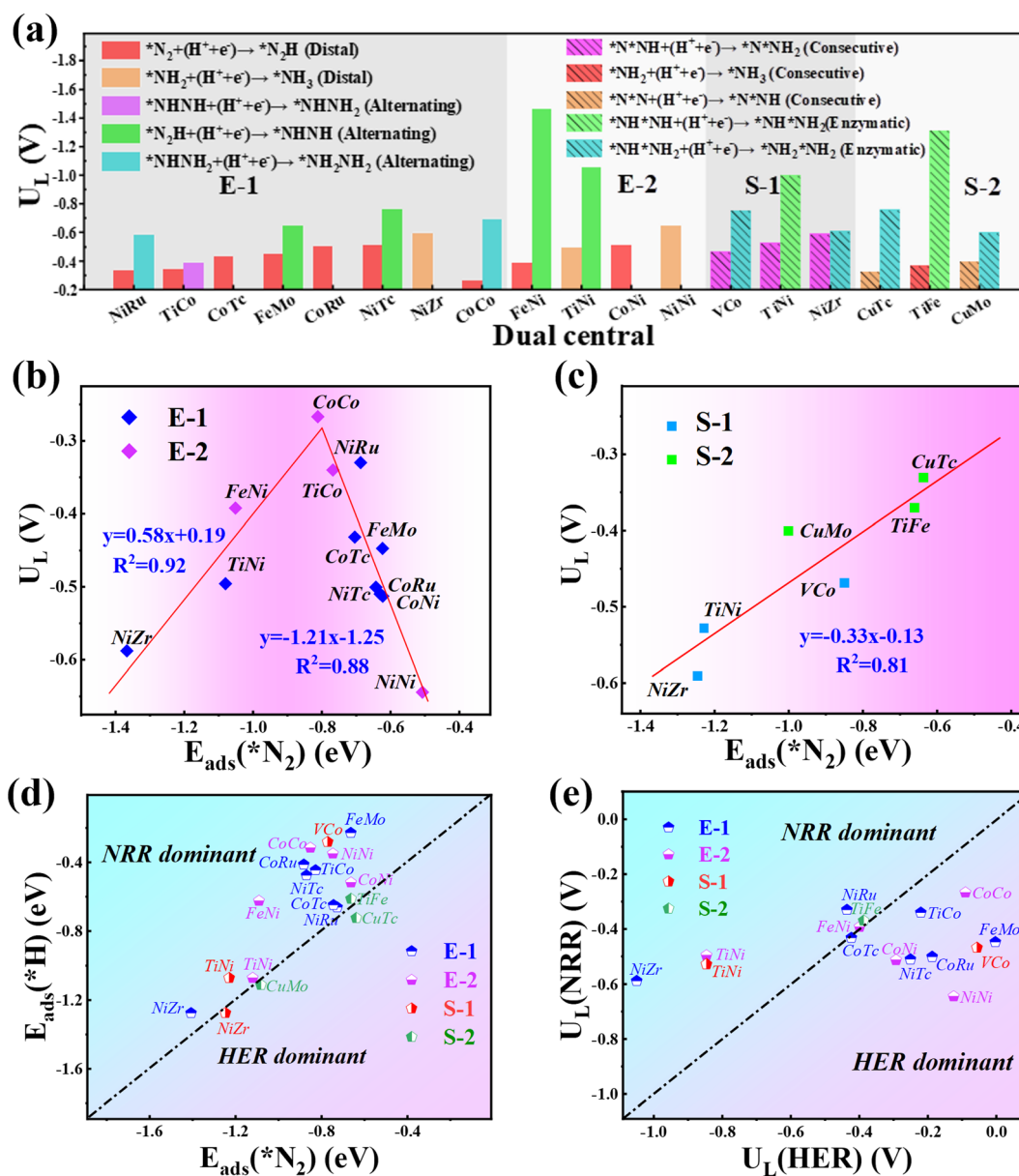


Fig. 4 (a) Theoretical limiting potentials for the NRR on the 12 and 6 promising $\text{TM}_1\text{TM}_2@C_9N_4$ candidates through the end-on configuration and side-on configuration. (b) The volcano curve between U_L and $E_{\text{ads}}(*\text{N}_2)$ through (c) end-on and (d) side-on configurations. Comparison of $E_{\text{ads}}(*\text{H})$ and $E_{\text{ads}}(*\text{N}_2)$ on 18 $\text{TM}_1\text{TM}_2@C_9N_4$ catalysts with 12 end-on configuration and 6 side-on configuration. (e) The limiting potential of the NRR ($U_L(\text{NRR})$) and HER ($U_L(\text{HER})$) for 15 $\text{TM}_1\text{TM}_2@C_9N_4$ catalysts with 12 end-on adsorption configuration and 3 side-on adsorption configuration.

the catalytic activity will move away from the highest activity region. For example, the $\Delta E_{\text{ads}}(*\text{N}_2)$ values of $\text{Ni}_2@\text{C}_9\text{N}_4$ and $\text{NiZr}@\text{C}_9\text{N}_4$ are -0.51 eV and -1.37 eV, corresponding to the U_L of -0.64 V and -0.59 V, respectively. Similarly, a nearly linear relationship is found between U_L s and $\Delta E_{\text{ads}}(*\text{N}_2)$ for potentially highly active catalysts with the side-on configuration (see Fig. 4c), where $\text{CuTc}@\text{C}_9\text{N}_4$ shows optimal activity of the NRR, with $\Delta E_{\text{ads}}(*\text{N}_2)$ of -0.64 eV.

3.4. The NRR selectivity of $\text{TM}_1\text{TM}_2@\text{C}_9\text{N}_4$

To ensure high faradaic efficiency in the ammonia production process, it is crucial for the catalysts to overcome the challenges of competing reaction, hydrogen evolution reaction (HER), as the adsorption of H on the catalyst surface will block the active sites and cause H poisoning. Therefore, in order to determine whether the candidate catalysts are more favorable for the NRR,

the higher adsorption energy of the H atom than that of the N_2 molecule ($E_{\text{ads}}(*\text{H}) > E_{\text{ads}}(*\text{N}_2)$) is set as the fifth screening criterion. As shown in Fig. 4d, the $E_{\text{ads}}(*\text{H})$ values below the diagonal line are more negative than $E_{\text{ads}}(*\text{N}_2)$, indicating that H can easily cover the active site of the catalyst and inhibit the progress of the NRR. After the fifth step of screening, four candidates with side-on adsorption configurations like $\text{V}_2@\text{C}_9\text{N}_4$, $\text{NiZr}@\text{C}_9\text{N}_4$, $\text{CuMo}@\text{C}_9\text{N}_4$, and $\text{CuTc}@\text{C}_9\text{N}_4$ were eliminated. Therefore, 15 candidates with 12 end-on adsorption configurations and 3 side-on adsorption configurations remained.

To further explore the effect of the relative limiting potential (U_L) of the NRR and HER, the Gibbs free energy for H (ΔG_{H}) of the remaining candidates was investigated (see Fig. S5, ESI†). Also, the U_L difference between the NRR and HER ($\Delta U_L = U_L(\text{NRR}) - U_L(\text{HER})$) was used to estimate the selectivity of the

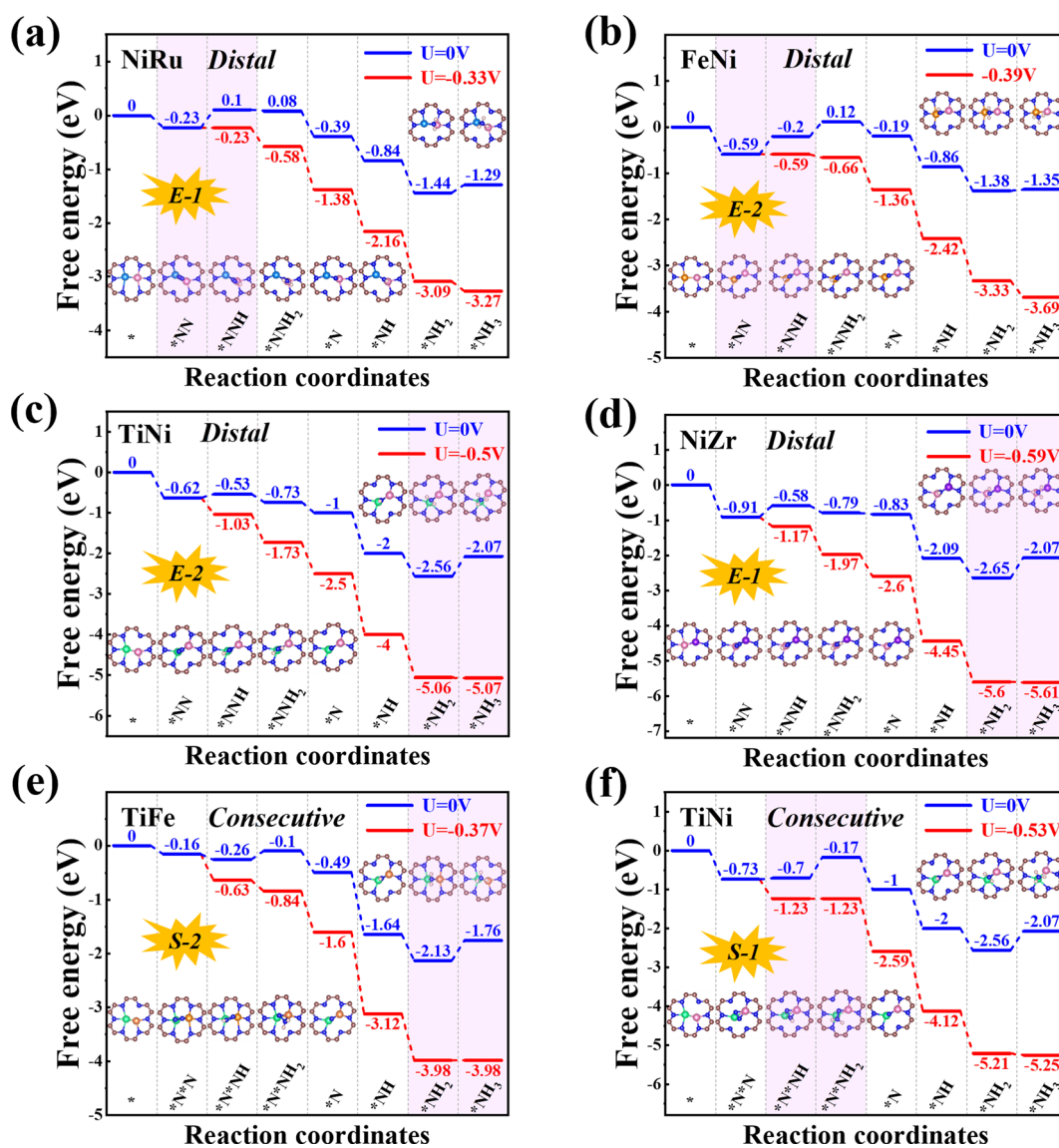


Fig. 5 Free energy diagrams of the NRR on (a) $\text{NiRu}@\text{C}_9\text{N}_4$, (b) $\text{FeNi}@\text{C}_9\text{N}_4$, (c) $\text{TiNi}@\text{C}_9\text{N}_4$ and (d) $\text{NiZr}@\text{C}_9\text{N}_4$ in the distal mechanism, (e) $\text{TiFe}@\text{C}_9\text{N}_4$ and (f) $\text{TiNi}@\text{C}_9\text{N}_4$ in the consecutive mechanism. Blue and red lines indicate free energy changes for the NRR at $U = 0$ V and U_L , respectively.

NRR (see Fig. 4e), and $\Delta U_L > 0$ V is set as the sixth step screening criterion. Unfortunately, the most active CoCo@C₉N₄, which cannot guarantee a relatively positive relative limiting potential, was eliminated. After the screening, only 6 candidates with 4 end-on configurations like NiRu@C₉N₄, FeNi@C₉N₄, TiNi@C₉N₄, and NiZr@C₉N₄ and 2 side-on configurations of TiFe@C₉N₄ and TiNi@C₉N₄ remained. On the other hand, to further confirm the HER performance of these TM₁TM₂@C₉N₄ systems, we calculated the ΔG_{HIS} of 14 screened TM₁TM₂@C₉N₄ candidates (see Fig. S5, ESI[†]) based on third and fourth step screening criteria. Three different sites for H adsorption were considered, namely, S(TM₁), S(TM₂), and B(bridge) sites. The optimized structures with optimal adsorption for *H are shown in Fig. S6 (ESI[†]) and the hydrogen adsorption free energy diagrams ($\Delta G(*\text{H})$) of all the candidates are shown in Fig. S7 (ESI[†]). Our results showed that four systems FeMo@C₉N₄, FeNi@C₉N₄, NiTe@C₉N₄, and CoTe@C₉N₄ have the optimal H adsorption site on top of the transition metal atom, while the other systems are found to have optimal H adsorption sites on the bridge site. Except FeMo@C₉N₄ and VCo@C₉N₄ that display $\Delta G(*\text{H})$, e.g. -0.16 eV and -0.18 eV, respectively, all the other TM₁TM₂@C₉N₄ systems showed bad HER performance with more negative $\Delta G(*\text{H})$ (< -0.2 eV).

3.5 NRR performance of efficient TM₁TM₂@C₉N₄

Next, we will explore the reaction mechanism and activity origin of the NRR of the six screened catalysts. Fig. 5a and d give the optimal NRR reaction pathways for NiRu@C₉N₄ ($U_L = -0.33$ V), FeNi@C₉N₄ ($U_L = -0.35$ V), TiNi@C₉N₄ ($U_L = -0.50$ V), and NiZr@C₉N₄ ($U_L = -0.53$ V) with N₂ adsorption through the end-on configuration. Taking NiRu@C₉N₄ as an example (see Fig. 5a), the reaction of adsorbed N₂ with hydrated protons produces an *N₂H intermediate with an energy barrier of 0.33 eV. Next, H* attacks the N atom of the *N₂H intermediate to form *N₂H₂ or *NHNH species, and H* favors the distal path due to the lower energy consumption for the formation of *N₂H species. The proton–electron pair then reacts with *NNH₂ to release the first ammonia molecule with a free energy drop of 0.27 eV. After that, the hydrated protons then attack the remaining *N atom three times in a row, eventually releasing a second NH₃. Notably, the PDS of NiRu@C₉N₄ *via* a distal mechanism is the first hydrogenation step (*N₂ + *H⁺ + e⁻ → *N₂H), resulting in a U_L of -0.33 V to make the whole NRR process spontaneously exothermic. A similar PDS is observed for FeNi@C₉N₄ (see Fig. 5b), while for TiNi@C₉N₄ (see Fig. 5c) and NiZr@C₉N₄ (see Fig. 5d), their PDSs are a remote mechanism of the last protonation step (*NH₂ + *H⁺ + e⁻ → *NH₃). The proton–electron pair needs to overcome a large energy barrier to attack the *NH₂ intermediate of N atoms; the energy barriers are 0.50 eV and 0.59 eV, respectively.

As shown in Fig. 5e and f, the optimal NRR reaction pathways for TiFe@C₉N₄ and TiNi@C₉N₄, whose N₂ adsorption is through the side-on configuration, are consecutive pathways. Taking TiFe@C₉N₄ with the S-2 adsorption configuration as an example, its second protonation of the consecutive mechanism requires only 0.16 eV, so hydrated protons tend to attack the

same N atom in succession. After the first NH₃ was dissociated, H continued to attack the remaining N atom three times consecutively, and the last protonation step (*NH₂ + *H⁺ + e⁻ → *NH₃) was a PDS with an energy barrier of 0.37 eV (see Fig. 5e). Differently, the PDS of TiFe@C₉N₄ adsorbed by N₂ through the S-1 configuration is the second protonation step (*N₂H + *H⁺ + e⁻ → *N₂H₂) with an energy barrier of 0.53 eV.

In order to further understand the NRR behaviors of the five screened catalysts, TM₁TM₂@C₉N₄ (TM₁TM₂ = NiRu, FeNi, TiNi, NiZr, and TiFe), as shown in Fig. 6b–g, the partial densities of states (PDOS) of the catalysts after N₂ adsorption and the crystal orbital Hamiltonian population (COHP) of the N₂ molecule are analyzed. The PDOS and COHP of free N₂ indicate that the 2π* orbital of N₂ gas is far from the Fermi level and is an antibonding component, revealing the strong inertness of free N₂ (see Fig. 6a). After N₂ adsorption, obvious hybridization is found for the d states of TM₁ and TM₂ atoms and the 2p state of adsorbed N₂ near the Fermi level for all catalysts, indicating that there is a strong bond between the catalysts and the adsorbed N₂, ensuring that N₂ can spontaneously adsorb on the active sites on the catalyst surface and being activated by the catalyst (see Fig. 6b–g). Obviously, some electron-occupied antibonding components of N₂ appear below the Fermi level in all the systems, which also demonstrates its activation. Taking NiRu@C₉N₄ as an example, the 3σ and 2π orbitals of adsorbed N₂ molecules donate electrons to the unoccupied d orbitals of Ni and Ru of the NiRu@C₉N₄ substrate, thereby enhancing the adsorption of N₂ molecules. In addition, the occupied d orbitals of Ni and Ru atoms donate electrons back to the 2π* antibonding orbitals of N₂ molecules, resulting in the separation of the 2π* antibonding orbitals into occupied and unoccupied orbitals.

In addition, the activation of the N≡N bond can also be confirmed by analyzing the integrated crystal orbital Hamiltonian population (ICOHP) values (see Fig. 6b–g). Our results show that the ICOHP values for N₂ on all the studied catalysts are negative, around -6.94 to -1.45 eV, indicating that the N₂ molecule is well activated. Interestingly, there is a strong linear relationship between the ICOHP value and the N≡N bond length of the adsorbed N₂; that is, a more negative ICOHP corresponds to a longer N≡N bond length. Similarly, such a linear relationship can also be determined between ICOHP and the charge transferred to the adsorbed N₂ (ΔQ) (see Fig. 6i). It is noted that the more charges transferred to the N₂, the weaker the interaction between the N≡N bonds and the more negative the values of ICOHP.

In order to confirm the influence of the solvent effect, we chose NiRu@C₉N₄ and TiFe@C₉N₄ to perform several test calculations with and without considering the effect of solvation (see Fig. S8, ESI[†]). Although the free energies of the adsorbed species for both NiRu@C₉N₄ and TiFe@C₉N₄ in the distal mechanism are slightly more negative with the consideration of the solvation effect, similar energy diagrams are identified for both cases. Moreover, the differences of U_L during the full NRR processes of NiRu@C₉N₄ and TiFe@C₉N₄ with and without considering the solvation effect are only -0.12 V and -0.08 V.

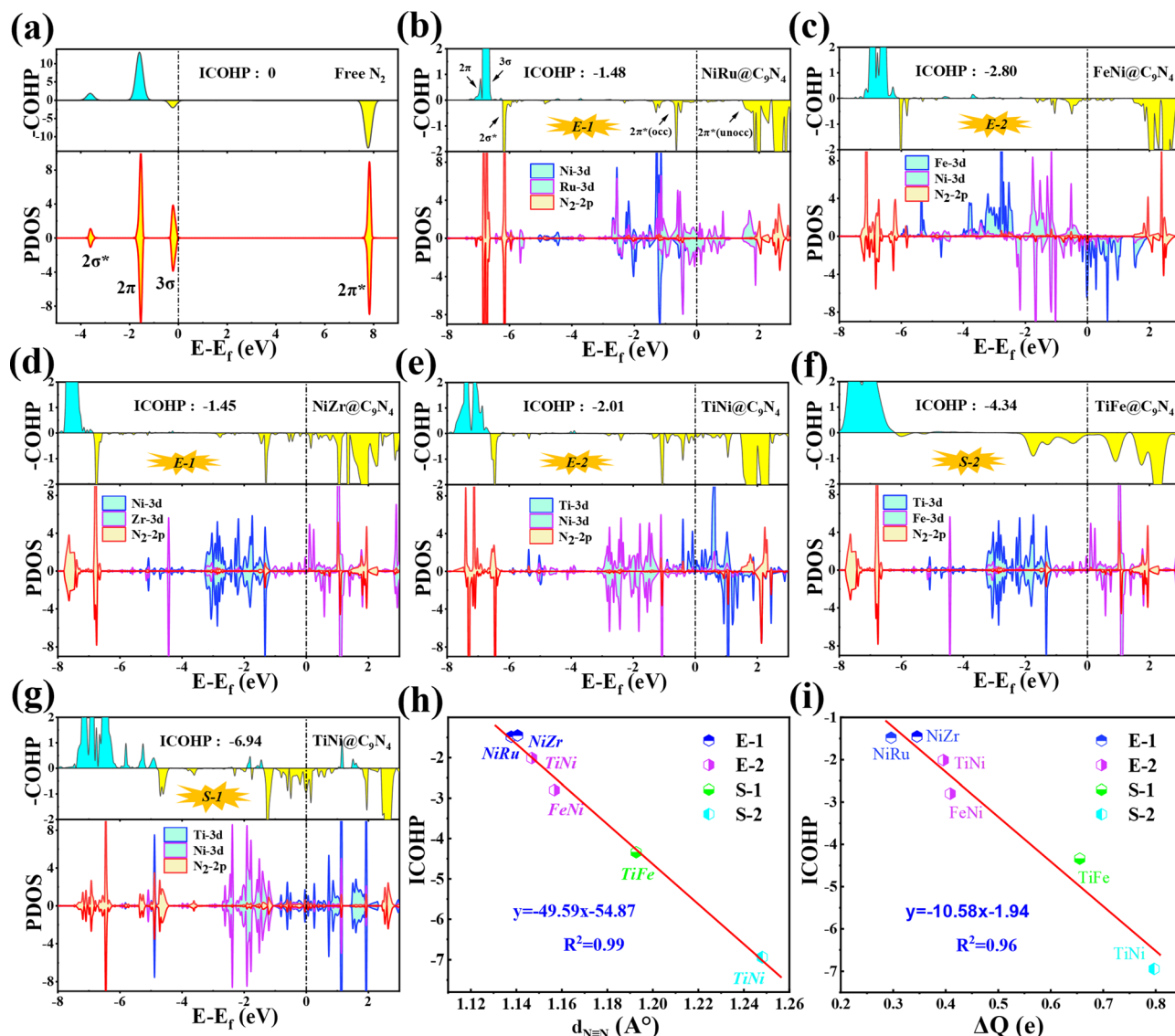


Fig. 6 (a) Partial density of states (PDOS) and molecular orbitals of a free N_2 molecule. (b–f) PDOS, crystal orbital Hamilton populations (COHPs), and integrated COHP (ICOHP) of $*N_2$ on NiRu@C₉N₄, FeNi@C₉N₄, TiNi@C₉N₄, and NiZr@C₉N₄ through the end-on configuration, and (g) TiFe@C₉N₄ and (h) TiNi@C₉N₄ through the side-on configuration. (h) Illustration of the correlation between ICOHP and N≡N bond length of N_2 ($d_{N≡N}$). (i) Illustration of the correlation between ICOHP and ΔQ . The bonding and antibonding states in COHP are denoted by cyan and yellow, respectively.

Based on this, we can conclude that the reaction energies are not significantly affected by those solvation molecules.

3.6. Possibility of the experimental synthesis of $TM_1TM_2@C_9N_4$

Finally, we extended the possibility of the experimental synthesis of these screened $TM_1TM_2@C_9N_4$ catalysts. First, we calculated their formation energies using the following equation:

$$E_f = \frac{E_{TM_1TM_2@C_9N_4} - E_{C_9N_4} - E_{TM_1} - E_{TM_2}}{2} \quad (4)$$

Here, $E_{TM_1TM_2@C_9N_4}$ is the energy of monolayer C₉N₄ anchored with the two TM atoms, and $E_{C_9N_4}$ is the energy of monolayer C₉N₄. E_{TM_1} and E_{TM_2} represent the energies of single TM atoms in their stable bulk phase. As shown in Fig. 7a, the formation

energies of $TM_1TM_2@C_9N_4$ are 0.18 eV, -0.07 eV, -0.1 eV, -0.79 eV, and -1.13 eV at $TM_1TM_2 = NiRu, FeNi, NiZr, TiNi,$ and $TiFe$, respectively. Besides, as shown in Fig. S9–S13 (ESI[†]), *ab initio* molecular dynamics (AIMD) simulations of NiRu@C₉N₄, FeNi@C₉N₄, NiZr@C₉N₄, TiNi@C₉N₄, and TiFe@C₉N₄ are performed at a time step of 2 fs at 500 K to explore their thermal stability. Obviously, the total energy converges rapidly, and no obvious structural distortion occurs during the entire simulation time (see Fig. 7b–f), which indicates that they have relatively high thermodynamic stability, hopefully synthesized experimentally.

It is well known that the NRR active sites of catalyst basal planes can be easily covered by various functional groups under certain reaction conditions; if yes, the reaction areas in their basal planes will be largely decreased.^{53,54} To address the concern whether the surfaces of the catalysts are blocked by

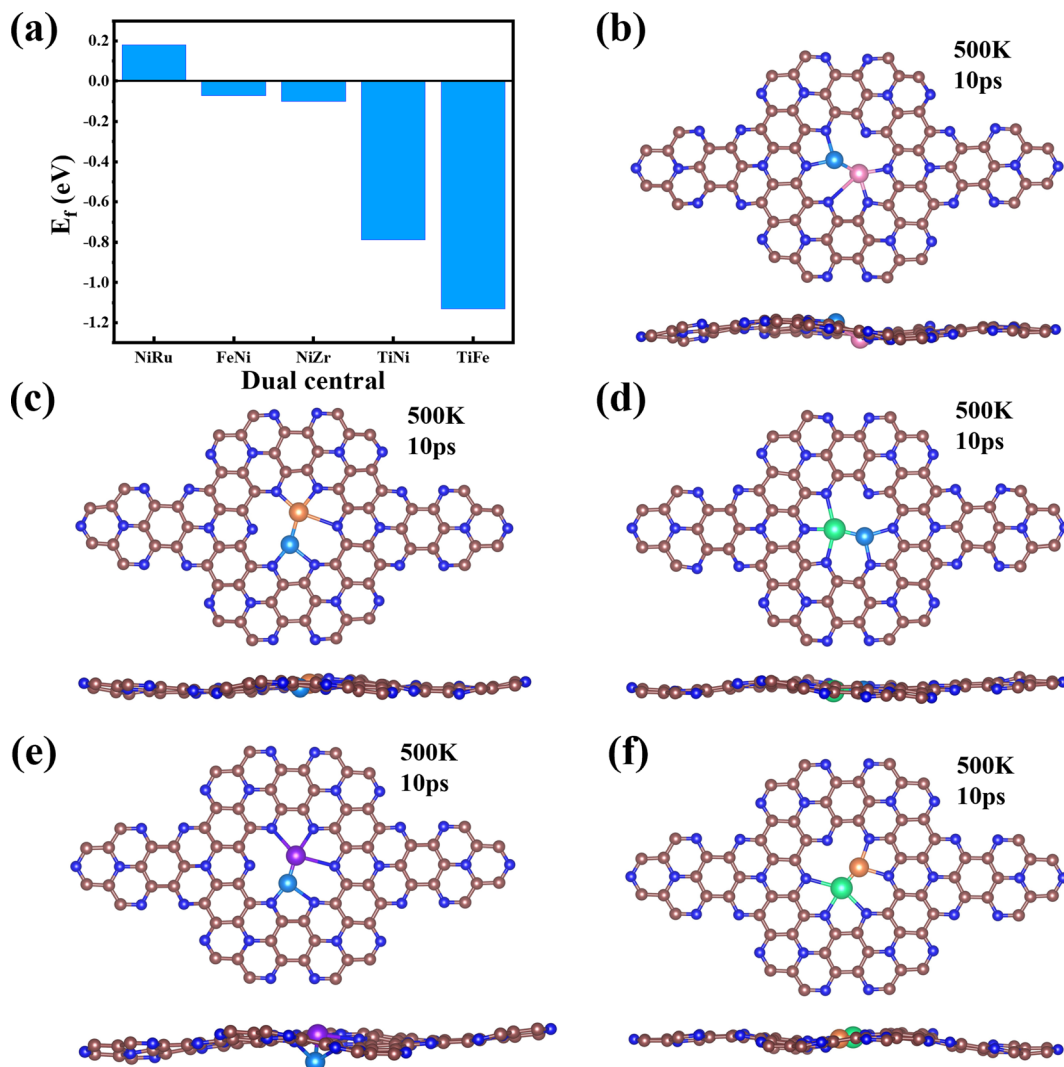


Fig. 7 (a) Formation energies of NiRu@C₉N₄, FeNi@C₉N₄, TiNi@C₉N₄, NiZr@C₉N₄, and TiFe@C₉N₄. (b–f) Top and side views of the configurations of NiRu@C₉N₄, FeNi@C₉N₄, TiNi@C₉N₄, NiZr@C₉N₄, and TiFe@C₉N₄ after AIMD simulations. The simulations were performed at 500 K for 10 ps with a time step of 2 fs.

O/OH like electron-accepting species or not, we constructed the surface Pourbaix diagrams of the 5 screened TM₁TM₂@C₉N₄ (TM₁TM₂ = NiRu, FeNi, TiNi, TiFe, and NiZr) catalysts by plotting the equilibrium potential between different surface terminations, including -O, -OH, and -H₂O terminated systems, as a function of pH (see Fig. S14, ESI[†]). The optimal structures for *O, *OH, and *H₂O adsorption are provided in Fig. S15 (ESI[†]). We first considered the situation with 0 V vs. SHE to unveil their surface composition at the cathode surface under operating conditions. Clearly, all the TM₁TM₂@C₉N₄ systems can adsorb the oxygen and hydroxyl groups onto their bare surfaces to form O*/OH*. Specifically, 3 TM₁TM₂@C₉N₄ (TM₁TM₂ = TiNi, TiFe, and NiZr) can be fully terminated by O*; FeNi@C₉N₄ can be occupied by OH*; whereas for NiRu@C₉N₄, both O* and OH* can be adsorbed on the basal plane depending on the pH value of the electrolyte. When an electrode potential is applied, the protonation of O*/OH* is gradually favorable on these TM₁TM₂@C₉N₄ surfaces. The redox potential (U_R), which

is defined as the electrode potential needed to remove the surface O*/OH* species, could be compared to the U_L of the NRR. Except NiZr@C₉N₄ with U_R being higher than U_L , the four other TM₁TM₂@C₉N₄ systems cannot be influenced by the *O*/OH* species under working conditions.

4. Conclusions

In conclusion, by first-principles high-throughput calculations, a 6-step screening criterion is set to identify promising candidate catalysts of TM₁TM₂@C₉N₄ for the NRR. Our calculations show that the heteronuclear dual-metal catalysts NiRu@C₉N₄, FeNi@C₉N₄, TiFe@C₉N₄, TiNi@C₉N₄, and NiZr@C₉N₄ are considered as promising NRR electrocatalyst candidates with good confinement potentials of -0.33 V, -0.35 V, -0.37 V, -0.50 V, and -0.59 V. In addition, we also confirmed the high selectivity and stability of these 5 catalysts. The systematic study shows

that for the $\text{TM}_1\text{TM}_2\text{@C}_9\text{N}_4$ catalyst with dual-atom active sites, the different adsorption configurations of N_2 have obvious differences in the origin of the catalytic activity, indicating that it is of great significance to explore the most stable adsorption configuration of N_2 . Our findings not only provide a useful dataset for the experimental exploration of $\text{TM}_1\text{TM}_2\text{@C}_9\text{N}_4$ catalysts, but also provide a reference to guide the rational design of novel high-performance NRR catalysts for the sustainable production of ammonia.

Conflicts of interest

There are no conflicts to declare.

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