

Article

Electrocatalytic Nitrate Reduction to Ammonia on Conductive Metal-Organic Frameworks with Varied Metal Centers

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Abstract

Nitrate pollution in groundwater poses severe threats to ecosystems and human health, making the electrochemical nitrate reduction reaction (NO₃RR) a promising remediation technology. Conductive metal–organic frameworks (cMOFs) with π -d conjugation, dispersed active sites, and tunable structures are ideal candidates for electrocatalysis. Herein, we synthesized a series of cMOFs (M₃(HHTP)₂, M = Fe, Zn, Cu, Co, Ni) via conjugated coordination between hexahydroxytriphenylene (HHTP) ligands and metal ions and systematically investigated their NO₃RR performance. Electrochemical tests revealed that Fe₃(HHTP)₂ exhibits superior catalytic performance for nitrate reduction, achieving a high NH₃ selectivity of 99.5% and a yield rate of 676.4 mg·g_{cat}^{−1}·h^{−1} at −1.0 V vs. RHE (reversible hydrogen electrode), along with excellent cyclic and structural stability. In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy identified key intermediates (*NO₂, *NH₂OH) and proposed the reaction pathway: NO₃[−] → *NO₃ → *NO₂ → *NO → *NOH → *NH₂OH → *NH₂ → *NH₃. DFT calculations revealed that Fe center exhibited a lower energy barrier for NO₃RR compared to other metal ions (Zn, Cu, Co, Ni). This study demonstrates the significant potential of Fe₃(HHTP)₂ for efficient NO₃RR and provides new insights into the structure-function relationship of cMOF-based electrocatalysts.

Keywords: conductive metal–organic frameworks (cMOFs); electrochemical nitrate reduction (NO₃RR); iron-based electrocatalyst



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1. Introduction

Nitrate is one of the most prevalent water pollutants worldwide, posing a significant threat to human health and the ecological environment [1]. Excessive discharge of nitrate (NO₃[−]) from agricultural runoff, urban sewage, industrial emissions, and other sources disrupts the nitrogen cycle, creating risks to ecosystems and human health [2–4]. The electrochemical nitrate reduction reaction (NO₃RR) powered by renewable energy offers greater kinetic advantages, thus having attracted considerable attention in recent years [5–8]. Electrochemical nitrate reduction can produce valuable ammonia (NH₃), but nitrogen dioxide, as the main byproduct, causes serious health issues such as birth defects and methemoglobinemia. It also lacks recovery value and therefore requires further reduc-

tion [9,10]. Consequently, it is necessary to design electrocatalysts with high selectivity for ammonia (NH_3) in low-concentration nitrate environments.

The elaborate design and regulation of catalysts are crucial for efficient and highly selective electrocatalytic nitrate-to-ammonia reduction reactions. Over the past few years, metal nanoparticles, alloys, metal oxides, and single-atom catalysts (SACs) have been extensively studied for nitrate reduction reactions [9–15]. Recently, metal–organic frameworks (MOFs) assembled from metal ions and organic ligands have shown great potential as electrocatalysts [16–19]. Their high chemical stability, accessible metal sites, and well-ordered coordination structures enable the formation of active centers with uniform distribution, high density, and tunable electronic properties [20]. Specifically, two-dimensional conductive metal–organic frameworks (2D cMOFs) constitute a unique subclass with their structures typically constructed via two-dimensional coordination between π -conjugated linkers and metal nodes [11,16]. This structural feature endows cMOFs with continuous electron transport pathways that guarantee efficient charge transfer and well-defined catalytic active sites.

The metal centers in MOFs as active sites plays an essential role in electrocatalytic process. Previous study demonstrated that ultrathin Ni-based MOFs (Ni-BDC) exhibit low activation energy (0.507 eV) for the NO_3RR . At -1.4 V vs. RHE (reversible hydrogen electrode), the nitrate reduction rate, rate constant, NH_3 selectivity, and NH_3 yield reached 96.4%, 0.448 h^{-1} , 80%, and $110.13\text{ }\mu\text{g}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$, respectively [21]. Other study reported that Cu-BTC indicated a higher NH_3 yield of $13.06\text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ at optimized -0.7 V vs. RHE [22]. Moreover, Co-based ZIF-67 and Co-HHTP catalysts can achieve an NH_3 yields of $87.41\text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and $79.11\text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$, respectively, at -1.0 V vs. RHE [23]. Despite extensive research on different metal centers, systematic comparison of MOFs with different metal centers in the same framework structure remains insufficient [21–23]. Considering the complex reaction pathways and intermediates of NO_3RR —which involves a multi-step reaction mechanism with nine protons and eight electrons—it has become imperative to understand the structure-performance relationship based on catalysts with well-defined metal centers [24,25].

Therefore, we constructed cMOFs through conjugated coordination between the organic ligand HHTP and metal ions (named as $\text{M}_3(\text{HHTP})_2$, where $\text{M} = \text{Fe}, \text{Zn}, \text{Cu}, \text{Co}$, or Ni) to investigate their nitrate reduction performance and mechanisms. In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) was performed to determine the intermediates and reaction pathways. Furthermore, density functional theory (DFT) calculations were employed to confirm the reaction pathway and energy. This work may provide valuable insights for the design of efficient metallized MOFs for NO_3RR and other reactions.

2. Materials and Methods

2.1. Materials and Reagents

2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), iron (II) acetate, cobalt acetate, nickel acetate, copper acetate monohydrate, zinc acetate, aqueous ammonia, N,N -dimethylformamide (DMF), potassium sulfate, Nafion (5 wt.%), ethanol, acetone, K_2SO_4 , and KNO_3 were all purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All chemicals were used without further purification.

2.2. Synthesis of $\text{M}_3(\text{HHTP})_2$ Material

The synthesis of $\text{M}_3(\text{HHTP})_2$ was performed with modifications to a previously reported procedure [26]. Briefly, copper acetate monohydrate (1 mmol) was dissolved in 25 mL of ultrapure water, while HHTP (1 mmol) and 0.6 mL of aqueous ammonia were

dissolved in 25 mL of N,N-dimethylformamide (DMF). The two freshly prepared solutions were mixed in a 50 mL beaker under ultrasonication for 20 min. The mixture was then heated in a constant temperature oven at 85 °C for 3 h, followed by natural cooling to room temperature. The resulting solid was washed with deionized water and acetone six times, respectively, and dried overnight in a vacuum oven at 60 °C. The synthesis of other $M_3(\text{HHTP})_2$ ($M = \text{Fe, Zn, Co, Ni}$) followed the same procedure, except that copper acetate monohydrate was replaced with the corresponding metal acetates.

2.3. Material Characterization

The morphology of the catalyst was characterized by scanning electron microscopy (SEM, Thermo Fisher Quattro, Waltham, MA, USA) and transmission electron microscopy (TEM, JEOL JEM-2100F, Tokyo, Japan) combined with energy-dispersive X-ray spectroscopy (EDS) elemental mapping. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS50R spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in the range of 400–4000 cm^{-1} . The crystal structure was analyzed by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with a scattering angle (2θ) range of 3–50°. X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS Supra, Shimadzu Corporation, Kyoto, Japan) was employed to determine the elemental valence states on the sample surface. Absorbance measurements were performed using an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu Corporation, Kyoto, Japan).

2.4. Electrochemical Testing

2.4.1. Nitrate Reduction

Electrochemical measurements were conducted using a three-electrode cell configuration on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China), where carbon cloth (CC), a silver/silver chloride electrode (SSCE), and a platinum electrode served as the working, reference, and counter electrodes, respectively. First, 5 mg of the as-prepared $M_3(\text{HHTP})_2$ was dispersed in a mixture of 400 μL anhydrous ethanol and 85 μL acetone, followed by the addition of 15 μL 5 wt.% Nafion solution to form a catalyst ink. The ink was ultrasonically dispersed for 0.5 h to ensure homogeneity. A 100 μL aliquot of the ink was then uniformly drop-cast onto a 1 cm $\times$ 1 cm carbon cloth substrate and air-dried to fabricate the working electrode.

The electrochemical measurements were performed in an H-type cell separated by a proton exchange membrane. The electrolyte for nitrate reduction experiments consisted of 0.1 $\text{mol}\cdot\text{L}^{-1}$ K_2SO_4 and 100 $\text{mg}\cdot\text{L}^{-1}$ NO_3^- . A silver/silver chloride (Ag/AgCl) electrode was used as the reference electrode. All potentials measured in the experiments were converted to the reversible hydrogen electrode (RHE) scale using the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \text{ V} \quad (1)$$

Linear sweep voltammetry (LSV) tests were performed in the aforementioned Ar-saturated electrolyte at a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$. Subsequently, potentiostatic electrolysis was conducted for 30 min at each potential interval of 0.1 V within the range of -0.7 V to -1.1 V (vs. RHE) to quantify the NH_3 yield, the yield of ammonia (NH_3) was calculated using the following equation:

$$\text{Yield } (\text{NH}_3) = \frac{C_{\text{NH}_3} \times V}{m \times t} \quad (2)$$

where C is the concentration of aqueous NH_3 in the electrolyte, V is the volume of the electrolyte, m is the mass of the loaded catalyst, and t is the reaction time. The mass-

normalized yield of nitrite (NO_2^-) was determined using the same formula, with C_{NH_3} replaced by the concentration of aqueous $C_{\text{NO}_2^-}$.

The Faradaic efficiency (FE) for NH_3 or NO_2^- production was determined by the equation:

$$\text{Faradaic Efficiency} = \left(\frac{C \times V \times F \times n}{Q} \right) \times 100\% \quad (3)$$

where C denotes the concentration of target product (NH_3 or NO_2^-) in the electrolyte, V is the volume of the electrolyte, n is the number of electrons transferred ($n = 8$ for NO_3^- reduction to NH_3 ; $n = 2$ for NO_3^- reduction to NO_2^-), F is the Faraday constant ($96,485 \text{ C} \cdot \text{mol}^{-1}$), and Q is the total charge passed through the electrode during electrolysis. To further evaluate the catalytic performance, the partial current density for NH_3 production (j_{NH_3}) and selectivity toward NH_3 (S_{NH_3}) were calculated. The partial current density, which reflects the current contribution of NH_3 production, was determined using the equation:

$$j_{\text{NH}_3} = \frac{C_{\text{NH}_3} \times V \times F \times n}{S \times t} \quad (4)$$

where C_{NH_3} is the concentration of NH_3 in the electrolyte, V is the electrolyte volume, $n = 8$ for NO_3^- reduction to NH_3 , F is the Faraday constant ($96,485 \text{ C} \cdot \text{mol}^{-1}$), S is the geometric area of the working electrode, and t is the reaction time.

The selectivity toward NH_3 , representing the fraction of NO_3^- reduced to NH_3 relative to total reduction products ($\text{NH}_3 + \text{NO}_2^-$), was calculated as:

$$S_{\text{NH}_3} = \left(\frac{n_{\text{NH}_3} \times 8}{n_{\text{NH}_3} \times 8 + n_{\text{NO}_2^-} \times 2} \right) \times 100\% \quad (5)$$

Here, n_{NH_3} and $n_{\text{NO}_2^-}$ are the molar amounts of produced NH_3 and NO_2^- , respectively; the factors 8 and 2 correspond to the electron transfer numbers for NO_3^- reduction to NH_3 and NO_2^- , ensuring normalization by electron consumption.

To determine the double-layer capacitance (C_{dl}), cyclic voltammetry (CV) measurements were conducted at scan rates of 10, 20, 30, 40, and 50 $\text{mV} \cdot \text{s}^{-1}$ within the non-Faradaic potential window near the open-circuit potential (OCP). Capacitive currents were extracted from this non-Faradaic region, and a linear plot of capacitive current density versus scan rate was constructed. The C_{dl} value was then derived from the slope of the fitted linear curve. The electrochemical active surface area (ECSA) represents the total area of surface-active sites on the catalyst that can participate in electrochemical reactions. It was derived by normalizing the measured double-layer capacitance C_{dl} against a literature-accepted specific capacitance (C_s) standard of $40 \mu\text{F} \cdot \text{cm}^{-2}$ for neutral aqueous electrolytes, as expressed by the equation:

$$\text{ECSA} = \frac{C_{\text{dl}}}{C_s} \times S \quad (6)$$

where S denotes the geometric area of the working electrode [27,28].

2.4.2. Detection of N-Containing Species

Prior to determining the concentration, the solution was diluted to an appropriate concentration.

1. Determination of Nitrate

1 mL of 1 M HCl solution and 0.01 mL of 0.8 wt% sulfamic acid solution were added to the diluted mixture. Nitrate ions exhibit a characteristic strong absorption at 220 nm, which is the basis for the quantitative determination of nitrate concentration. However, dissolved organic compounds in the electrolyte also produce non-negligible background

absorption at this wavelength. Notably, nitrate ions show negligible absorption at 275 nm, while the background absorption from organic compounds persists at this wavelength. Thus, the absorbance measurement at 275 nm serves to correct the background interference, ensuring the calculated absorbance accurately reflects the actual nitrate concentration. After 15 min, the color development was completed, and the absorbance was measured via UV-Vis spectrophotometry at wavelengths of 220 nm and 275 nm.

The final absorbance of NO_3^- -N was calculated using the following equation:

$$A = A_{220\text{nm}} - 2 \times A_{275\text{nm}} \quad (7)$$

A standard calibration curve was established based on the absorbance values of NO_3^- -N standard solutions with known concentrations.

2. Determination of Nitrite

To prepare the chromogenic reagent, 0.4 g of sulfanilamide and 0.02 g of N-(1-naphthyl)ethylenediamine dihydrochloride were dissolved in a mixed solution containing 5 mL of ultrapure water and 1 mL of phosphoric acid (density, $\rho = 1.70 \text{ g/mL}$). Subsequently, 0.1 mL of the chromogenic reagent was added to 5 mL of the diluted electrolyte. The solution was allowed to stand for 20 min, and then the absorbance was measured via UV-vis spectrophotometry at a wavelength of 540 nm. A standard calibration curve was established using a series of NO_2^- -N standard solutions with known concentrations.

3. Determination of Ammonium

Potassium sodium tartrate solution and Nessler's reagent were sequentially added to 5 mL of the diluted sample solution. The mixture was allowed to stand for 15–30 min, and then the absorbance was measured via UV-Vis spectrophotometry at a fixed wavelength of 420 nm. The standard calibration curve was established using a series of NH_4^+ standard solutions with known concentrations.

2.4.3. In Situ Fourier Transform Infrared (FTIR) Measurement

The electrolyte employed in this study was a mixed aqueous solution consisting of 0.1 M K_2SO_4 and $100 \text{ mg}\cdot\text{L}^{-1}$ NO_3^- (as the target reactant, sourced from KNO_3 with analytical purity). Prior to electrochemical measurements, high-purity argon (Ar , 99.999%) was purged through the electrolyte at a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$ for 30 min to completely eliminate dissolved oxygen, thus avoiding interference from oxygen reduction reactions. Electrochemical tests were conducted in a standard three-electrode system using a CHI 660E electrochemical workstation, operated in potentiostatic mode. The applied potentials were set to range from the open-circuit potential (OCP) to -1.0 V vs. RHE. For in situ Fourier transform infrared (FTIR) spectral collection, each set potential was maintained for 10 min to ensure a stable electrochemical state (Figure S1).

In situ FTIR spectra were acquired using a Thermo Nicolet iS50R (Thermo Fisher Scientific Inc., Waltham, MA, USA) spectrometer equipped with an MCT (Mercury Cadmium Telluride) detector. The spectral resolution was set to 4 cm^{-1} with 128 scans for each spectrum to improve signal-to-noise ratio.

2.5. DFT Calculations

DFT calculations were performed in VASP 5.4 using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). Projected augmented wave (PAW) potentials and a 500 eV plane-wave cutoff were employed to describe ionic cores and valence electrons, respectively. Gaussian smearing (0.05 eV) was used for partial occupation of Kohn-Sham orbitals. Self-consistency was achieved when the energy change was $<10^{-5} \text{ eV}$. Structural optimizations (full atomic relaxation) converged at a force tolerance of $0.01 \text{ eV}/\text{\AA}$, with

$1 \times 1 \times 1$ Monkhorst-Pack k-point sampling for Brillouin zone integration. Grimme's DFT-D3 method accounted for dispersive interactions, and a 15 Å vacuum thickness minimized interlayer effects. The free energy was calculated by the equation:

$$\Delta G = \Delta E + \text{ZPE} - T \times \Delta S \quad (8)$$

where E is the total energy, ZPE is the zero-point energy, S is the entropy, and T is set as 298.15 K.

3. Results

3.1. Material Properties

As observed from the SEM and TEM images, the $M_3(\text{HHTP})_2$ materials presented as irregular nanoparticles with an average particle size of approximately 50 nm (Figures 1a,b and S2). The elemental mapping demonstrates the uniform distribution of metal elements, carbon, and oxygen throughout the materials (Figures 1b and S2). X-ray diffraction (XRD) patterns show that $\text{Zn}_3(\text{HHTP})_2$ exhibits characteristic diffraction peaks at 2θ values of approximately 4.8° , 9.7° , 12.8° and 28.1° (Figure 1c), corresponding to the (110), (200), (210), and (001) crystal planes of AA-stacked $\text{Zn}_3(\text{HHTP})_2$ [29]. Slight shifts in peak positions were observed for MOFs containing different central metals (Figure 1c), indicating variations in local symmetry arising from differences in metal–ligand bonding.

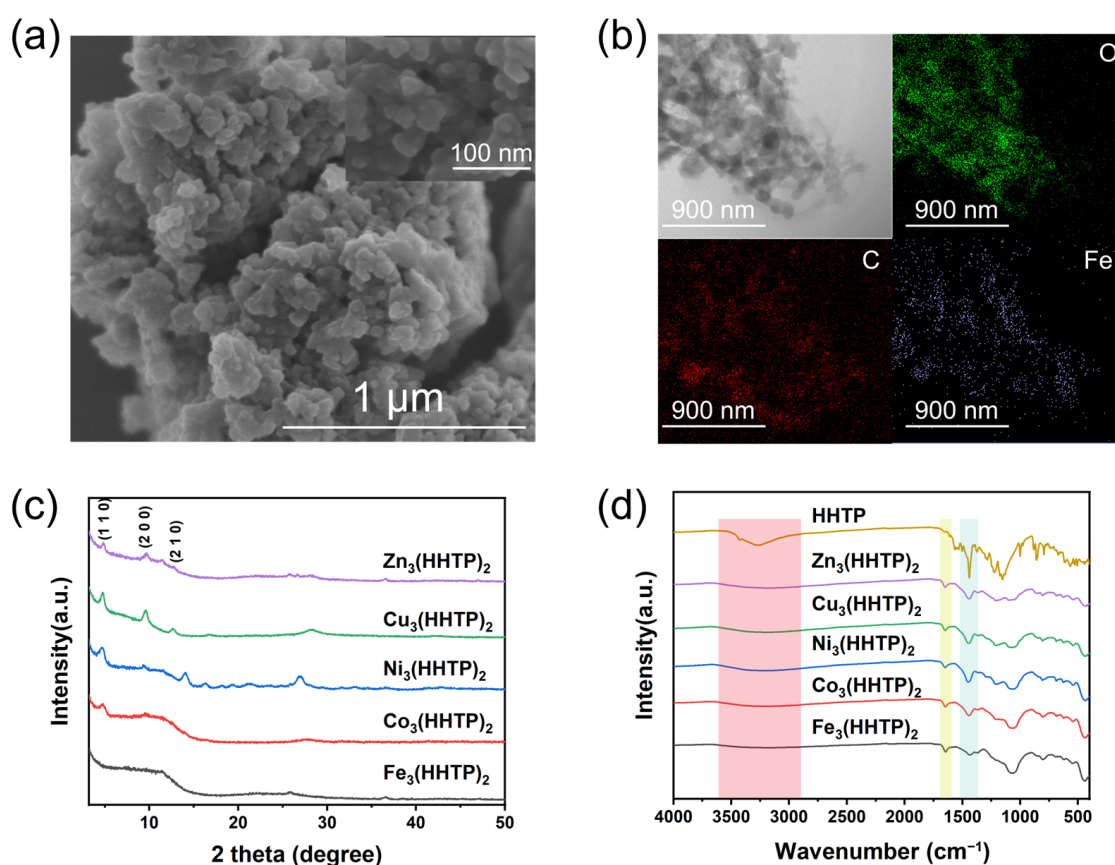


Figure 1. (a) SEM and (b) TEM image and elemental mapping of $\text{Fe}_3(\text{HHTP})_2$. (c) X-ray diffraction (XRD) patterns and (d) Fourier transform infrared (FTIR) spectra of $M_3(\text{HHTP})_2$ samples.

As shown in the Fourier transform infrared (FTIR) spectrum (Figure 1d), HHTP exhibits typical $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ stretching peaks at 1621 cm^{-1} and 1214 cm^{-1} , and the peaks below 1000 cm^{-1} corresponded to M-O stretching modes, respectively [30]. With introduction of metal ions for $M_3(\text{HHTP})_2$, the $\nu(\text{C}-\text{O})$ intensity of HHTP de-

creases while the $\nu(\text{C}=\text{O})$ intensity increases. This is because phenolic hydroxyl groups in HHTP are partially oxidized to quinones during MOF synthesis [29]. These results confirm the successful synthesis of $\text{M}_3(\text{HHTP})_2$. In summary, via a facile hydrothermal method, $\text{M}_3(\text{HHTP})_2$ coordination polymers were synthesized using metal acetates and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) as raw materials.

In addition, X-ray photoelectron spectroscopy (XPS) confirms the valence states of metal, C, and O elements (Figure 2). For $\text{Fe}_3(\text{HHTP})_2$, the Fe 2p XPS identified peaks at 710.98 and 724.38 eV, assigned to the +3 valence state (Figure 2a). The asymmetric C 1s peak can be deconvoluted into three peaks located at 284.58 eV, 285.60 eV, and 288.33 eV (Figure 2b), which are assigned to C-C, C-O, and C=O groups, respectively [31]. The O 1s peak can be deconvoluted into two peaks at 531.12 eV and 532.62 eV, correspond to C=O and C-O bonds (Figure 2c).

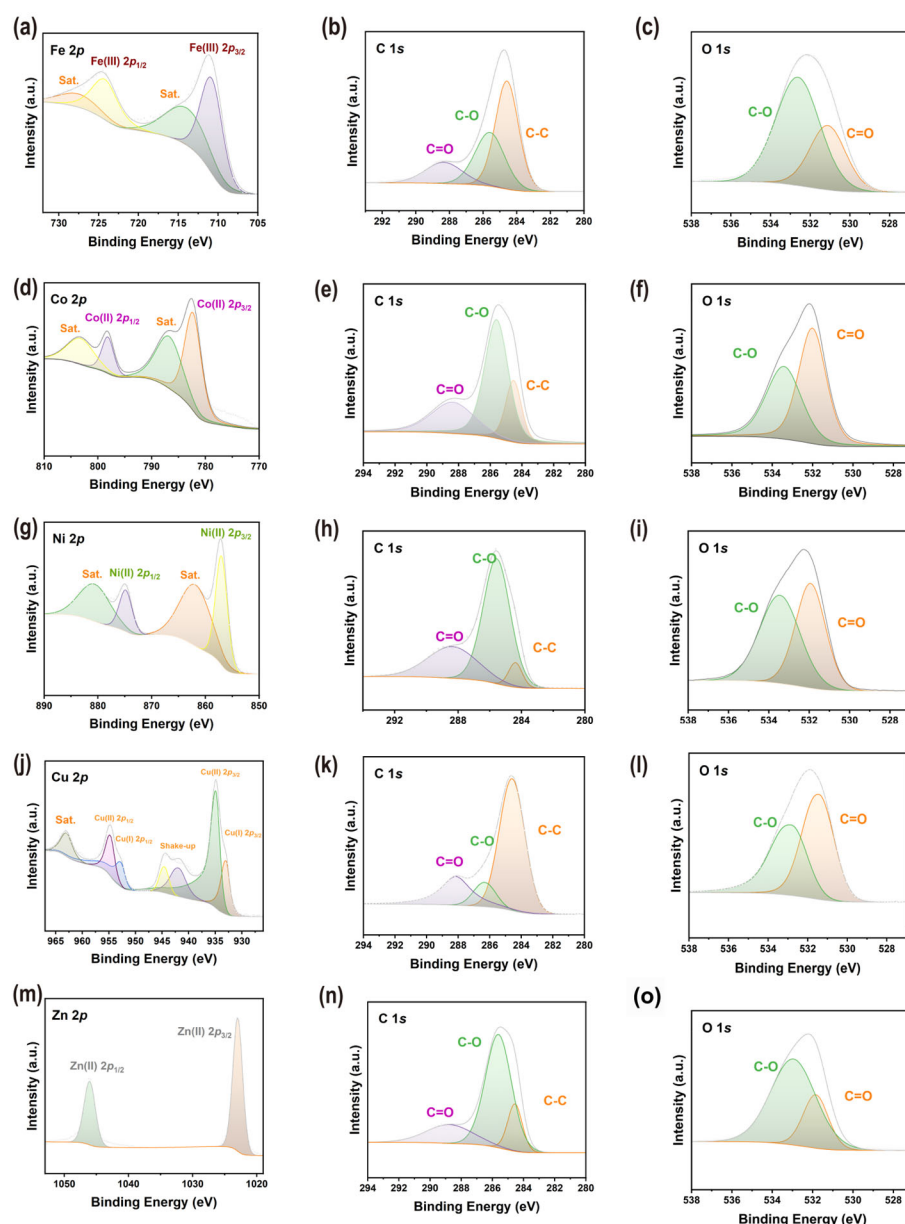


Figure 2. X-ray photoelectron spectroscopy (XPS) spectra of $\text{M}_3(\text{HHTP})_2$: (a) Fe 2p, (b) C 1s, and (c) O 1s of $\text{Fe}_3(\text{HHTP})_2$; (d) Co 2p, (e) C 1s, and (f) O 1s of $\text{Co}_3(\text{HHTP})_2$; (g) Ni 2p, (h) C 1s, and (i) O 1s of $\text{Ni}_3(\text{HHTP})_2$; (j) Cu 2p, (k) C 1s, and (l) O 1s of $\text{Cu}_3(\text{HHTP})_2$; (m) Zn 2p, (n) C 1s, and (o) O 1s of $\text{Zn}_3(\text{HHTP})_2$.

Similar chemical binding state characteristics are observed for MOFs with other metal centers. For $\text{Co}_3(\text{HHTP})_2$, the Co 2p XPS spectrum shows peaks at 782.13 and 797.93 eV, which are ascribed to the +2 valence state (Figure 2d) [32]. For $\text{Ni}_3(\text{HHTP})_2$, the Ni 2p XPS spectrum exhibits peaks at 856.13 and 874.63 eV, corresponding to the +2 valence state (Figure 2g). For $\text{Cu}_3(\text{HHTP})_2$, the Cu 2p XPS spectrum displays peaks at 792.80, 952.65, 934.65, and 954.60 eV, indicating mixed +1 and +2 valence states (Figure 2j). For $\text{Zn}_3(\text{HHTP})_2$, the Zn 2p XPS spectrum has peaks at 1022.67 and 1045.75 eV, assigned to the +2 valence state (Figure 2m). The asymmetric C 1s spectra of the other metal-centered MOFs can all be deconvoluted into three peaks in the range of 284.48–288.76 eV, which are assigned to C-C, C-O, and C=O groups, respectively (Figure 2e,h,k,n). Similarly, the O 1s peak of each MOF can be split into two peaks between 531.12 and 532.95 eV, corresponding to C=O and C-O bonds (Figure 2f,i,l,o).

3.2. Electrochemical Characteristics

To evaluate the electrocatalytic activity of $\text{M}_3(\text{HHTP})_2$, linear sweep voltammetry (LSV) measurements were conducted in 0.1 M K_2SO_4 solution with and without 100 mg L^{-1} NO_3^- (Figures 3a and S3). Compared to the LSV curve in the absence of NO_3^- , a pronounced increase in catalytic current was observed when NO_3^- was present, indicating that $\text{M}_3(\text{HHTP})_2$ exhibits distinct activity toward nitrate electroreduction. Specifically, $\text{Co}_3(\text{HHTP})_2$ displayed the highest reductive activity in the presence of NO_3^- (Figure 3b).

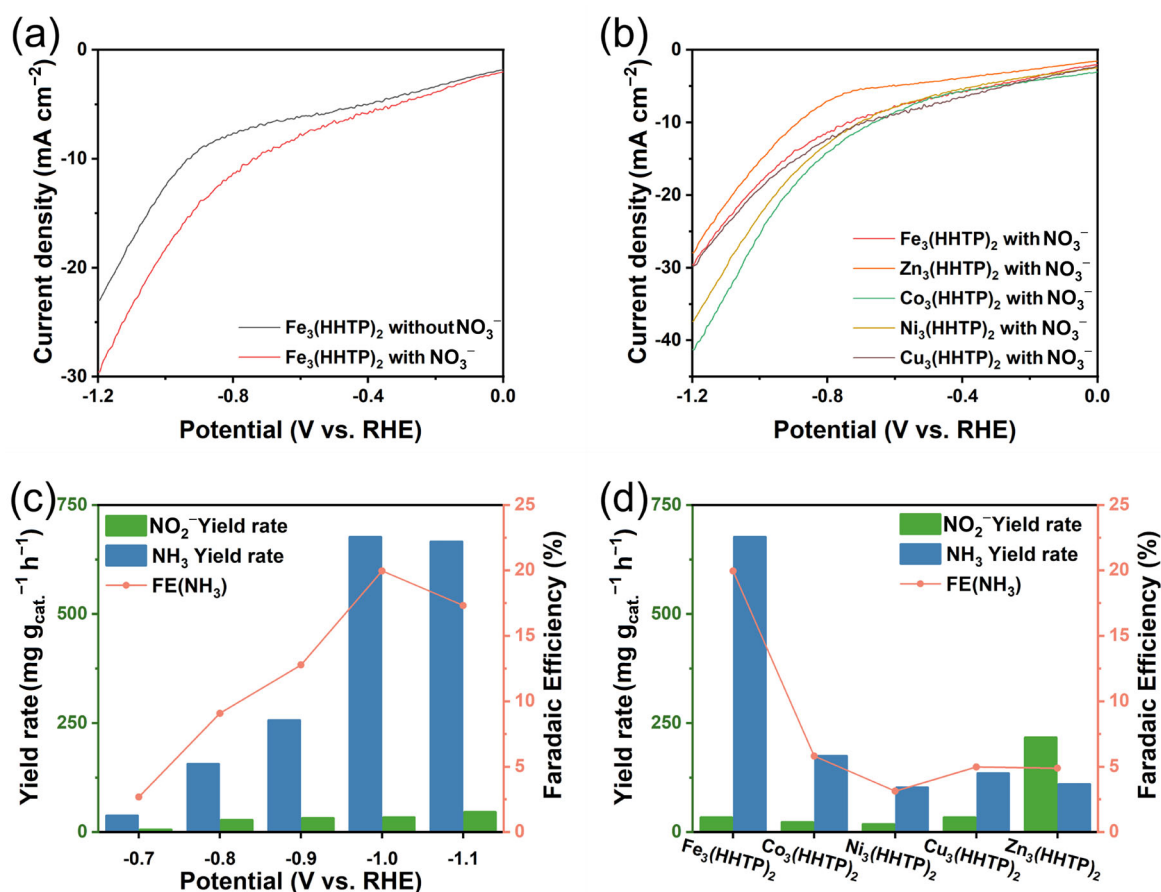


Figure 3. (a) Linear sweep voltammetry (LSV) curves of $\text{Fe}_3(\text{HHTP})_2$ in the presence and absence of 100 mg/L nitrate ions; (b) LSV curves of different $\text{M}_3(\text{HHTP})_2$ samples in the presence of 100 mg/L nitrate ions; (c) Nitrate/nitrite yields and Faradaic efficiencies of different $\text{M}_3(\text{HHTP})_2$ samples at a potential of -1.0 V vs. RHE; (d) Nitrate/nitrite yields and Faradaic efficiencies of $\text{Fe}_3(\text{HHTP})_2$ at different potentials.

To evaluate the efficiency of nitrate electroreduction, potentiostatic electrolysis experiments were performed on various $M_3(\text{HHTP})_2$ catalysts (Figures 3c and S4). As summarized in Table 1, $\text{Fe}_3(\text{HHTP})_2$ demonstrates the most superior NO_3RR performance among all tested catalysts. In terms of ammonia yield rate—a critical indicator of catalytic activity—it reaches $676.4 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, which is significantly higher than that of $\text{Co}_3(\text{HHTP})_2$ ($174.2 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), $\text{Cu}_3(\text{HHTP})_2$ ($134.7 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), $\text{Zn}_3(\text{HHTP})_2$ ($109.3 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), and $\text{Ni}_3(\text{HHTP})_2$ ($101.8 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$). In terms of ammonia Faradaic efficiency (FE), which reflects the selectivity of the catalyst for ammonia production over competing reactions, $\text{Fe}_3(\text{HHTP})_2$ also exhibits the highest value of 20.0%. This is substantially higher than the FE of $\text{Co}_3(\text{HHTP})_2$ (5.8%), $\text{Cu}_3(\text{HHTP})_2$ (5.0%), $\text{Zn}_3(\text{HHTP})_2$ (4.9%), and $\text{Ni}_3(\text{HHTP})_2$ (3.1%). Notably, $\text{Zn}_3(\text{HHTP})_2$ shows a high nitrite yield rate of $216.8 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, but a low ammonia FE, suggesting that Zn center tends to cause incomplete nitrate reduction rather than further conversion to ammonia. These results confirm that the metal center in $M_3(\text{HHTP})_2$ plays a decisive role in regulating NO_3RR activity and selectivity, with the Fe center being the most favorable for efficient and selective nitrate reduction to ammonia. Compared with previously reported literature (Table S1), $\text{Fe}_3(\text{HHTP})_2$ shows advantages in NH_3 selectivity and yield. The nitrate reduction performance of $\text{Fe}_3(\text{HHTP})_2$ was further evaluated at various applied potentials (Figure 3d). A volcano-type relationship was observed, where both the ammonia yield rate and Faradaic efficiency reached their maximum at -1.0 V vs. RHE.

Table 1. NH_3 and NO_2^- yield rate as well as Faradaic efficiency (NH_3) of different $M_3(\text{HHTP})_2$ at -1.0 V vs. RHE.

	Yield Rate (NH_3) / $\text{mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$	Yield Rate (NO_2^-) / $\text{mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$	Faradaic Efficiency (NH_3)/%
$\text{Fe}_3(\text{HHTP})_2$	676.4	33.5	20.0
$\text{Co}_3(\text{HHTP})_2$	174.2	22.6	5.8
$\text{Ni}_3(\text{HHTP})_2$	101.8	18.1	3.1
$\text{Cu}_3(\text{HHTP})_2$	134.7	33.4	5.0
$\text{Zn}_3(\text{HHTP})_2$	109.3	216.8	4.9

To gain insight into the intrinsic properties of the catalysts, CV measurements were performed in the non-Faradaic region. The electrochemical active surface area (ECSA) can indirectly reflect the activity of materials. The ECSA values were determined via CV measurements within the non-Faradaic potential range, and the calculated ECSA values are presented in Figure 4b. The ECSA followed the order of $\text{Fe}_3(\text{HHTP})_2$ (37.0 cm^2) < $\text{Cu}_3(\text{HHTP})_2$ (40.3 cm^2) < $\text{Zn}_3(\text{HHTP})_2$ (50.5 cm^2) < $\text{Co}_3(\text{HHTP})_2$ (51.5 cm^2) < $\text{Ni}_3(\text{HHTP})_2$ (54.5 cm^2), suggesting that although $\text{Fe}_3(\text{HHTP})_2$ exhibited the highest Faradaic efficiency, its ECSA was relatively low. The ammonia yield normalized by ECSA was calculated for $M_3(\text{HHTP})_2$ catalysts at -1.0 V vs. RHE. The obtained values were $18.3 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ (Fe), $3.4 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ (Co), $1.9 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ (Ni), $3.4 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ (Cu), and $2.2 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ (Zn). This ECSA-normalized yield reflects the ammonia production efficiency per unit active surface area, eliminating the influence of differences in active site accessibility among different catalysts. Evidently, $\text{Fe}_3(\text{HHTP})_2$ exhibits the most prominent intrinsic catalytic activity across the series.

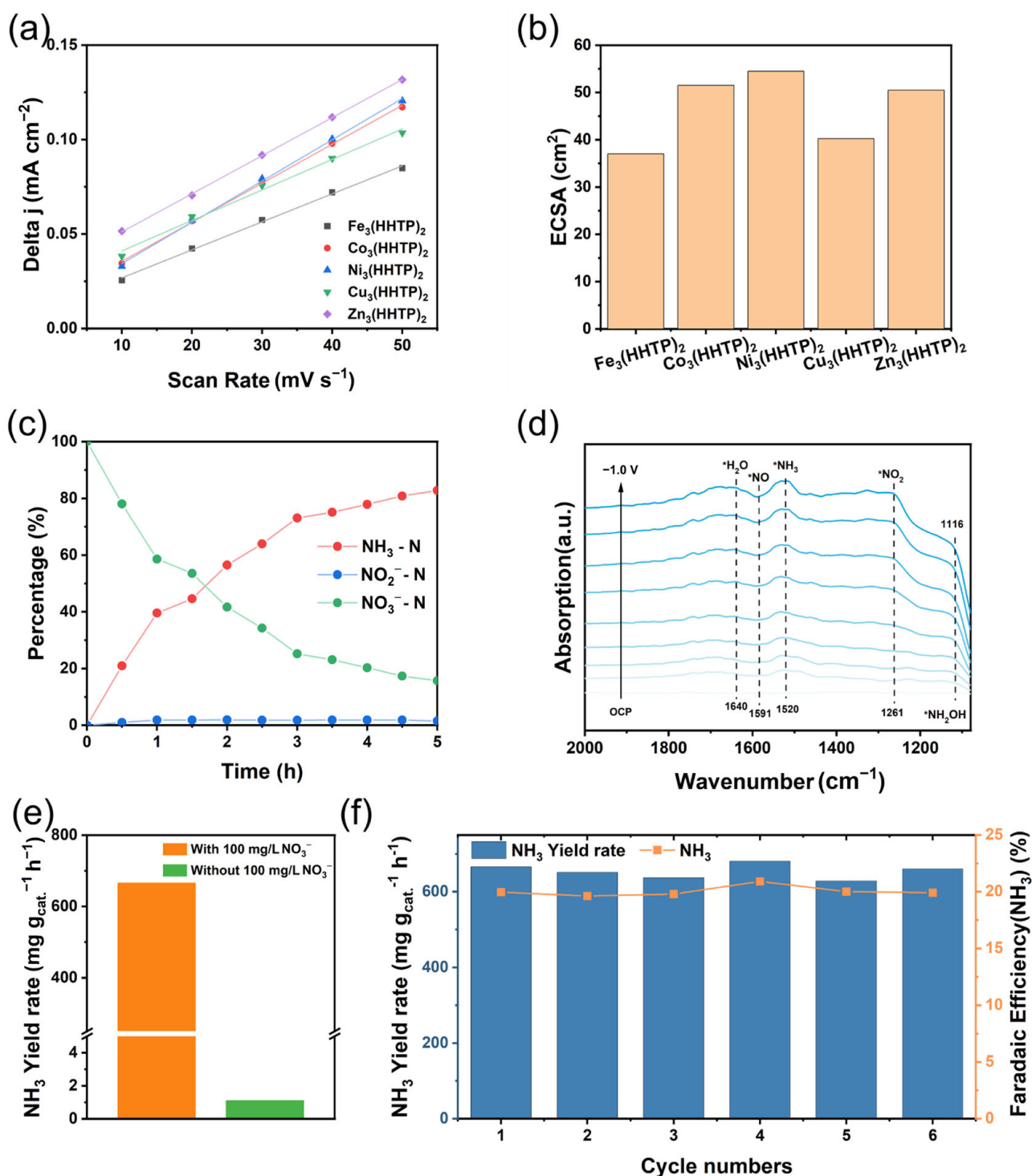


Figure 4. (a) Calculated C_{dl} and (b) ECSA of various $M_3(\text{HHTP})_2$ catalysts; (c) Concentration changes in nitrate, ammonium, and nitrite ions during electrolysis; (d) In situ ATR-FTIR spectra on $\text{Fe}_3(\text{HHTP})_2$; (e) Ammonia yield of $\text{Fe}_3(\text{HHTP})_2$ at -1.0 V vs. RHE in the presence and absence of nitrate ions; (f) NH_3 yield and Faradaic efficiency for NH_3 of $\text{Fe}_3(\text{HHTP})_2$ in consecutive recycling tests at -1.0 V vs. RHE.

This phenomenon may be attributed to the fact that all surface species capable of forming a double-layer structure contribute to the ECSA. Nevertheless, surface sites involved in non-Faradaic charging/discharging do not necessarily participate in Faradaic processes [33].

To verify the nitrate removal efficiency of $\text{Fe}_3(\text{HHTP})_2$ in aqueous solution, a 5 h long-term electrolysis was carried out at -1.0 V. With an initial nitrate concentration of 100 mg/L, the nitrate concentration decreased by 84.3% after 5 h, with only 1.5% of NO_3^- converted to NO_2^- (Figure 4c). This demonstrates that $\text{Fe}_3(\text{HHTP})_2$ exhibits excellent nitrate removal capability, ammonia conversion efficiency, and high ammonia selectivity for nitrate reduction.

To better understand the nitrate reduction reaction pathway and identify catalytic intermediates, we performed in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic measurements. Since $\text{Fe}_3(\text{HHTP})_2$ exhibits the highest ammonia yield rate, we addressed NO_3RR pathways on this catalyst. Figure 4d presents the in situ ATR-FTIR spectra on $\text{Fe}_3(\text{HHTP})_2$ as the potential was gradually decreased from the open circuit potential (OCP) to -1.0 V in a 0.1 mol·L $^{-1}$ K_2SO_4 solution containing 100 mg/L NO_3^- . The positive absorption peak at 1116 cm $^{-1}$ corresponds to the $-\text{N}-\text{O}-$ stretching vibration of $^*\text{NH}_2\text{OH}$, indicating that $^*\text{NH}_2\text{OH}$ is an intermediate of the reaction. The positive absorption peak at 1261 cm $^{-1}$ is attributed to the $\text{N}-\text{O}$ asymmetric stretching vibration of NO_2^- [34], demonstrating that NO_3^- is converted to NO_2^- as the nitrate reduction reaction proceeds. The negative absorption peak at 1591 cm $^{-1}$ corresponds to adsorbed $^*\text{NO}$ [35], and its intensity gradually decreases with the negative shift in potential, indicating the consumption of NO . The positive absorption peak at 1520 cm $^{-1}$ corresponds to $^*\text{NH}_3$ [36], and its intensity continuously increases with the negative shift in potential, confirming the formation of NH_3 . Notably, the absorption peak at 1640 cm $^{-1}$ is assigned to the $\text{O}-\text{H}$ stretching vibration of H_2O [37], suggesting that water dissociation occurs during NO_3RR to provide H for the hydrogenation of NO_x intermediates. For comparison, we also performed an in situ FTIR experiment without nitrate addition (Figure S5). The resulting spectrum displays only the characteristic 1640 cm $^{-1}$ peak of H_2O , this confirms that the peaks assigned to $^*\text{NO}$ (1591 cm $^{-1}$) and $^*\text{NH}_3$ (1520 cm $^{-1}$) in the nitrate-containing system are indeed derived from reaction intermediates, rather than from the cMOF framework or solvent background vibrations. Therefore, we propose the reaction pathway of $\text{Fe}_3(\text{HHTP})_2$ in nitrate reduction as $\text{NO}_3^- \rightarrow ^*\text{NO}_3 \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO} \rightarrow ^*\text{NOH} \rightarrow ^*\text{NH}_2\text{OH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$, where $*$ is denoted as the adsorption site on the $\text{M}_3(\text{HHTP})_2$ catalyst surface.

To verify the source of N in ammonia, electrocatalytic nitrate reduction experiments of $\text{Fe}_3(\text{HHTP})_2$ were conducted in the presence and absence of 100 mg/L nitrate, respectively. As shown in Figure 4e, $\text{Fe}_3(\text{HHTP})_2$ produces almost no ammonia only when nitrate is absent, demonstrating that the N in ammonia during nitrate reduction originated from nitrate.

Catalytic stability of electrocatalysts is another crucial factor for practical applications. To evaluate the cyclic stability of $\text{Fe}_3(\text{HHTP})_2$, six consecutive NO_3RR tests were performed at -1.0 V vs. RHE (Figure 4f). The results show that after six successive electrolysis cycles, the ammonia yield rate and Faradaic efficiency of $\text{Fe}_3(\text{HHTP})_2$ exhibited negligible change, indicating that $\text{Fe}_3(\text{HHTP})_2$ possesses excellent electrocatalytic stability. In addition, to confirm the structural stability of the material, LSV tests were conducted on $\text{Fe}_3(\text{HHTP})_2$ before and after the 5 h electrolysis. As shown in Figure S6, the LSV curves of $\text{Fe}_3(\text{HHTP})_2$ barely changed after the long-term electrolysis, indicating that the material itself possesses excellent structural stability.

3.3. Theoretical Calculations

To gain mechanistic insights into the effect of metal centers on the nitrate electroreduction reaction (NO_3RR), theoretical calculations were further performed to evaluate the reaction energies. Based on in situ ATR-FTIR spectroscopy studies (Figure 4d), the overall NO_3RR pathway on $\text{M}_3(\text{HHTP})_2$ conductive metal-organic frameworks (cMOFs, $\text{M} = \text{Fe}$,

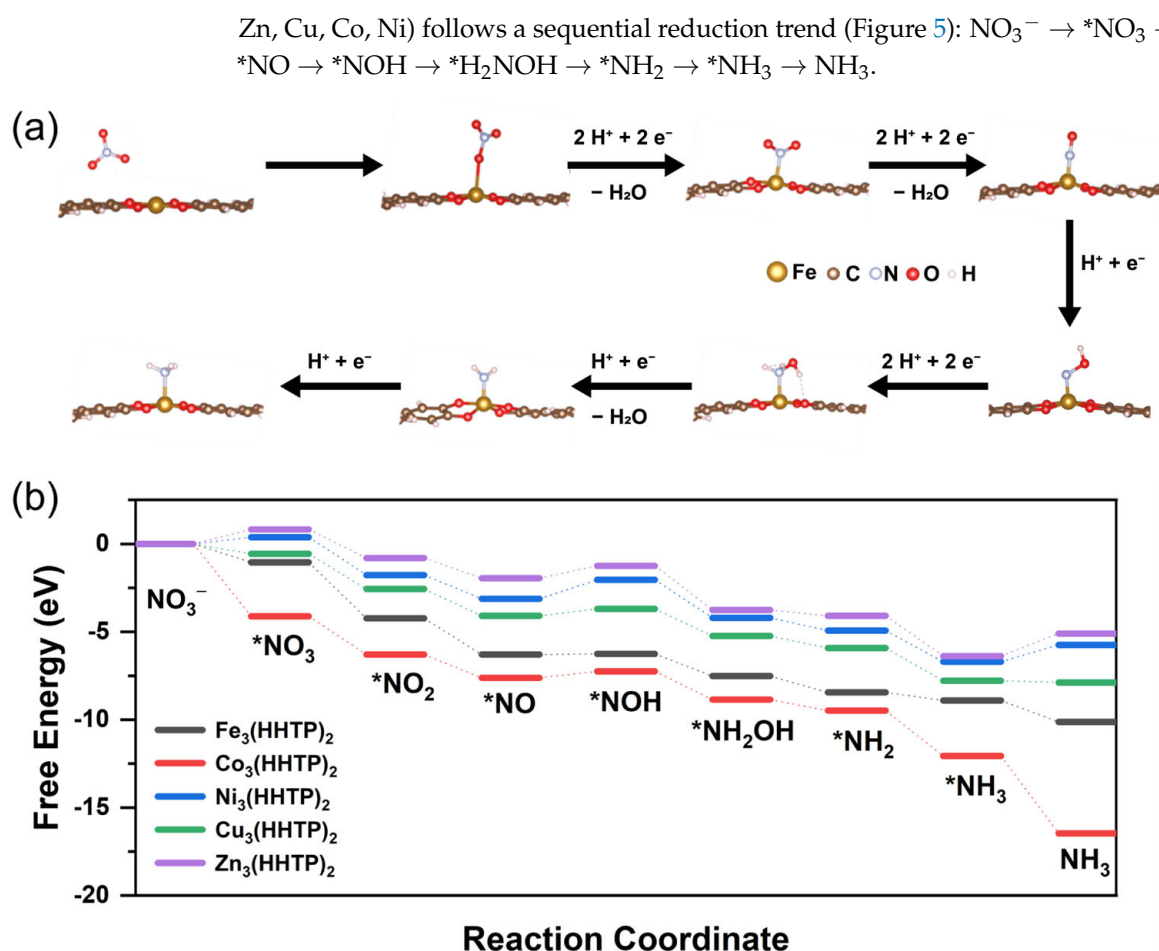


Figure 5. DFT calculations for the electronic structures and reaction mechanism. (a) The reaction mechanism of $\text{M}_3(\text{HHTP})_2$ catalyst for nitrate reduction to NH_3 . (b) Free-energy diagrams for nitrate reduction to NH_3 on the surfaces of $\text{M}_3(\text{HHTP})_2$.

The first step corresponds to the adsorption of NO_3^- to form $^*\text{NO}_3$ ($\text{NO}_3^- \rightarrow ^*\text{NO}_3$). For $\text{Fe}_3(\text{HHTP})_2$, $\text{Co}_3(\text{HHTP})_2$, and $\text{Cu}_3(\text{HHTP})_2$, the free energy change for $^*\text{NO}_3$ adsorption are -1.04 eV, -4.11 eV, and -0.57 eV, respectively, indicating spontaneous nitrate adsorption. In contrast, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Zn}_3(\text{HHTP})_2$ exhibit positive free energy change for $^*\text{NO}_3$ adsorption (0.38 eV and 0.83 eV), suggesting that nitrate adsorption on these catalysts requires overcoming a thermodynamic barrier.

The second step involves the reduction of $^*\text{NO}_3$ to $^*\text{NO}_2$ ($^*\text{NO}_3 \rightarrow ^*\text{NO}_2$). All $\text{M}_3(\text{HHTP})_2$ catalysts exhibit significant negative free energy changes in this step: -3.19 eV for $\text{Fe}_3(\text{HHTP})_2$, -2.18 eV for $\text{Co}_3(\text{HHTP})_2$, -2.15 eV for $\text{Ni}_3(\text{HHTP})_2$, -2.00 eV for $\text{Cu}_3(\text{HHTP})_2$, and -1.64 eV for $\text{Zn}_3(\text{HHTP})_2$. These negative values confirm the spontaneity of this reaction on all catalysts. Among them, $\text{Fe}_3(\text{HHTP})_2$ shows the largest free energy decrease, indicating the strongest thermodynamic driving force for this step.

Similarly to the second step, the third step ($^*\text{NO}_2 \rightarrow ^*\text{NO}$) also proceeds with significant negative free energy changes for all catalysts: -2.06 eV for $\text{Fe}_3(\text{HHTP})_2$, -1.32 eV for $\text{Co}_3(\text{HHTP})_2$, -1.35 eV for $\text{Ni}_3(\text{HHTP})_2$, -1.52 eV for $\text{Cu}_3(\text{HHTP})_2$, and -1.14 eV for $\text{Zn}_3(\text{HHTP})_2$. Notably, $\text{Fe}_3(\text{HHTP})_2$ still exhibits the largest free energy drop, which further supports its superior catalytic activity by virtue of the strongest driving force for this reduction step.

Distinct differences among the catalysts are observed in the next step ($^*\text{NO} \rightarrow ^*\text{NOH}$), all $\text{M}_3(\text{HHTP})_2$ materials show positive free energy changes, indicating an endothermic process. The energy barriers are 0.53 eV for $\text{Fe}_3(\text{HHTP})_2$, 0.93 eV for $\text{Co}_3(\text{HHTP})_2$, 1.59 eV for

$\text{Ni}_3(\text{HHTP})_2$, 0.94 eV for $\text{Cu}_3(\text{HHTP})_2$, and 1.23 eV for $\text{Zn}_3(\text{HHTP})_2$. Notably, the Fe-based cMOF has the lowest energy barrier, which further confirms its optimal catalytic activity.

For the subsequent $^*\text{NOH} \rightarrow ^*\text{H}_2\text{NOH}$ step, all catalysts exhibit negative free energy changes: -1.75 eV ($\text{Fe}_3(\text{HHTP})_2$), -2.16 eV ($\text{Co}_3(\text{HHTP})_2$), -2.68 eV ($\text{Ni}_3(\text{HHTP})_2$), -2.09 eV ($\text{Cu}_3(\text{HHTP})_2$), and -3.04 eV ($\text{Zn}_3(\text{HHTP})_2$), indicating spontaneous hydrogenation. The $^*\text{H}_2\text{NOH} \rightarrow ^*\text{NH}_2$ step also proceeds spontaneously for all metal centers, with free energy changes of -0.93 eV ($\text{Fe}_3(\text{HHTP})_2$), -0.63 eV ($\text{Co}_3(\text{HHTP})_2$), -0.72 eV ($\text{Ni}_3(\text{HHTP})_2$), -0.68 eV ($\text{Cu}_3(\text{HHTP})_2$), and -0.34 eV ($\text{Zn}_3(\text{HHTP})_2$).

The conversion of $^*\text{NH}_2$ to $^*\text{NH}_3$ is thermodynamically favorable for all catalysts, as reflected by their negative free energy changes: -0.45 eV ($\text{Fe}_3(\text{HHTP})_2$), -2.59 eV ($\text{Co}_3(\text{HHTP})_2$), -1.78 eV ($\text{Ni}_3(\text{HHTP})_2$), -1.85 eV ($\text{Cu}_3(\text{HHTP})_2$), and -2.29 eV ($\text{Zn}_3(\text{HHTP})_2$). Finally, the last step ($^*\text{NH}_3 \rightarrow \text{NH}_3$) shows divergent trends: $\text{Fe}_3(\text{HHTP})_2$, $\text{Co}_3(\text{HHTP})_2$, and $\text{Cu}_3(\text{HHTP})_2$ exhibit negative free energy changes (-1.23 eV, -4.40 eV, and -0.11 eV), enabling spontaneous NH_3 desorption. In contrast, Ni- and Zn-based cMOFs face specific thermodynamic limitations: their $^*\text{NH}_3 \rightarrow \text{NH}_3$ steps show positive free energy changes (0.96 eV for $\text{Ni}_3(\text{HHTP})_2$ and 1.29 eV for $\text{Zn}_3(\text{HHTP})_2$), which may lead to $^*\text{NH}_3$ accumulation on the catalyst surface and thus hinder the final formation of free NH_3 .

4. Conclusions

This work focuses on developing efficient cMOF-based electrocatalysts for nitrate reduction to address the critical need for highly selective NH_3 production from nitrate-contaminated water. Five $\text{M}_3(\text{HHTP})_2$ cMOFs ($\text{M} = \text{Fe}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}$) were successfully synthesized via a facile hydrothermal method. These materials exhibit uniform nanostructured morphologies and homogeneous distributions of metal, carbon, and oxygen elements, which together enhance electrolyte contact and active-site accessibility. Among them, $\text{Fe}_3(\text{HHTP})_2$ demonstrated the most outstanding performance, achieving an NH_3 yield rate of $676.4 \text{ mg} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ and a selectivity of 99.5%, along with excellent stability over six cyclic tests and 5 h continuous electrolysis (84.3% nitrate removal efficiency). In situ ATR-FTIR analysis identified

key intermediates and supported a stepwise nitrate reduction pathway ($\text{NO}_3 \rightarrow ^*\text{NO}_3 \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO} \rightarrow ^*\text{NOH} \rightarrow ^*\text{NH}_2\text{OH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$). DFT calculations further revealed a lower energy barrier for NO_3RR on $\text{Fe}_3(\text{HHTP})_2$ compared to other cMOFs. Overall, this study expands the application scope of cMOFs in electrochemical nitrate reduction, establishes a design strategy for high-performance electrocatalysts through central metal tuning, and highlights the potential of $\text{Fe}_3(\text{HHTP})_2$ for practical water remediation. These findings also provide guidance for future optimization of cMOFs by tailoring HHTP ligands or metal centers to minimize charge-transfer resistance and enhance catalytic performance in complex real-water systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations13020043/s1>, Figure S1: Photograph of the in-situ FTIR characterization setup; Figure S2: SEM and element mapping images of $\text{M}_3(\text{HHTP})_2$; Figure S3: Linear sweep voltammetry (LSV) curves of $\text{M}_3(\text{HHTP})_2$; Figure S4: Nitrate/nitrite yields and Faradaic efficiencies of $\text{M}_3(\text{HHTP})_2$ at different potentials; Figure S5: In-situ ATR-FTIR spectra on $\text{Fe}_3(\text{HHTP})_2$ without NO_3^- ; Figure S6: LSV curves of $\text{Fe}_3(\text{HHTP})_2$ before and after 5 h long-term electrolysis; Table S1: Comparisons of electrocatalytic denitrification performance between this work and other reported electrocatalysts [38–42].

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