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Rational Design of Electrocatalysts Comprising Single-Atom-Modified Covalent Organic Frameworks for the N₂ Reduction Reaction: A First-Principles Study

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KEYWORDS

Nitrogen reduction reactions, Single-atom electrocatalysts, Covalent organic frameworks, Density functional theory

ABSTRACT

The electrocatalytic N_2 reduction reaction (NRR) is one of the most promising methods for the on-site and on-demand production of NH_3 . Single-metal-atom-doped covalent organic frameworks (COFs) are expected to function as efficient NRR electrocatalysts because a designed coordination environment of metal centers is available as a consequence of the wide range of possible designs of COFs. Herein, we used density functional theory (DFT) to systematically investigate the theoretical NRR activity of various single-3*d*-metal atoms doped into COFs with different coordination numbers to attain a general design guideline for the development of efficient NRR catalysts. The adsorption strength of NRR intermediates decreased as either the coordination number or the number of *d*-electrons of the metal centers increased. The potential-determining step switched between N–N bond activation and NH_3 desorption depending on the adsorption strength of the NRR intermediates. Therefore, an optimal NRR catalyst exhibits a moderate binding strength with intermediates. Among the investigated metal-doped COFs, an Fe metal center with a coordination number of three exhibited the highest theoretical onset potential (-0.49 eV vs computational hydrogen electrode). In this catalyst, the charge-density and density-of-state analyses revealed moderate π back-donation and σ donation between Fe 3*d* orbitals and the π^* orbital of N–N bonds, which resulted in the optimal binding strength of intermediates.

Introduction

NH₃ is an important raw material for various chemical products, including resins and fertilizers.¹⁻
² The present industrial technology for NH₃ synthesis, the Haber–Bosch process, is conducted on a large scale because it requires high pressures and temperatures.³⁻⁴ Recently, the aqueous electrochemical reduction of N₂ to NH₃ has attracted much attention as an on-demand technology for NH₃ synthesis because it can be carried out under ambient conditions.⁵⁻⁸ The development of active electrocatalysts that split the stable N $\equiv$ N bonds in N₂ is required for efficient electrochemical devices for the N₂ reduction reaction (NRR).⁹

Organometallics are promising candidates as NRR electrocatalysts because their structure can be precisely tuned to effectively activate N $\equiv$ N bonds. However, the instability of these materials, especially the ligand substitution to water molecules in aqueous solutions, remains a substantial problem; these metal complexes have therefore been used in organic electrolytes.¹⁰⁻¹² Single-atom electrocatalysts (SACs), which comprise singly isolated metal sites immobilized on a heterogeneous support, have attracted attention as the new category of analogue of organometallics. SACs exhibit unique electrocatalytic activity and selectivity compared with bulk metal catalysts; thus, SACs are expected to be a new platform for heterogeneous electrocatalysts in aqueous electrolytes, even for the NRR. For example, Wang et al. have reported that single Fe atoms supported on N-doped carbons exhibited a Faradaic efficiency of 56% for NH₃ production.⁶ In addition, Ru single atoms distributed on N-doped carbon showed an NH₃ production rate of 120.9 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$, which is the highest value ever reported for an aqueous NRR reaction.⁸ Even from the viewpoint of theoretical calculations, a single metal supported on an inorganic

substrate, such as Fe-doped N-doped carbon,¹³ Ru-doped carbon nitride (C_3N_4),¹⁴ and Mo-modified boron nitride,¹⁵ have been predicted to efficiently catalyze the NRR. However, developing a defined coordination structure of single-metal atoms on conventional supports, including N-doped carbon and C_3N_4 , is difficult because of the low structural flexibility of these supports. Significantly, the coordination numbers (CNs) of metal centers are known to directly affect the adsorption strength of electrocatalytic intermediates (i.e. free energies of elementary reactions).¹⁶⁻¹⁹

Covalent organic frameworks (COFs) have attracted intensive attention as novel polymeric materials for use in heterogeneous catalysts and electrical and optical materials.²⁰⁻²⁵ COFs are expected to become novel platforms for SACs with defined coordination structures because their structures can be freely designed through the selection of monomers and because COFs have abundant heteroatoms with a lone electron pair, such as N, S, and O, to immobilize metal atoms through coordination bonds.²⁶⁻²⁸ In previous reports, it has been experimentally demonstrated that various 3d metal atoms (Co, Ni, and Cu) doped into triazine-linked COFs exhibited unique electrocatalytic activity, such as O_2 , NO_3^- , and CO_2 reduction reactions.^{26, 29-33} In parallel, we theoretically investigated the relationship among the metal species, their CNs, and the adsorption strength of oxygen reduction reaction (ORR) intermediates in M-COFs using density functional theory (DFT) calculations.³⁴ As a result, *d*-electron numbers and CNs were found to independently serve as a descriptor for the adsorption strength of ORR intermediates (i.e., ORR activity). Given that the adsorption strength of intermediates on electrocatalysts is one of the determining factors for NRR activity,^{3, 14, 35-36} M-COFs are becoming promising electrocatalysts even for the NRR because CNs and metal centers can be freely chosen using appropriate monomers and metal precursors. In the present work, we investigated the relationships between the CN, adsorption

strength of reaction intermediates, and various modified 3d metal species on several types of COFs using the DFT method with the aim of obtaining a systematized design direction for efficient SACs for the NRR.

Computational details

We used Phase/0 as a code for carrying out DFT calculations of structural relaxation and the adsorption energy of NRR intermediates.³⁷⁻³⁸ The implemented method was the generalized gradient approximation of the Perdew–Burke–Ernzerhof model (GGA-PBE) with a kinetic cutoff energy of 400 Ry. We made all atoms mobile in all directions and obtained the total electronic energy by DFT (E_{DFT}). The reciprocal space was sampled using $2 \times 2 \times 1$ k -points for the atomic relaxations until the maximum force was less than 10^{-2} eV/Å for all moiety units. The residual minimization method–direct inversion in the iterative subspace (RMM–DIIS) method that considers spin polarization was applied in the Self-consistent field (SCF) method.

On the basis of the experimentally synthesized COFs in the previous report, we modeled single-metal active centers with different coordination numbers of N atoms such as metal–bipyridine ($M\text{--}N_2$), terpyridine ($M\text{--}N_3$), and porphyrin ($M\text{--}N_4$)-like structures.^{28-29, 39} We used a slab model with a space greater than 15 Å between successive slabs—specifically, the single-layer M-COFs—to simplify the calculation and eliminate interactions between successive slabs. The adsorption energies of each NRR intermediate (N, NH, NNH) were calculated using the following formulas on the basis of previous reports:³⁴

$$\Delta E_{\text{N}} = E_{*N} - E_{*} - \frac{1}{2}E_{N_2} \quad (1)$$

$$\Delta E_{\text{NH}} = E_{\text{NH}}^* - E^* - \left(\frac{1}{2}E_{\text{N}_2} + \frac{1}{2}E_{\text{H}_2}\right) \quad (2)$$

$$\Delta E_{\text{NNH}} = E_{\text{NNH}}^* - E^* - E_{\text{N}_2} - \frac{1}{2}E_{\text{H}_2} \quad (3)$$

where E^* , E_{ads}^* , and E_{molecule} represent the total electronic energies of the M-COFs, the M-COFs with each adsorbed intermediate, and the M-COFs with each adsorbed molecule. The Gibbs free energy of formation (ΔG) for each reaction intermediate was calculated using the following equations:

$$\Delta G(\text{NNH}^*) = G(\text{NNH}^*) - G(^*) - G(\text{N}_2) - \frac{1}{2}G(\text{H}_2) \quad (4)$$

$$\Delta G(\text{N}^*) = G(\text{N}^*) - G(^*) - \frac{1}{2}G(\text{N}_2) \quad (5)$$

$$\Delta G(\text{NH}^*) = G(\text{NH}^*) - G(^*) - \frac{1}{2}G(\text{N}_2) - G(\text{H}_2) \quad (6)$$

$$\frac{1}{2}G(\text{H}_2) = G(\text{H}^+ + \text{e}^-) + eU \quad (7)$$

The free energy of each chemical state can be calculated by

$$G = E_{\text{DFT}} + E_{\text{ZPE}} - TS \quad (8)$$

where E_{DFT} , E_{ZPE} , and TS denote the total energies obtained from DFT calculations, the zero-point energy, and an entropy correction, respectively. E_{ZPE} and TS were obtained from previous reports.⁴⁰⁻⁴¹ (Table S1)

On the basis of a report by Nørskov *et al.*,⁴² the concept of the computational hydrogen electrode (CHE) was applied to establish the free-energy diagram for the NRR. In this model, the chemical potential of a proton and electron pair $G(\text{H}^+ + \text{e}^-)$ is equivalent to one-half of the

chemical potential of gaseous hydrogen ($0.5G(H_2)$) (0 V vs. standard hydrogen electrode). The external potential U could shift the free energy of the reaction intermediates by $-eU$.

Results and discussion

Model Structures of M-COFs and Stability of Their Single-Metal Sites: First, we explain the details of the model M-COF structures shown in Figure 1a–c. The COFs with bipyridine (Figure 1a), terpyridine (Figure 1b), and porphyrin moieties (Figure 1c), in which the metal atoms are coordinated by two, three, and four N atoms of frameworks, respectively, are adopted as the model structures. Notably, these structures have been experimentally prepared,^{28-29, 39} and we computationally investigated their ORR activity in a previous report.³⁴ We first evaluated the stability of single-metal sites in M-COFs by calculating the computational stabilizing energies using equation (9):

$$E_{\text{stabilize}} = E(\text{M-support}) - E(\text{support}) - E(\text{M}_{\text{single}}) \quad (9)$$

where $E(\text{M-support})$, $E(\text{support})$, and $E(\text{M}_{\text{single}})$ indicate the total energy of the unit cell for a metal-modified support (metal-modified COFs), the energy of the support without metal modifications, and the energy of single metal atoms in vacuum, respectively.^{34, 43-44} The stabilized energies for the M-COFs are summarized in Table 1. The single-metal atoms coordinated with N atoms in COFs were much more stable on pristine sp^2 carbon surfaces. For example, an Fe atom in Fe–N₃ exhibits a lower stabilization energy (higher stability) by 2.7 eV than an Fe atom on a pristine graphene layer. As expected, the $E_{\text{stabilize}}$ decreases (i.e., the metal atoms become more stable) when increasing CNs. These results indicate that the single-metal sites with a CN of 2 or 3 are metastable. In addition, the metal stabilization energies increase with increasing d -electron number

when the metal atoms with the same CN are compared. This result is consistent with those in previous papers related to single-metal active centers.^{34, 45} However, several previous studies showed that the interaction between pristine graphene and single-metal atoms is relatively weak.⁴⁶⁻⁴⁸ Thus, the stabilization energies were also compared with the cohesive energy calculated using bulk metals, as also listed in Table 1. The calculated values revealed that the metal atoms with $M-N_4$ structures are more stable than those in bulk metal atoms, whereas the stabilized energies for metal atoms with $M-N_2$ and $M-N_3$ structures are more positive than the corresponding cohesive energies. Therefore, these single-metal sites with $M-N_2$ and $M-N_3$ structures would be metastable. However, it should be noted here that the metal nanoclusters formed through the aggregation of single metals are energetically more unfavorable than bulk metals.⁴⁹ In addition, the previous experimental studies demonstrated that single-atoms with $M-N_2$ and $M-N_3$ type COFs can be fabricated using the wet-impregnation methods and were stable during electrochemical reactions.^{29, 32, 50-51} On the basis of these considerations, it is worth investigating the theoretical NRR activity for these structures.

Adsorption of NRR Intermediates onto M-COFs: We used the reaction scheme shown in Figure 1d, which is known as an associative pathway, to investigate N_2 reduction to NH_3 on M-COFs. Actually, in situ Fourier transform infrared spectroscopy experiments have demonstrated that the associative pathway efficiently proceeds on single-Fe-modified N and P co-doped porous carbons.⁵²⁻⁵³ Therefore, NNH_2 , N, NH, and NH_2 were considered as NRR intermediates in the present work.

We subsequently investigated the adsorption structure and energies of NRR intermediates onto M-COFs. The representative structures of NNH and other adsorbates on $Fe-N_3$ after structural

relaxation are shown in Figure 2 and Figure S1, respectively. The results confirmed that NNH binds to open coordination sites of the metal atoms with a CN of 3 because the open coordination sites exhibit low steric hindrance. The extent of N₂ activation is reflected by the change of the N–N bond length (i.e., the bond order). Table S2(a) and Table S2(b) show the N–N bond length for N₂* and NNH* on M-COFs. With decreasing *d*-electron number of the active metal center, the N–N bond length increased, indicating that the bond order decreased.⁵⁴⁻⁵⁶ In addition, the decrease in CN led to lengthening of the N–N bond when the same metal centers were compared. The mechanism for the dependence of N–N bond activation on metal centers and CN will be discussed in the following section.

Figure 3 shows the adsorption energy ΔE for the NRR intermediates on M-COFs, which was calculated on the basis of equations (1)–(3). As shown in Figure 3(a), ΔE_N monotonically increased (i.e., the adsorption weakened) with increasing number of *d*-electrons for *M*–N₃ of M-COFs. As for the dependence of ΔE on CNs, ΔE_N decreased (i.e. stronger adsorption) with decreasing CN, as shown in Figure 3a. In addition to the trend for N*, a similar trend was observed for NNH* (Figure 3b) and NH* (Figure 3c) with respect to the dependence of the adsorption strength on the *d*-electron number and CN, consistent with the results for the bond order for NNH* (Table S2(b)).

We can explain the molecular-level mechanism of the adsorption-strength dependence on CNs and *d*-electron numbers as below. As for the CN dependence, *M*–N₂ and *M*–N₃ possess the open sites that are not coordinated with N atoms in the planar plane. Thus, *M*–N₂ and *M*–N₃ have more bindable orbitals for NRR intermediates. In addition, the steric hindrance for NRR intermediates decreased with CN. In the previous reports, Calle-Vallejo *et al.* demonstrated that metal sites with a lower CN tend to adsorb electrocatalytic intermediates more strongly in metal

nanoparticles.¹⁶⁻¹⁷ Next, let us consider the dependence on d-electron numbers. When the NRR intermediates interact with metal atoms, the bonding and antibonding orbitals are formed between them. The degree of filling of the antibonding states increases with the number of d-electrons, resulting in weakening the adsorption of NRR intermediates.⁵⁷

A linear relationship is known to exist for the adsorption energy for all of the intermediates for several electrochemical reduction reactions, including the ORR, CO₂RR, and even the NRR on metal electrodes (scaling relationship).^{3, 34, 58} We plotted ΔE_{NNH} and ΔE_{NH} as functions of ΔE_{N} for all of the M-COFs to confirm the scaling relationship in the NRR on the SACs (Figure 4a and b), respectively. Both ΔE_{NNH} and ΔE_{NH} show a linear relation with ΔE_{N} , indicating that a scaling relationship exists for the NRR on M-COFs. Therefore, we expect a so-called volcano-type relationship between the activity and adsorption strength accompanied with a single peak for the NRR on M-COFs. In the other word, precise modulation of the adsorption strength of NRR intermediates will enable optimization of the catalysts.

Free Energy Diagram and Volcano Relationship: We next calculated Gibbs free energy diagrams using the CHE model to elucidate the potential-determining step, which is the elementary reaction with the most unfavorable equilibrium potential. The potential-determining step obtained from the thermodynamic analysis is known to be an essential design guideline for developing better catalysts like the rate-determining step.⁵⁹⁻⁶⁰ Figure 5a, b, and c show free-energy diagrams for the NRR for $M\text{-N}_2$, $M\text{-N}_3$, and $M\text{-N}_4$ at -0.49 V vs. CHE, respectively. When we focus on $M\text{-N}_3$ in Figure 5b, the overall reaction pathway of the NRR on Fe- N_3 is exergonic. Some of the N-N bond activation steps (step 0-1, 1-2, or 2-3 in Figure 1d) become endergonic for Co- N_3 , Ni- N_3 , and Cu- N_3 , which exhibit weaker adsorption of NRR intermediates than Fe- N_3 . In

contrast, V-N₃, Cr-N₃, and Mn-N₃ exhibit stronger adsorption of NRR intermediates than Fe-N₃ and show that the NH₃ desorption is an uphill pathway. These results indicate that the potential-determining step switched at Fe-N₃ from NH₃ desorption to N-N bond activation with increasing *d*-electron number.

To gain further insight into the potential-determining step, the limiting potentials (ΔU) at which each reaction step becomes exergonic were plotted against ΔG_N for $M-N_3$, as shown in Figure 6. In addition, we defined the theoretical onset potential, which is determined as the potential at which all elementary steps become exergonic (i.e., the lowest ΔU in one catalyst), as ΔU_{all} . As expected from Figure 5, the limiting potential for step 5 $\rightarrow$ 6 ($\Delta U_{5 \rightarrow 6}$) is the lowest value for the earlier transition metals, whereas $\Delta U_{0 \rightarrow 1}$ or $\Delta U_{2 \rightarrow 3}$ became the potential-determining step for the later transition metals. As previously explained, Fe-N₃ exhibits the highest ΔU_{all} value (−0.49 V vs CHE) among the investigated $M-N_3$ M-COFs and a so-called volcano-type relationship with a single peak is obtained. We observed the same tendency with respect to the dependence of the free-energy diagrams and ΔU values on metal species, even for $M-N_2$ (Figures 5a and S2a) and $M-N_4$ (Figure 5c and S2b). We also investigated the free-energy diagrams for Fe atoms with different CNs, as shown in Figure 5d. The potential-determining step for Fe-N₂ and Fe-N₄ is step 5 $\rightarrow$ 6 (NH₃ desorption) and step 0 $\rightarrow$ 1 (N₂ activation), respectively.

We then plotted the ΔU_{all} values against the *d*-electron numbers for $M-N_2$, $M-N_3$, and $M-N_4$ (Figure 7). The metal species at the peak where the potential-determining step switched were Co, Fe, and Mn for $M-N_2$, $M-N_3$ and $M-N_4$, respectively. Even among these three M-COFs, Fe-N₃ exhibited the highest theoretical onset potential.

We now consider the mechanism by which the potential-determining step changes and the dependence of the mechanism on the *d*-electron number and CNs. As mentioned in the previous

sections, increasing the d -electron number in the metal centers led to a decrease in the adsorption strength of NRR intermediates on the M-COFs. Stronger adsorption can facilitate N–N bond activation because of the efficient π back-donation (for details, refer to the next section),^{41, 54, 61} however, accordingly, stronger adsorption of NH_3 impedes its desorption. Conversely, weak adsorption of NRR intermediates accelerates NH_3 desorption but inhibits effective N–N bond activation. Therefore, increasing the d -electron number of metal centers leads to a switch of the potential-determining step from NH_3 desorption to N–N bond activation. Even for the CN dependence, a decrease in the CN for the M-COFs induced strong adsorption, resulting in the metal species at the peak of the volcano plot shifting to the noble side. The aforementioned results clearly indicate that the number of d -electrons and the CN simultaneously serve as control parameters of the adsorption of NRR intermediates. An optimal metal species shifts to the noble side with increasing CN. The wide range of possible designs of COFs enables us to freely choose the CN of metal centers. That is, the modulation of the CN by the choice of COF can reveal the potential of metal species thought to exhibit poor activity as electrocatalytic centers.

Electronic Structure of NRR Intermediates on Fe–N₃: We next attained molecular-level insights into M-COFs as NRR catalysts using density-of-states and charge-density analyses, mainly focusing on Fe–N₃. We investigated the electronic structure of Fe–N₃ binding the NRR intermediate in detail. Figure S3 shows the projected density of states (PDOS) of N₂ binding Fe–N₃ and the PDOS with N₂ and Fe–N₃ at various distances (i.e., with l_0 (optimized distance after structural relaxation), $l_0+0.3$, and $l_0+1.0$ Å separation between Fe–N₃ and N₂). The π^* orbital of N–N bonds gradually shifted to negative potential and became broader with decreasing gap distance. Thus, the π^* -orbital of the N–N bond interacted with the Fe-3*d* orbital of Fe–N₃. Figure

8 shows the charge-density difference between before and after N₂ adsorption onto Fe–N₃. The charge density of the π -orbital and σ -orbital of the N–N bond was accumulated and depleted after the adsorption, respectively. Bader charge analysis reveals that the N₂ molecule gained a total of 0.40 e charge from the Fe atoms. These results indicate that both π back-donation and σ donation decreased the bond order of N₂.^{41, 54} In the case of N–NH on Fe–N₃, similar electronic interactions were observed (Figure S4).

Finally, let us summarize the NRR reaction scheme of optimal Fe–N₃ based on our study, as shown in Scheme S1. Firstly, the N₂ adsorption at the open coordination site of Fe atoms occurred through both π back-donation and σ donation, resulting in weakening N–N bonds. Then, the electrons were sequentially transferred to the π^* orbital of N–N bonds, and the N–N bond was broken. The resulting NH₂ on Fe sites was reduced to NH₃, and diffused into electrolytes.

Conclusion

We identified the relationship in 3*d*-metal-atom-doped COFs among the ΔE_{ads} of NRR intermediates, metal species (V, Cr, Mn, Fe, Co, Ni, and Cu), and their CNs (2, 3, and 4) using first-principles calculations. Although single 3*d* metal atoms are (meta)stably immobilized on all of the COFs with a CN of 2, 3, or 4, a decrease in the CN resulted in a weaker interaction between the frameworks and the metal centers. The adsorption strength of NRR intermediates, such as NNH, NH, and NH₃, depends on both the metal species and the CN of the M-COFs. Primarily, the adsorption energy monotonically increased (weakened) with decreasing number of *d*-electrons and increasing CN of the metal. The energy diagram analyses based on the adsorption strength of NRR intermediates indicated that the potential-determining process shifted from the N–N bond activation step to the NH₃ desorption step with increasing adsorption energy. The optimal metal species gradually shifted from Co to Fe and Mn as the CN was varied from 2 to 3 and 4, respectively. Among these three M-COFs, Fe–N₃ exhibited the smallest potential at which all elementary steps became exergonic. Both π back-donation and σ donation occurred upon the adsorption of N₂ or N₂ intermediates onto Fe–N₃, causing efficient weakening of the N–N bond. The COF linked with a terpyridine moiety (i.e., CN = 3) has already been reported to support a wide variety of single-metal sites in its micropores via coordinate bonds, and the metal-doped COFs exhibited various electrocatalytic activities depending on their metal species.²⁹ Therefore, the results obtained in this study directly provide design guidelines for efficient NRR catalysts composed of COFs. In addition, the knowledge about designed coordination environments for NRR obtained in this study would be applicable to the SACs on other supports. More importantly, this design principle can accelerate the development of efficient M-COF electrocatalysts for other useful reactions.

FIGURES and TABLES

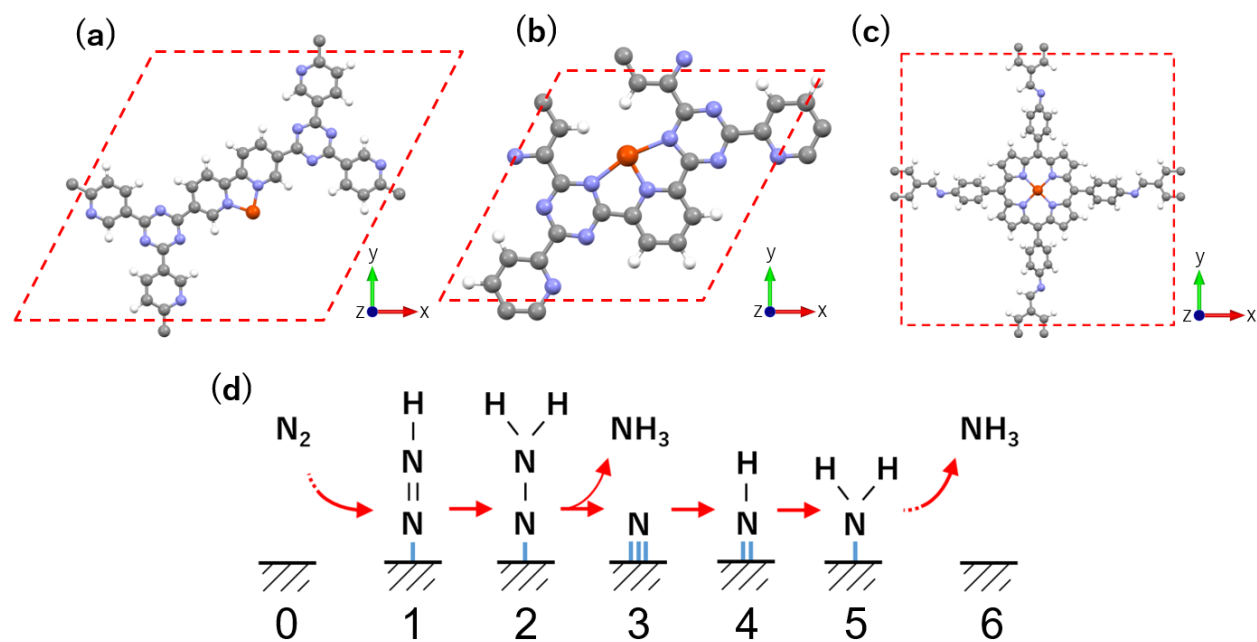


Figure 1. Optimized structures of (a) bipyrindine-type ($M-N_2$), (b) terpyridine-type ($M-N_3$), and (c) porphyrin-type ($M-N_4$) M-COFs. Red, blue, black, and white balls represent metal, N, C, and H atoms, respectively. Red dashed lines represent the unit cell for each structure. (d) The reaction pathway used in this study. The numbers below the reaction pathway indicate the reaction step.

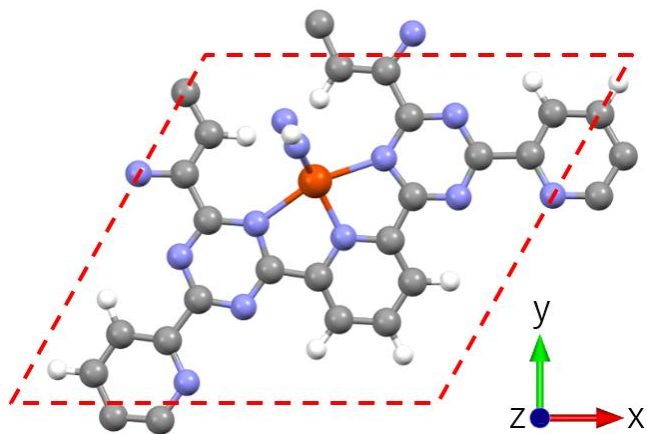


Figure 2. Top view of optimized structures of N_2H -adsorbed Fe-N_3 . Red, blue, black, and white balls represent Fe, N, C, and H atoms, respectively. Red dashed lines represent the unit cell for the structure.

Table 1 Stabilization energy of single metal atoms for $M-N_2$, $M-N_3$, $M-N_4$. The stabilization energies for M-pristine graphene, and the calculated and experimental cohesive energies are also listed as references. Energy values in this table are expressed in eV.

		V	Cr	Mn	Fe	Co	Ni	Cu
	$M-N_2$	-4.47	-4.63	-4.88	-4.23	-4.68	-3.80	-1.32
	$M-N_3$	-5.81	-5.81	-5.98	-5.40	-5.10	-3.80	-2.49
	$M-N_4$	-11.82	-11.55	-11.56	-10.98	-10.74	-9.84	-7.10
	M-pristine graphene	-3.27	-3.71	-3.63	-2.67	-2.85	-2.06	-0.53
$E_{coh}^{(a)}$	calc.	-5.55	-4.00	-3.62	-4.26	-4.89	-4.71	-3.55
	exp.	-5.3	-4.1	-2.9	-4.3	-4.4	-4.4	-3.5

$^{(a)}E_{coh}$ is the cohesive energy of metals. The method of the calculation and experimental data were referred to the previous paper.^{41, 49}

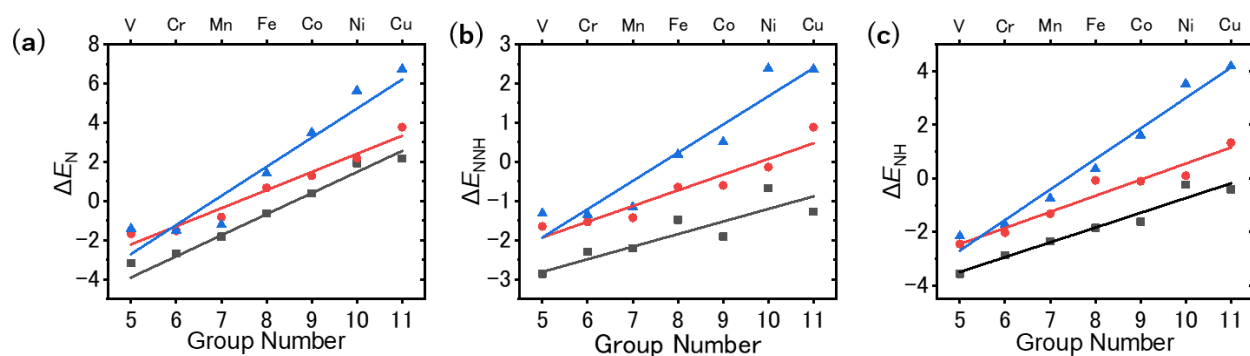


Figure 3. Adsorption energies (ΔE) for (a) N^* , (b) NNH^* , and (c) NH^* plotted against the group number of the metal species. Black: $M-N_2$; red: $M-N_3$; blue: $M-N_4$. The solid lines in each graph represent guidelines for the trends of the ΔE values of NRR intermediates.

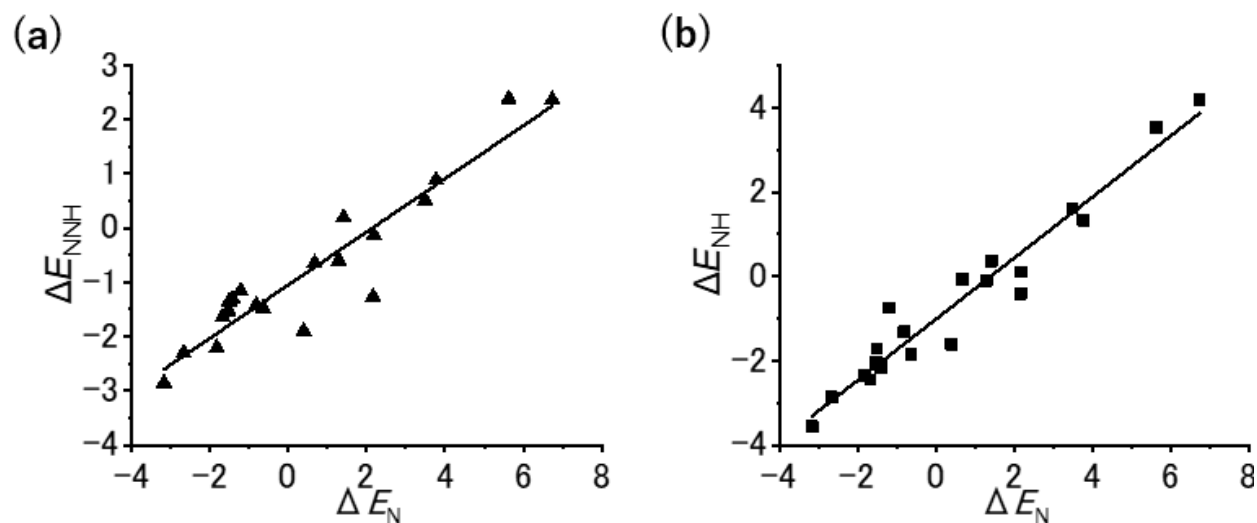


Figure 4. The relationship (a) between ΔE_{NNH} and ΔE_{N} and (b) between ΔE_{NH} and ΔE_{N} . In these graphs, ΔE_{NH} or ΔE_{NNH} for all of the investigated M-COFs (i.e., $M = \text{V to Cu}$; $\text{CN} = 2, 3, 4$) are plotted against ΔE_{N} . The solid lines in each graph are trend guidelines.

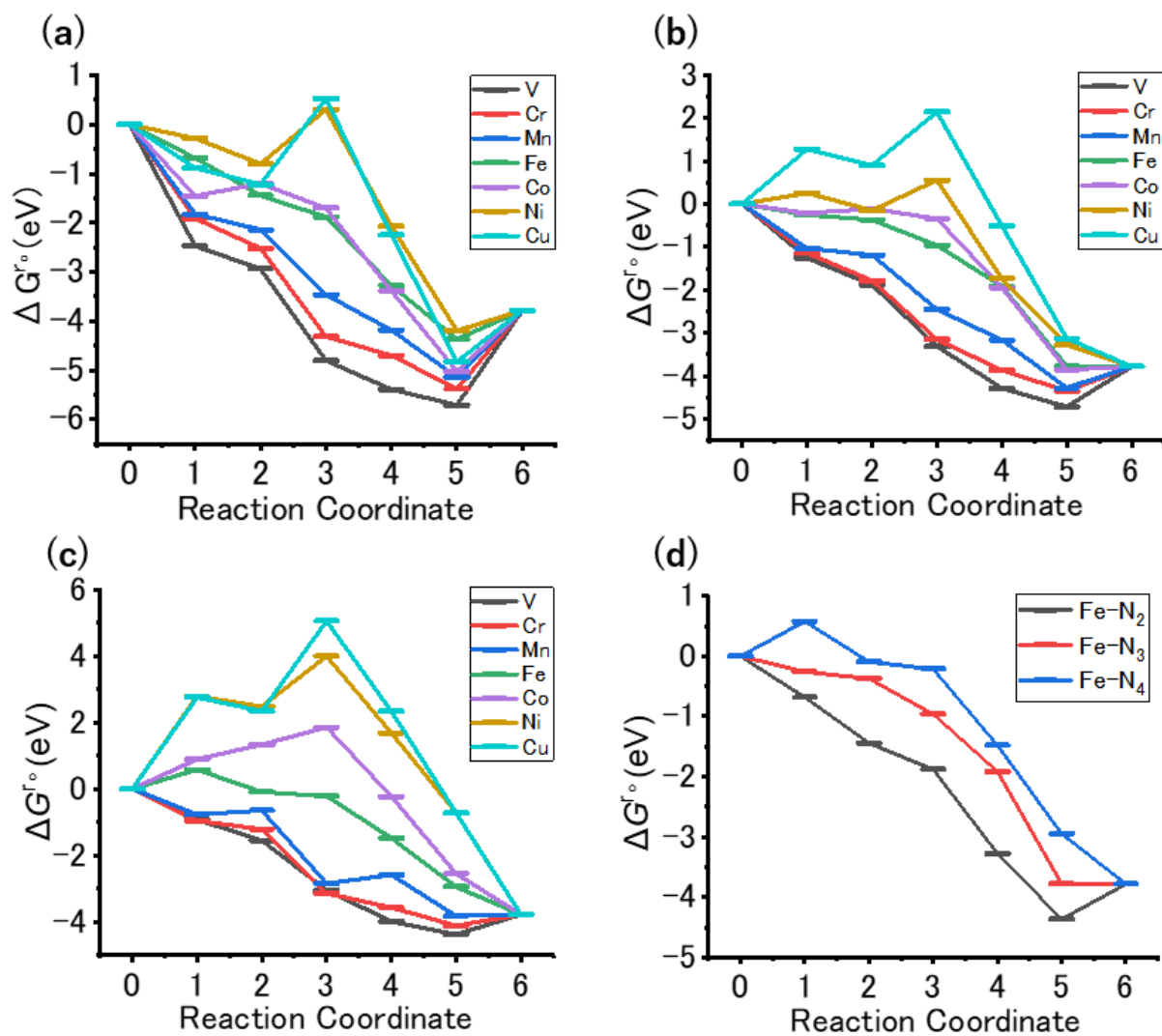


Figure 5. Free energy diagrams of the NRR on (a) $M-N_2$, (b) $M-N_3$, and (c) $M-N_4$. (d) Free energy diagrams for $Fe-N_x$. Electrode potential = -0.49 V vs CHE.

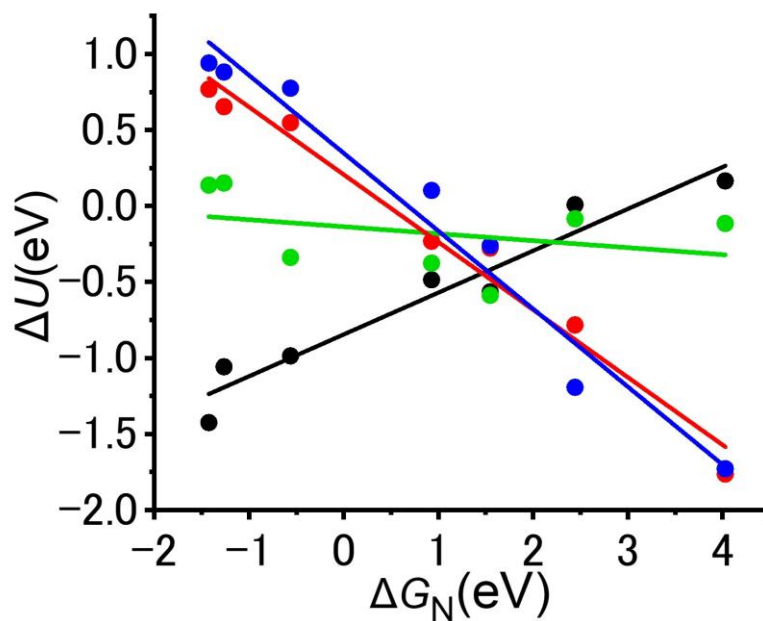


Figure 6. The limiting potential (ΔU) of each NRR step (red: $0 \rightarrow 1$ step; green: $1 \rightarrow 2$; blue: $2 \rightarrow 3$; black: $5 \rightarrow 6$ step) for $M\text{-N}_3$ plotted against ΔG_N . The colored solid lines in the graph are trend guidelines.

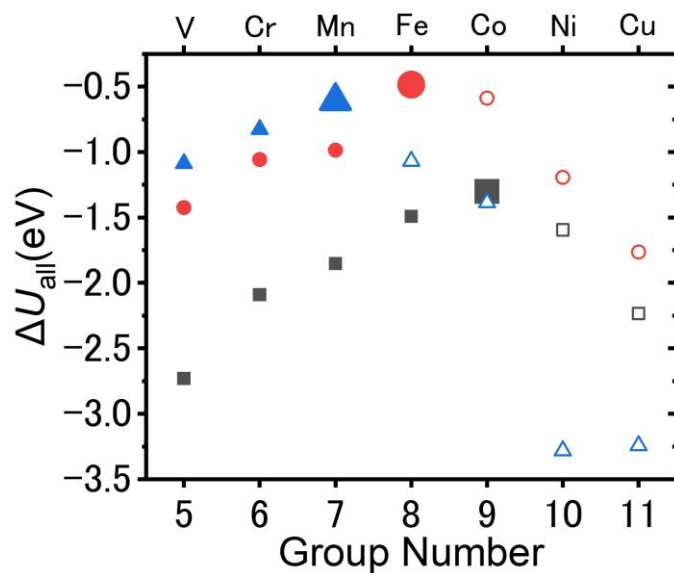


Figure 7. Plots of ΔU_{all} , at which all elementary steps become exergonic, for $M\text{-N}_2$ (black), $M\text{-N}_3$ (red), and $M\text{-N}_4$ (blue). Closed symbols and open symbols indicate that the potential-determining step was the desorption step ($5 \rightarrow 6$) or the adsorption step ($0 \rightarrow 1$, $1 \rightarrow 2$, or $2 \rightarrow 3$), respectively. Each large symbol represents the lowest limiting potential when comparing metal species with the same CN.

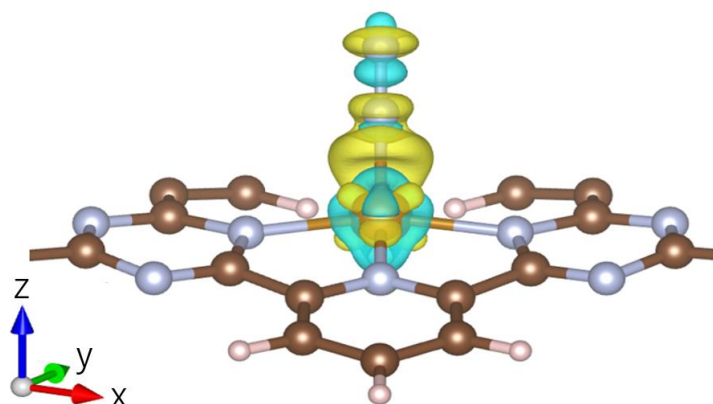


Figure 8. Charge density difference for Fe–N₃ before and after N₂ adsorption. The isosurface levels is 0.006 (e₀ a.u.⁻³). The positive and negative charges are represented by yellow and cyan, respectively. Ocher, light blue, brown, and white balls represent metal, N, C, and H atoms, respectively.

ASSOCIATED CONTENT

Supporting Information.

The adsorption structures of NRR intermediates on Fe-N₃. Limiting potentials for *M*-N₂ and *M*-N₄. Projected DOS. Charge density difference of N₂H-Fe-N₃. The bond length of N₂ and N₂H. The proposed NRR mechanism over Fe-N₃.

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Notes

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