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Modulating Electronic Structure of Cu-based MOF via Ni Doping for Efficient CO₂ Electroreduction to C₂₊ Products

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Abstract: Copper-based catalysts were used in electrochemical CO₂ reduction reactions (CO₂RR) to provide a sustainable way to convert CO₂ into valuable chemicals, but achieving high selectivity for multi-carbon (C₂₊) products such as ethylene remains challenging. Herein, we report a series of Ni-modified copper-based metal organic frameworks (MOFs) catalysts were synthesized by solvothermal method and subsequently subjected to calcination to obtain its derivatives. Among the prepared catalysts, CuNi-2 catalyst achieved a high Faradaic efficiency of 55.56 % for C₂₊ and 32.35% for ethylene at -1.0 V vs. RHE, along with excellent stability over 40 hours of continuous operation. Systematic characterization revealed that the introduction of Ni modulated the electronic structure of Cu, stabilizes Cu⁺ active species, and enriches the surface coverage of *CO intermediates, thereby promoting C-C coupling (a critical step toward C₂H₄ formation). Additionally, the porous MOFs-derived structure facilitates mass transport and confines reactive intermediates, further boosting ethylene selectivity. This work provides a bimetallic electronic modulation strategy offers a promising pathway for designing efficient Cu-based electrocatalysts toward high-value C₂₊ products.

Keywords: CO₂ reduction, ethylene, bimetallic catalyst, MOF derivatives,

electrocatalysis

1. Introduction

In recent decades, the continuous development of industrialization has led to excessive emissions of greenhouse gases, primarily CO₂, causing various environmental issues such as climate anomalies and sea-level rise [1, 2]. To address this challenge, extensive research efforts have been conducted on carbon emission reduction [3], and Carbon Capture, Utilization, and Storage (CCUS) technology has been recognized as one of the most effective strategies for mitigating CO₂ emissions [4]. As a promising approach, using renewable electricity electrocatalytic CO₂ reduction reaction (CO₂RR) has been widely investigated due to its ability to convert CO₂ into value-added chemicals under ambient conditions [5, 6]. The main products of CO₂RR include C₁ products (e.g., CO, CH₄) and multi-carbon (C₂₊) products (e.g., C₂H₆, C₂H₄) [7, 8]. While significant progress has been made in electrochemically reducing CO₂ to C₁ products, the efficient conversion of CO₂ into higher-value C₂₊ products remains challenging [9, 10].

Copper (Cu) has been reported as the only heterogeneous metallic catalyst capable of catalyzing the production of various oxygenates and hydrocarbon fuels, including ethylene (C₂H₄), ethanol (C₂H₅OH), and propanol (C₃H₇OH) [11, 12]. This exceptional capability established Cu-based catalysts as the most promising candidates for electrocatalytic CO₂ reduction to C₂₊ products [13-15]. However, Cu-based catalysts often suffered from insufficient selectivity toward specific hydrocarbons, high overpotentials, and competitive hydrogen evolution reaction (HER) [16, 17]. Therefore, designing Cu-based electrocatalysts with high activity and selectivity became a significant challenge. Numerous strategies have been developed to enhance the C₂₊ product selectivity of Cu-based catalysts, such as crystal facet and morphology control, doping effects, oxidation state modulation, and interface engineering [18, 19]. Metal-organic frameworks (MOFs) were recognized for their high specific surface area,

tunable morphology, adjustable porosity, accessible active sites, and diverse electronic structures, making them ideal platforms for CO₂ adsorption and activation [20, 21]. Nevertheless, the inherently poor electrical conductivity and limited structural stability of MOFs significantly hindered their direct application as electrocatalysts [12, 13, 22]. Consequently, Cu-based MOFs catalysts, which combined the catalytic activity of Cu for multi-electron reduction with the structurally controllable effects of MOFs [20, 23], demonstrated markedly higher selectivity toward C₂₊ products compared to conventional Cu-based nano catalysts [24, 25]. In summary, the modification of Cu-based MOFs catalysts presented considerable research potential for enhancing C₂₊ product selectivity, improving stability, and suppressing the hydrogen evolution reaction [26, 27].

In previous studies, Bai et al [28]. developed a Cu-Ni atomic pair catalyst co-existing with bimetallic atom-cluster sites (CuNiAC@Ni/Cu-N-C) via pyrolysis of a Ni/Cu-ZIF-8 precursor. This unique configuration, featuring CuN₃ and NiN₄ dual sites adjacent to CuNi clusters, achieved outstanding CO₂ electroreduction performance with a CO Faradaic efficiency of 98.2 % at -0.7 V vs. RHE and remarkable stability over 70 hours. Combined experimental and theoretical analyses revealed that the synergistic interaction between the atomic clusters and dual atomic sites optimizes electron redistribution, narrows the bandgap, and lowers the energy barrier for the rate-determining *COOH formation step. Wang et al [29]. synthesized Cu-Ni alloy nanoparticles anchored on nitrogen-doped carbon nanotubes via a hydrothermal method followed by pyrolysis. The optimized CuNi/NCNT catalyst exhibited excellent CO₂ electroreduction performance, achieving a high CO Faradaic efficiency of 94.8 % and a current density of 26.6 mA·cm⁻² in an H-cell. Combined experimental and DFT studies revealed that the Cu-Ni alloy facilitates the formation of the key *COOH

intermediate, thereby enhancing CO production. Wu et al [30]. conducted a density functional theory (DFT) study on stepped Cu-M (M = Pt, Ni, Pd, Zn, Ag, Au) bimetallic catalysts for CO₂ reduction reaction (CO₂RR). They analyzed CO₂ activation, C₁ and C₂ reaction pathways, and key descriptors such as d-band center, charge transfer, and ICOHP. Their results show that Cu-Ni exhibits superior CO₂ activation with elongated C–O bonds and enhanced electron transfer, leading to a lower overpotential (1.03 eV) for the C₁ pathway favoring *CHO production.

In this study, a series of Cu-Ni bimetallic MOFs derivatives catalysts were prepared via the solvothermal method by different molar ratios of Cu and Ni. The influence of catalysts with different molar ratios on the electrocatalytic CO₂ reduction performance was compared. The results demonstrated that the incorporation of Ni into Cu-based MOFs catalysts exerted significant influences on the surface properties, structure, and electrochemical performance. At -1.0 V vs. RHE, CuNi-2 catalyst achieved a Faradaic efficiency of 32.35 % for the reduction of CO₂ to ethylene, while exhibiting good selectivity and excellent stability. A possible catalytic reaction mechanism was discussed in detail. Overall, this study provided a new insight for promoting the development and application of CO₂RR.

2. Experimental section

2.1 Catalysts synthesis

The specific catalysts synthesis steps were described in Supporting Information. Here, for clarity and simplicity in subsequent discussions, the Cu-Ni bimetallic MOFs derivatives catalysts of different precursor molar ratios were labeled with concise codes as summarized in Table 1. Subsequently, following the identical preparation procedure described above, a pure Ni MOFs derivatives catalyst could not be successfully synthesized. Thus, comparative experiments with this material were not included in the

subsequent testing.

Table 1 Catalyst codes and their corresponding nominal compositions

Catalyst Code	Material Description (precursor molar amount Cu/Ni)
CuNi-0	10 mmol/0
CuNi-1	7.5 mmol/2.5mmol
CuNi-2	5 mmol/5mmol
CuNi-3	2.5 mmol/7.5mmol

2.2 Materials characterization

The Cu-Ni bimetallic MOFs derivatives catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), N₂ adsorption and desorption experiment and scanning electron microscopy/elemental mapping (SEM/EDS), inductively coupled plasma optical emission spectrometry (ICP-OES). The detailed catalysts characterization methods were described in Supporting Information.

2.3 Preparation of working electrode

For the preparation, 10 mg of the catalyst powder was accurately weighed and dispersed into a mixture of 100 μ L Nafion (D520) and 300 μ L ethanol. The mixture was ultrasonicated at 100 % power for 1 hour to form a homogeneous ink. The resulting ink was then drop-cast onto a $1 \times 1 \text{ cm}^2$ carbon paper substrate. The coated electrode was allowed to dry naturally under ambient conditions to obtain the working electrode.

2.4 Electrochemical measurements

To evaluate the catalytic performance for electrocatalytic carbon dioxide reduction, a reaction system was designed and constructed as shown in Figure 1. All electrochemical CO₂ reduction measurements were performed in an H-type electrolytic cell controlled

by an electrochemical workstation (CHI660E, China). The airtight H-cell (Figure S1) was separated into cathode and anode compartments by a cation exchange membrane (Nafion 117, Dupont, USA), with 30 mL of 0.5 M KHCO_3 solution used as the catholyte and anolyte, respectively. A Pt foil ($10 \times 10 \times 0.2$ mm, Gooss Union, China) was used as the counter electrode, an Ag/AgCl electrode (Gooss Union, China) served as the reference electrode, and the working electrode was prepared by drop-casting the catalyst onto carbon paper. During testing, the catholyte was stirred at 200 rpm using a magnetic stirrer to prevent bubble accumulation on the working electrode. A flow rate controller was used to regulate the CO_2 gas flow. Before the reaction, CO_2 was continuously introduced into the catholyte at a flow rate of 20 mL/min for 30 minutes to ensure complete saturation, followed by continuous CO_2 bubbling at 20 mL/min throughout the experiment.

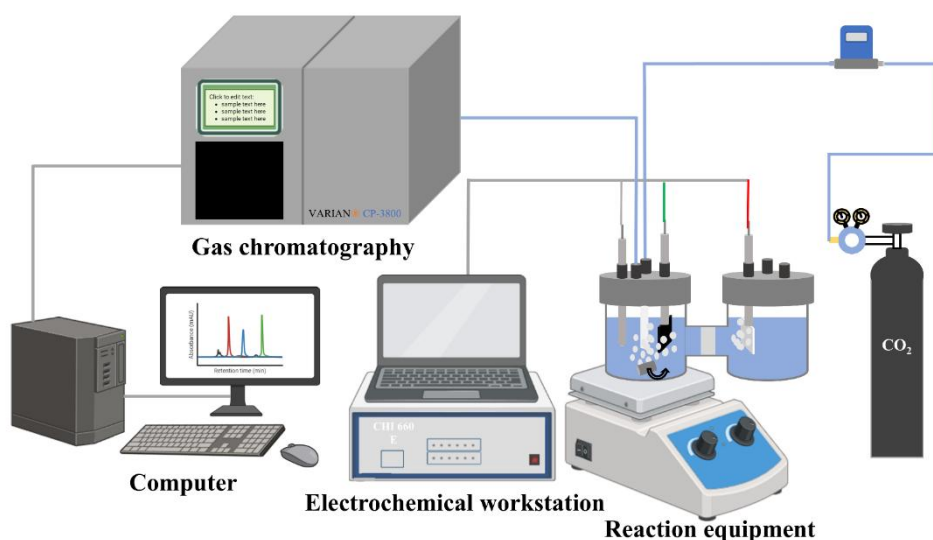


Fig. 1. Schematic diagram of electrochemical reaction system.

After 10 minutes of reaction, the gaseous products were collected using a gas bag for 18 minutes. The effluent gas, carried by the CO_2 stream from the cathode compartment, was analyzed online by gas chromatography (CP-3800, Varian) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The FID was used

to detect C₁ and C₂₊ products, while the TCD was employed to quantify H₂. After the reaction, liquid products in the catholyte were collected and analyzed by ¹H-NMR (Bruker Avance III 400 MHz). All potentials measured against the Ag/AgCl reference electrode in this study were converted to the reversible hydrogen electrode (RHE) scale using the equation 1.

$$E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \times pH + 0.210 \text{ V} \quad (1)$$

The Faradaic efficiencies for various gaseous reaction products were calculated using the following equation 2.

$$FE (\%) = \frac{i_{\text{product}}}{i_{\text{total}}} \times 100\% = \frac{V_{\text{product}} \times Q \times \frac{KF}{V_m}}{i_{\text{total}}} \times 100\% \quad (2)$$

The Faradaic efficiencies for various liquid reaction products were calculated using the following equation 3.

$$FE (\%) = \frac{Q_{\text{product}}}{Q_{\text{total}}} \times 100\% = \frac{F \times C \times V_{\text{liquid}} \times K}{i_{\text{total}} \times t} \times 100\% \quad (3)$$

Where F represents the Faraday constant (96485 C/mol), *i*_{total} is the total current measured during the electrochemical reaction (mA), *V*_{product} is the volume fraction of the gas product in the outlet gas, Q is the flow rate of the outlet gas, K is the number of electrons transferred by the generated product, *V*_m is the molar volume of the gas under ambient temperature and pressure (24.5 L/mol), C is the concentration of the target product (mol/L), *V*_{liquid} represents the volume of the electrolyte (L), t represents reaction time (min).

3. Results and discussion

3.1 Construction and characterization

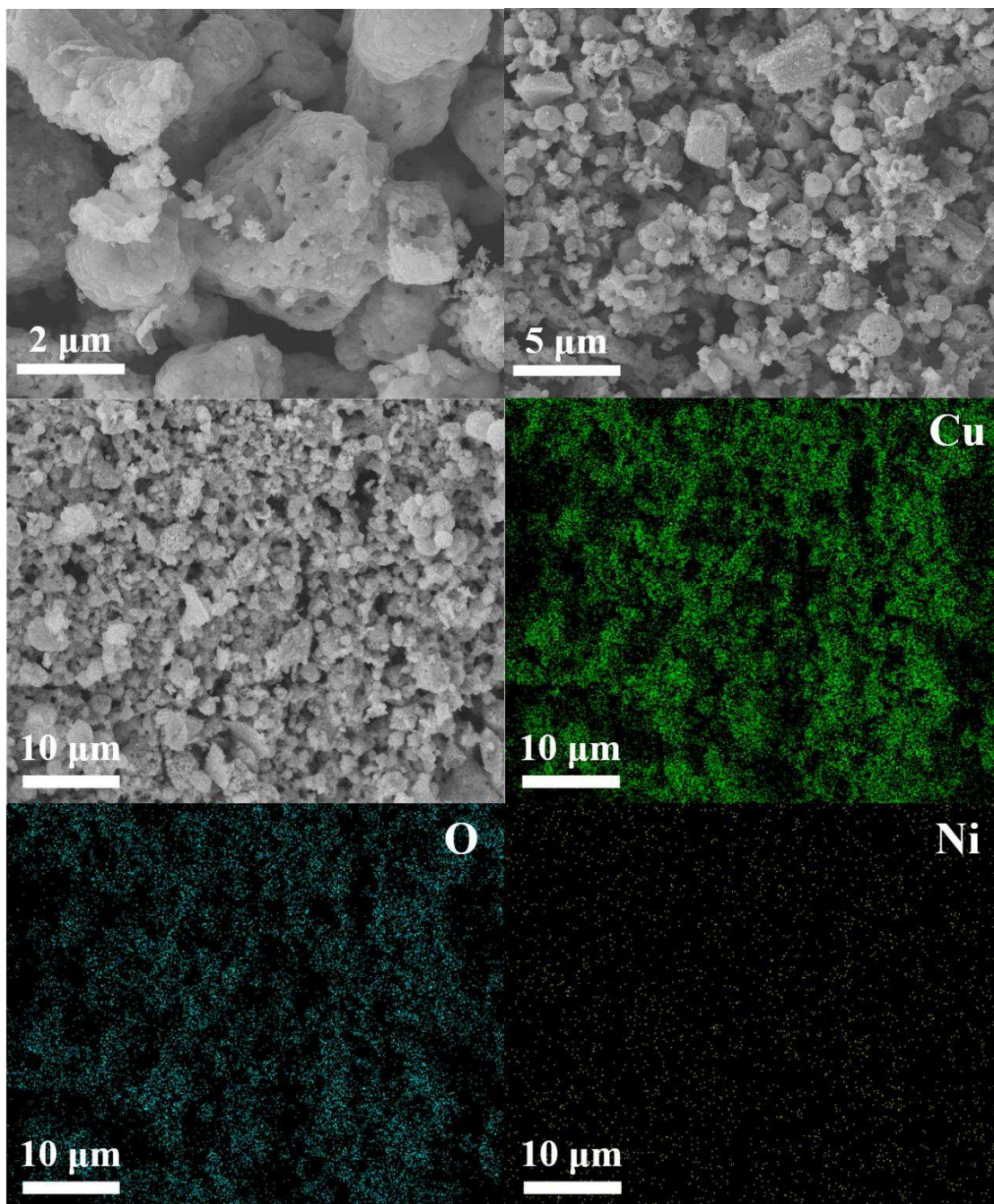


Fig. 2. SEM images of different proportions and EDS elemental maps of CuNi-2 catalyst.

The morphological characteristics of Cu-Ni bimetallic MOFs derivatives catalysts were examined by scanning electron microscopy (SEM) and EDS elemental mapping, as shown in Figure 2 and Figure S3. The surfaces of all four catalysts were covered with abundant and uniformly distributed granular materials. However, numerous nanoparticles were agglomerated in a disordered manner, which likely contributed to the formation of substantial interparticle porosity [31]. As shown in Figures S3(a) and

S3(b), both CuNi-0 and CuNi-1 catalysts exhibited massive block-like structures formed by the aggregation of a large number of nanoparticles. Furthermore, when the precursor content of Ni was increased (Figures 2 and S3(c)), catalysts (CuNi-2 and CuNi-3) displayed agglomerated nanoparticles assembling into individual ellipsoidal structures, with relatively independent spheres. This phenomenon was likely attributed to the increased Ni content in the precursor solution, which promoted particle agglomeration on the catalyst surface. The EDS results indicated a homogeneous distribution of Cu, Ni, and O elements across the catalyst surfaces [32]. However, the Ni elemental map in Cu-Ni bimetallic MOFs derivatives catalysts appeared less distinct, possibly due to the relatively low Ni content on the surface [33, 34]. This observation was consistent with the relatively low peak intensity of NiO in the XRD patterns.

As shown in Figure S2, the uncalcined precursor catalyst exhibited characteristic diffraction peaks appeared at $2\theta = 6.8^\circ, 9.5^\circ, 11.6^\circ, 13.5^\circ, 15.0^\circ, 16.5^\circ, 17.6^\circ, 19.1^\circ, 20.3^\circ, 24.1^\circ, 26.0^\circ, 29.5^\circ, 35.3^\circ$ and 39.2° corresponding to the (200), (220), (222), (400), (420), (511), (440), (442), (551), (731), (751), (773) and (882) crystal planes, which was consistent with what has been reported previously [35]. The XRD patterns of Cu-Ni bimetallic MOFs derivatives catalysts were presented in Figure 3(a). The diffraction peaks observed at $32.5^\circ, 35.5^\circ, 38.7^\circ, 48.8^\circ, 53.4^\circ, 58.2^\circ, 61.5^\circ, 66.2^\circ$ and 68.1° corresponded to the crystalline phases of CuO (PDF#48-1548). The diffraction peaks observed at 43.3° and 75.2° corresponded to the crystalline phases of NiO (PDF#47-1049). As shown in the figure, the fundamental CuO lattice structure remained intact after the incorporation of NiO, confirming the preservation of structural integrity in Cu-Ni bimetallic MOFs derivatives catalysts. The characteristic peaks at 35.5° and 38.7° were indexed to the (11-1) and (200) crystal planes of CuO, which have

been identified as crucial for the formation of C₂ products [36]. Importantly, no significant peak shifts of Cu or Ni were observed, indicating the absence of CuNi alloy formation [37]. These results collectively demonstrated the successful formation of a well-defined MOFs structure in Cu-Ni bimetallic MOFs derivatives catalysts.

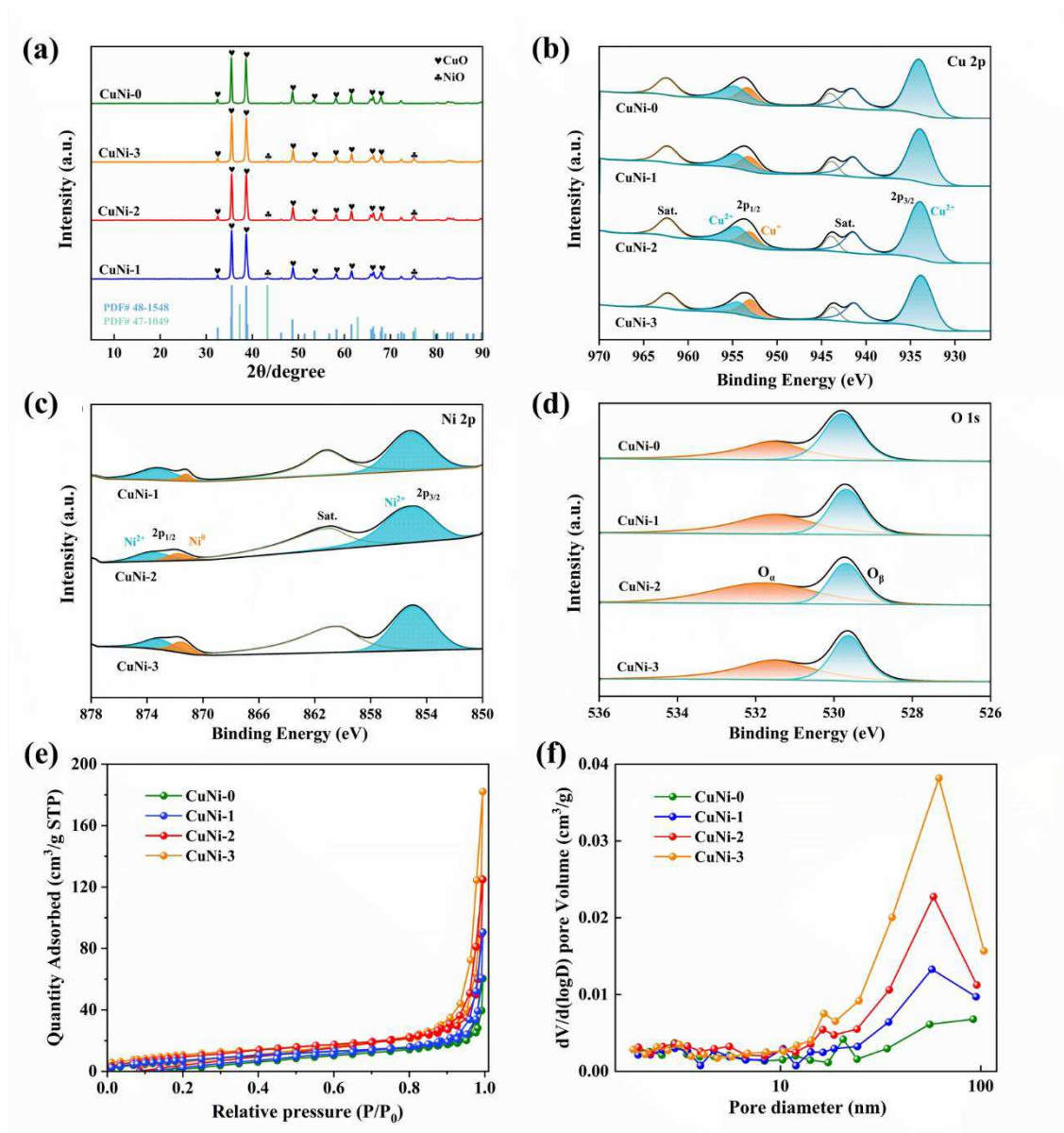


Fig. 3. (a) XRD patterns of CuNi-X catalysts. XPS spectra of CuNi-X catalysts (b) Cu 2p, (c) Ni 2p, (d) O 1s. (e) N₂ adsorption-desorption isotherms of CuNi-X catalysts. (f) Pore size distribution of CuNi-X catalysts.

To further determine the contents of Cu and Ni in the Cu-Ni bimetallic MOFs derivatives catalysts, inductively coupled plasma optical emission spectrometry

(ICP-OES) was performed, and the results are summarized in Table S4. In all catalysts, the Cu content exceeded 70 wt.%. Among the bimetallic samples, the highest Ni content reached 3.16 wt.% in the CuNi-3 series. These quantitative results further corroborated the trends observed in the XRD patterns and EDS elemental mapping.

X-ray photoelectron spectroscopy (XPS) was performed on Cu-Ni bimetallic MOFs derivatives catalysts to probe the oxidation state and chemical composition of the catalysts, as shown in Figure 3(b-d). As shown in Figure 3(b), the Cu 2p spectra displayed distinct doublet features for all catalysts. There were two distinct peaks were observed which were attributed to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, other peaks were matched with the satellite peaks [38]. The Cu 2p_{1/2} signal could be deconvoluted into two peaks at 953.1 eV and 954.6 eV, which were attributed to Cu⁺ and Cu²⁺ species [39], respectively. The Cu 2p_{3/2} peak at 933.9 eV was attributed to Cu²⁺ [15]. As summarized in Table S1, on the surfaces of all catalysts, the predominant copper species was identified as Cu²⁺, while Cu⁺ species accounted for less than 20 % of the total copper content. It is well-established that Cu⁺ species are recognized as key sites for promoting the adsorption of CO intermediates and their subsequent coupling to form C₂₊ products such as ethylene. However, the superior performance of the CuNi-2 catalyst was not solely attributed to its highest Cu⁺ proportion, but rather could be explained by the appropriate Ni doping which created a local environment capable of stabilizing a moderate proportion of Cu⁺ species [39]. This specific environment prevented the excessive reduction of Cu⁺ to Cu⁰ while also inhibiting over-oxidation under reaction conditions, thereby providing durable and highly efficient active sites.

The Ni 2p spectrum (Figure 3(c)) exhibited two distinct peaks corresponding to the Ni 2p_{1/2} and Ni 2p_{3/2} spin-orbit doublets, the other peak at 861.2 eV were matched with the satellite peak [38]. The Ni 2p_{1/2} signal could also be deconvoluted into two peaks at

871.2 eV and 873.2 eV, which were attributed to Ni⁰ and Ni²⁺ species [40], respectively. The Ni 2p_{3/2} peak at 855.1 eV was attributed to Ni²⁺ [41]. The Cu 2p and Ni 2p spectra revealed that with increasing Ni content, the binding energies of Cu 2p_{3/2} and Ni 2p_{3/2} exhibited slight shifts, suggesting electron transfer between Cu and Ni species. This indicated that Ni was not present as a separate metallic phase but was likely incorporated into the CuO lattice or existed as highly dispersed NiO clusters in close contact with CuO, forming a solid-solution-like interface or heterojunction structure rather than a bulk alloy. CuNi-2 catalyst possessed the highest proportion of Ni²⁺ (Table S2). As a moderate modifier, Ni²⁺ was able to donate electrons to Cu sites through electronic interactions, which contributed to stabilizing the Cu⁺ state of Cu and was likely a key factor in its superior electrocatalytic reduction performance. Furthermore, in the O 1s spectra (Figure 3(d)), two peaks at 531.5 eV and 529.7 eV were identified as chemisorbed oxygen (O_α) and lattice oxygen (O_β) [4], respectively.

Table 2 Surface area and pore size of Cu-Ni bimetallic MOFs derivatives catalysts

Catalyst	Surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
CuNi-0	24.4	14.8	0.009
CuNi-1	26.5	18.9	0.014
CuNi-2	39.2	20.5	0.019
CuNi-3	41.1	26.3	0.028

To investigate the physical properties of catalysts, N₂ adsorption-desorption tests were conducted on Cu-Ni bimetallic MOFs derivatives catalysts. The results were shown in Figure 3(e) and Table 2. As observed from the figure, the isotherms of all catalysts exhibited type III characteristics with no distinct inflection points and showed no apparent hysteresis loops, indicating a relatively simple pore structure. Among all the

catalysts, CuNi-3 demonstrated the largest specific surface area, while CuNi-0 showed the smallest. With the introduction and increasing content of Ni in the copper-based catalysts (from CuNi-0 to CuNi-3), the specific surface area and pore volume generally displayed an increasing trend. This suggested that Ni doping might alter the crystal nucleation and growth process, resulting in a looser and more open framework structure, thereby providing more surface area and space for adsorption. The results in the pore size distribution (Figure 3(f)) and Table 2 showed that the pore sizes of the catalysts ranged from 2 nm to 50 nm, exhibiting a well-defined mesoporous structure. All Ni-doped samples had significantly larger average pore sizes compared to CuNi-0, with CuNi-3 possessing the largest pore size. This further confirmed that the introduction of Ni promoted the formation of a porous structure. These results indicated that the increased specific surface area of Cu-Ni bimetallic MOFs derivatives catalysts might contribute to enhanced catalytic performance. The optimized pore structure likely facilitated easier access of reactants to the active sites, improves the utilization efficiency of these sites, and thereby promoted the CO₂RR reaction.

3.2 Electrocatalytic performance for CO₂RR

To investigate the influence of Cu-Ni bimetallic MOFs derivatives catalysts on the CO₂RR, their catalytic activities were evaluated in a CO₂-saturated 0.5 M KHCO₃ solution. Linear sweep voltammetry (LSV) was employed to assess the electrocatalytic activity at a scan rate of 50 mV/s over a potential range from -1.1 to -0.4 V vs. RHE, as shown in Figure 4(a). Compared to CuNi-0 catalyst, Cu-Ni bimetallic MOFs derivatives catalysts exhibited higher current densities, indicating that the bimetallic synergistic effect enhanced the catalytic activity in certain aspects [33]. At lower potentials, CuNi-2 catalyst demonstrated a greater current density than CuNi-1 and CuNi-3 catalysts, suggesting its potentially superior electrocatalytic activity under these

conditions. Notably, at higher overpotentials, the current density of CuNi-3 catalyst increased more rapidly than those of CuNi-2 and CuNi-1 catalysts. This result implies that a higher Ni content may play a key role in improving the electrical conductivity of the catalyst [38].

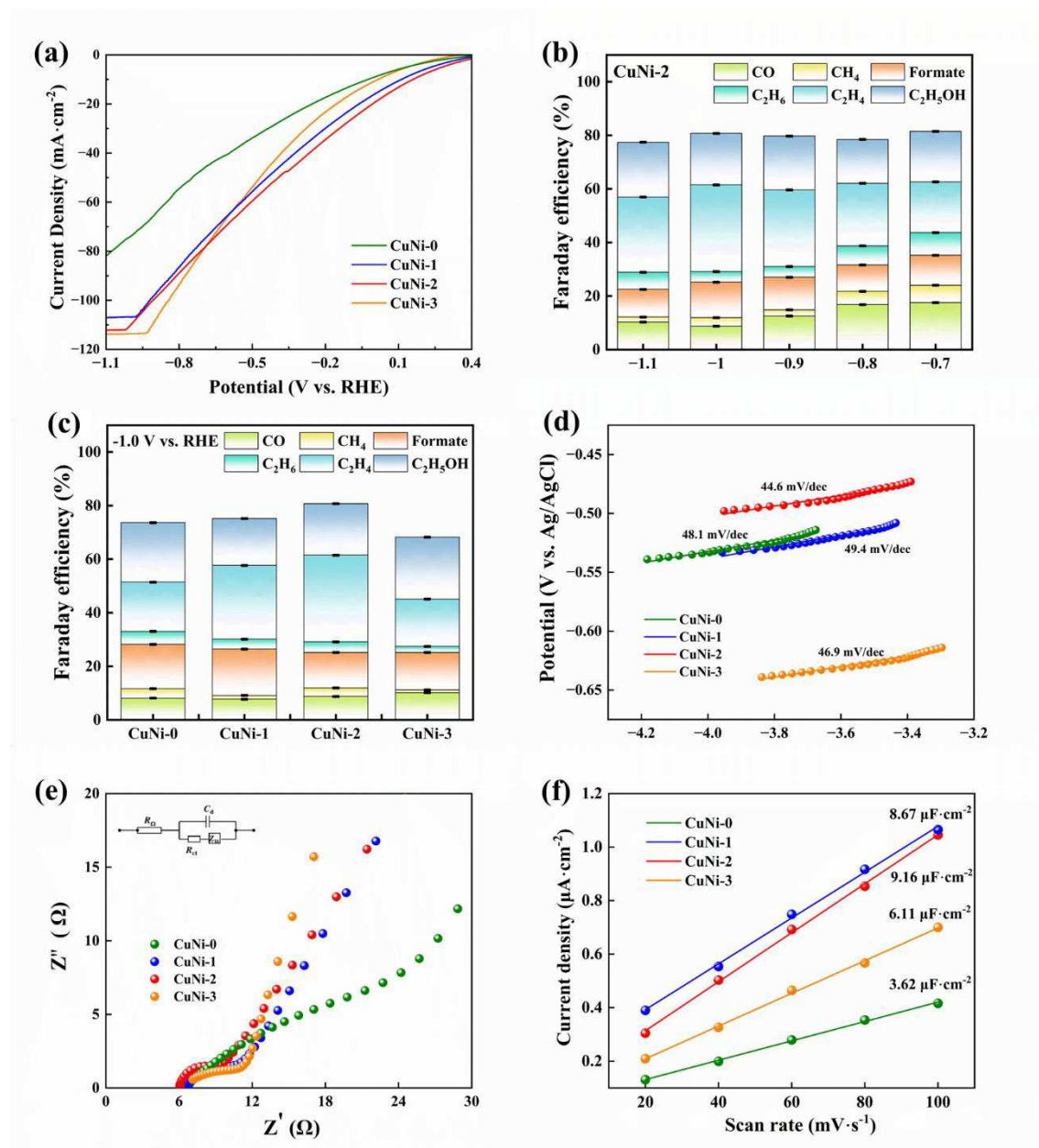


Fig. 4. (a) LSV curves of catalysts. (b) FE values of products of CuNi-2 catalyst, (c) FE values of products of CuNi-X catalysts at -1.0 V vs. RHE. (d) Tafel slopes of catalysts. (e) Nyquist plot of catalysts, (Inset: equivalent electrical circuit). (f) Electrochemical active surface area of catalysts.

The FE of CuNi-X catalysts at different potentials were presented in Figure 4(b-c) and

Figure S4. Figure 4(b) displayed the FE of CuNi-2 catalyst at different applied potentials. As the potential was lowered from -0.7 V to -1.0 V vs. RHE, the FE of C_{2+} increased significantly, reaching 55.56 % at -1.0 V vs. RHE, among which the FE of C_2H_4 is 32.35%. Figure S4(a-c) presents the FE of CuNi-0, CuNi-1 and CuNi-3 catalysts at various potentials, all of which exhibited a similar trend in the FE of C_{2+} variation. At -1.0 V vs. RHE, the FE of C_{2+} for these catalysts were 45.45 %, 48.74 %, and 43.05 % (the FE of C_2H_4 is 18.36 %, 27.54 %, and 17.66 %), respectively. Figure 4(c) compared the FE of C_{2+} of Cu-Ni bimetallic MOFs derivatives catalysts at -1.0 V vs. RHE. Therefore, CuNi-2 catalyst achieved the highest C_{2+} and C_2H_4 Faradaic efficiency. As shown in Table S5, compared with previous reported electrocatalysts, CuNi-2 catalyst demonstrated the highest selectivity toward C_{2+} , confirming the significant enhancement effect of an appropriate Cu/Ni molar ratio in promoting the selective electrocatalytic reduction of CO_2 to C_{2+} . Additionally, the total FE is frequently below 85%, this might be due to the detection methods were not precise enough, resulting in the failure to detect a small portion of the products (e.g., liquid oxygenates).

Subsequently, the Tafel slopes of the Cu-Ni bimetallic MOFs derivatives catalysts were fitted and calculated to investigate the kinetics of CO_2 reduction to C_{2+} , with the results shown in Figure 4(d). CuNi-2 catalyst exhibited the smallest slope of 44.6 mV/dec. This result indicated that CuNi-2 catalyst possessed a strong electron transfer efficiency. Therefore, Cu-Ni bimetallic MOFs derivatives catalysts with an optimized ratio could enhance the electron transfer capability, which would undoubtedly promote the reaction kinetics.

The electrochemical impedance spectroscopy (EIS) states were evaluated by equivalent circuit fitting, where R_Ω represents the electrolyte resistance and R_{ct} denotes the charge

transfer resistance. The Nyquist plots for Cu-Ni bimetallic MOFs derivatives catalysts are shown in Figure 4(e). The diameter of the semicircle in the Nyquist plot corresponds to the charge transfer resistance during the reaction. A smaller R_{ct} indicates faster charge transfer, which facilitates the activation of adsorbed CO_2 in the initial step of the reaction. The charge transfer resistances of the catalysts were determined as follows: CuNi-2 (6.017 Ω), CuNi-3 (6.131 Ω), CuNi-0 (6.395 Ω), and CuNi-1 (6.679 Ω). The results revealed that CuNi-2 catalyst exhibited the lowest R_{ct} , suggesting minimal interfacial impedance at the electrode/electrolyte interface and faster charge transfer during electrolysis, thereby favoring improved mass transport behavior in the CO_2RR process. Consequently, the lower charge transfer resistance of CuNi-2 catalyst further enhanced the reaction activity and accelerated the CO_2RR kinetics, which is consistent with the observations from the performance tests.

To investigate the electrochemical active surface area (ECSA) of the Cu-Ni bimetallic MOFs derivatives catalysts, estimation was performed using the double-layer capacitance (Cdl) technique. Based on double-layer capacitance theory, cyclic voltammetry (CV) was measured at scan rates ranging from 20 mV/s to 100 mV/s within a potential window of -0.35 V to -0.55 V vs. Ag/AgCl, yielding the CV curves shown in Figure S5. The current density difference (Δj) was calculated at the selected potential of -0.45 V vs. Ag/AgCl, and the slopes of these curves were used to determine the Cdl values (Figure 4(f)). The calculated Cdl values for the catalysts were as follows: CuNi-0 (3.62 $\mu F \cdot cm^{-2}$), CuNi-1 (8.67 $\mu F \cdot cm^{-2}$), CuNi-2 (9.16 $\mu F \cdot cm^{-2}$), and CuNi-3 (6.11 $\mu F \cdot cm^{-2}$). The highest Cdl value was observed for CuNi-2, indicating a larger electrochemical active surface area and consequently more accessible active sites during the actual reaction. This result was consistent with the EIS measurements, further confirming the favorable electrocatalytic properties of the CuNi-2 catalyst for

the reduction of CO₂ to C₂+

3.3 Reaction mechanism of CO₂ reduction to C₂H₄

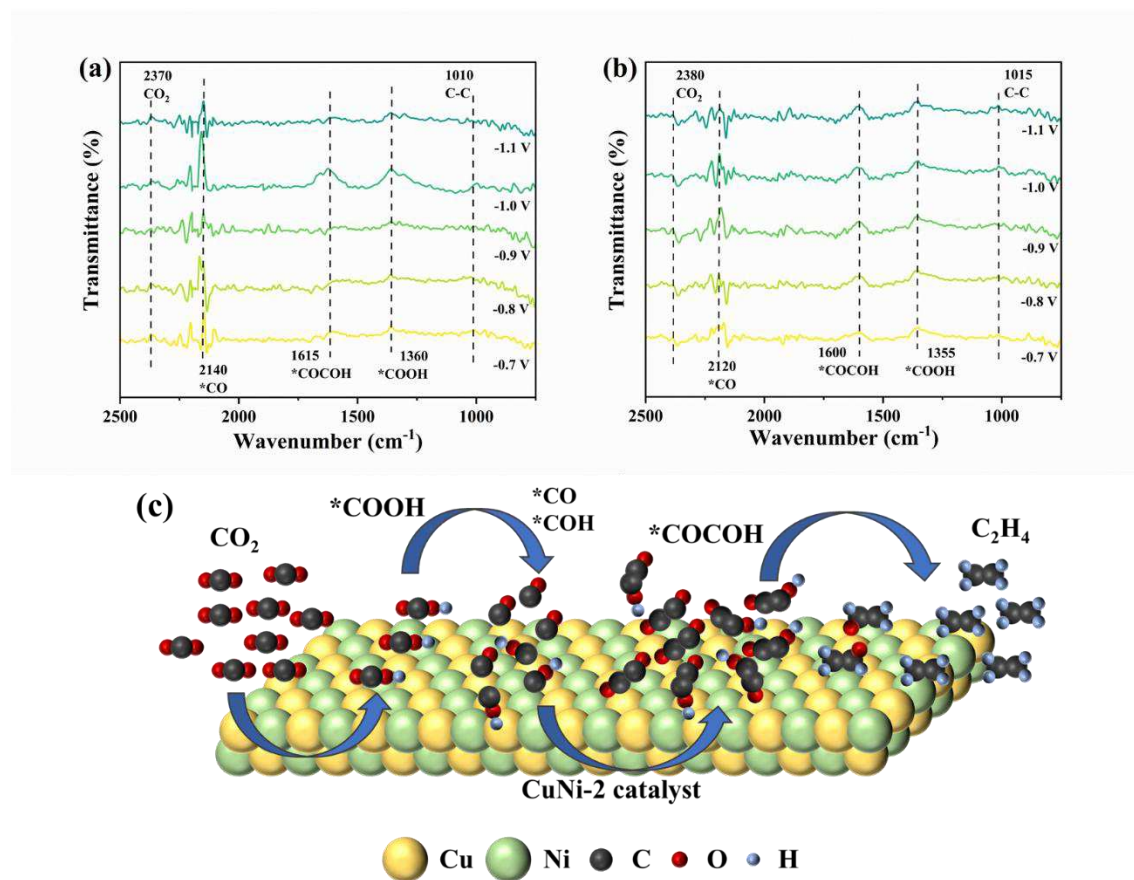


Fig. 5. FT-IR spectra of catalysts. (a) CuNi-0, (b) CuNi-2. (c) The possible catalytic mechanism of CO₂RR on the surface of CuNi-2 catalyst.

To further elucidate the reason for the high selectivity of CuNi-2 catalyst toward C₂H₄, an FT-IR study was conducted to investigate the reaction intermediates during the CO₂RR to ethylene, with the results presented in Figure 5(a-b). An absorption peak at 1355 cm⁻¹ corresponding to *COOH was observed, indicating the occurrence of CO₂ hydrogenation [32, 42, 43]. Subsequently, an asymmetric vibration peak of *COCO, a key intermediate for C-C coupling toward the final product C₂H₄ was detected at 1600 cm⁻¹ [44, 45]. Furthermore, the peak at 2120 cm⁻¹ was attributed to the *CO intermediate, where a high concentration of CO is favorable for C-C coupling and the formation of multi-carbon products [46]. As shown in Figure 5(b), under the combined

effect of CuNi-2 catalyst and the applied electric field, the peak intensity of *CO first increased and then decreased with increasing voltage, reaching its maximum at -1.0 V vs. RHE. This suggests that -1.0 V vs. RHE is more conducive to C-C coupling and the formation of multi-carbon products, which is consistent with the FE results. Figure 5(a) shows the FT-IR spectrum obtained for CuNi-0 catalyst. Compared with CuNi-2 catalyst, it exhibited the same reaction intermediates but with minor peak shifts, which may be related to Ni doping. In addition, compared to CuNi-0 catalyst, the presence of Ni in CuNi-2 catalyst significantly enhanced the peak intensities of various intermediates. This is likely because the introduction of Ni altered the electronic structure of Cu in the catalyst, thereby improving its ability to adsorb and stabilize intermediates. Thus, the bimetallic Cu-Ni active sites were more favorable for the adsorption of *CO and the stabilization of the *COCO₂H intermediate.

Figure 5(c) showed the possible catalytic mechanism of CO₂ reduction on the surface of CuNi-2 catalyst. During the electrocatalytic reduction of CO₂ to ethylene on the CuNi-2 catalyst, CO₂ first underwent chemisorption on the catalyst surface, followed by a proton-coupled electron transfer to form the first key intermediate, *COOH [47, 48]. *COOH was generated via the initial one-electron reduction of CO₂ to *CO₂, subsequent protonation, and further hydrogenation [49]. Subsequently, *COOH accepted another electron and underwent dehydration to form adsorbed *CO, which served as a critical precursor for C₂₊ products. Its surface coverage and binding strength directly influenced the efficiency of C-C coupling [20, 50]. C-C coupling is an essential step for C₂H₄ formation, primarily proceeding via two pathways: the first involved the dimerization of two adsorbed *CO species to form *OCCO, followed by hydrogenation to yield *OCCOH; the second pathway involved the hydrogenation of *CO to *COH, followed by its coupling with another *CO or *COH to produce *COCO₂H [51].

Numerous studies have indicated that $^*\text{COCO}^*\text{H}$ is a common early intermediate in the formation of C_2^+ products and a key species for C-C coupling toward the final product C_2H_4 [52]. $^*\text{COCO}^*\text{H}$ could then be sequentially hydrogenated and deoxygenated to eventually form C_2H_4 [53, 54]. In the Cu-Ni bimetallic MOFs derivatives catalyst system, Ni doping modulated the d-band center of Cu, influencing its chemical state, stabilizing partial Cu^+ species, enhancing $^*\text{CO}$ adsorption, and thereby promoting C-C coupling [55, 56]. Furthermore, BET results indicated that the introduction of an appropriate amount of Ni adjusted the specific surface area and pore structure of the catalyst. The spatial confinement effect of the pores likely helped to restrict reaction intermediates such as $^*\text{CO}$ near adjacent Cu-Ni sites, increasing their probability of collision and coupling, thus facilitating CO_2 mass transfer and intermediate stabilization. In the Cu-Ni bimetallic system, Ni sites exhibited high intrinsic activity for CO_2 activation to $^*\text{CO}$, while Cu sites were particularly favorable for further hydrogenation of $^*\text{CO}$ and C-C coupling, synergistically enhancing the selectivity toward C_2H_4 .

3.4 Stability of catalyst

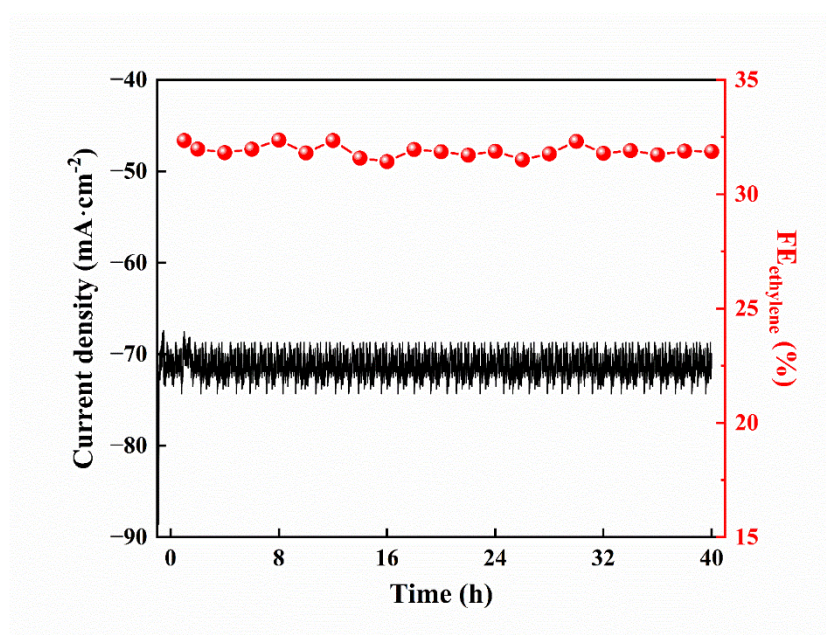


Fig. 6. Stability of CuNi-2 catalyst at -1.0 V vs. RHE during CO₂RR.

The stability of CuNi-2 catalyst was evaluated at -1.0 V vs. RHE via chronoamperometry, with the results presented in Figure 6. The current density of the CuNi-2 catalyst remained stable over a continuous 40 hours reaction period without significant decay. The Faradaic efficiency for C₂H₄ exhibited some fluctuations within an acceptable range, showing a decrease of no more than 1% over the 40-hour test. These results indicated that CuNi-2 catalyst possesses good stability during the CO₂RR process.

4. Conclusion

In this study, a series of Cu-Ni bimetallic MOFs derivatives catalysts with varying Cu/Ni molar ratios were successfully synthesized and evaluated for the electrocatalytic reduction of CO₂ to ethylene. The introduction of Ni markedly influences the textural properties, surface chemistry, and catalytic behavior of the Cu-based catalysts. Among the prepared catalysts, CuNi-2 exhibited a high Faradaic efficiency of 55.56 % for C₂⁺ products and 32.35 % specifically for ethylene at -1.0 V vs. RHE while maintaining good stability over 40 h of continuous operation. Detailed characterization revealed that Ni doping modulated the electronic structure of Cu, stabilized Cu⁺ active sites, enriched *CO intermediate coverage, and promoted C-C coupling kinetics. Furthermore, the optimized porous structure enhances mass transport and confines key reaction intermediates, contributing to improved ethylene selectivity. These findings demonstrate that the Cu-Ni bimetallic synergy offers an effective strategy for selective CO₂ electroreduction toward high-value C₂H₄ products, providing valuable insights for the rational design of efficient electrocatalysts.

Abbreviations

XRD X-ray diffraction

SEM Scanning electron microscope

EDS Energy dispersive X-ray

XPS X-ray photoelectron spectra

LSV Linear sweep voltammetry

FE Faraday efficiency

EIS electrochemical impedance spectroscopy

CV cyclic voltammetry

FT-IR Fourier transform infrared spectrometer

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Data Availability

No datasets were generated or analyzed during the current study.

Declaration

Competing Interests The authors declare no competing interests.

Ethics and Consent to Participate Not applicable.

Consent for Publication Not applicable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

References:

- [1]. Bhawnani RR, Sartape R, Gande VV, Barsoum ML, Kallon EM, Reis Rd, Dravid VP, Singh MR (2024) *Small* 21.
- [2]. Cui X, Wu M, Hou G, Li Y, Wang Y, Wang Y, Huang J, Zhao M, Luo Z-Z, Zou Z, Zhang Y, Shao M (2024) *ACS Catalysis* 14:11857-11864.
- [3]. Zhu Y, Xi H, Zhou S, Shreka M, Zhou P, Wang H, Yang W (2025) *Chemical Engineering Journal* 518.
- [4]. Song A, Han Z, Yang X, Zhang M, Wu X, Zhou Z, Liu D, Ma D (2025) *Separation and Purification Technology* 378.
- [5]. Fan D, Zhang S, Li Y, Bin H, Li R, Li Y, An M, Yang P, Zhang J (2024) *Journal of Colloid and Interface Science* 662:786-795.
- [6]. Guo P-P, He Z-H, Yang S-Y, Wang W, Wang K, Li C-C, Wei Y-Y, Liu Z-T, Han B (2022) *Green Chemistry* 24:1527-1533.
- [7]. Hao S, Elgazzar A, Zhang S-K, Wi T-U, Chen F-Y, Feng Y, Zhu P, Wang H (2025) *Science* 388.
- [8]. Jeon YE, Ko YN, Kim J, Choi H, Lee W, Kim YE, Lee D, Kim HY, Park KT (2022) *Journal of Industrial and Engineering Chemistry* 116:191-198.
- [9]. Kim D, Ka S, Han MH, Kim W, Yu S-H, Choi J-Y, Chae KH, Oh H-S, Lee WH (2025) *Journal of Energy Chemistry* 103:674-681.
- [10]. Sang JL, Zhang SD, Liu Q, Geioushy RA, Mahmoud T, Zhang Y, Liu M (2025) *Small* 21.
- [11]. Woldu AR, Huang Z, Zhao P, Hu L, Astruc D (2022) *Coordination Chemistry Reviews* 454.
- [12]. Xiong R-Z, Xu H-M, Zhu H-R, Zhang Z-J, Li G-R (2025) *Chemical Engineering Journal* 505.
- [13]. Xue L, Qi Y, Li Z, Yang H, Liu R, Zhang B (2025) *Journal of Energy*

Chemistry 110:88-108.

- [14]. Wang D, Li Y, Geng S, Li R, Chen K (2025) *Advanced Functional Materials* 35.
- [15]. Yan T, Guo J-H, Liu Z-Q, Sun W-Y (2021) *ACS Applied Materials & Interfaces* 13:25937-25945.
- [16]. Kim I, Lee G-B, Kim S, Jung HD, Kim J-Y, Lee T, Choi H, Jo J, Kang G, Oh S-H, Kwon W, Hong D, Kim HG, Lee Y, Kim U, Kim H, Kim M, Back S, Park J, Joo Y-C, Nam D-H (2025) *Nature Catalysis* 8:697-713.
- [17]. Rittirum M, Khamloet P, Ektarawong A, Atthapak C, Saelee T, Khajondetchairit P, Alling B, Prasertthdam S, Prasertthdam P (2024) *Applied Surface Science* 652.
- [18]. Liu M, Liu S, Xu Q, Miao Q, Yang S, Hanson S, Chen GZ, He J, Jiang Z, Zeng G (2023) *Carbon Energy* 5.
- [19]. Lu J, Ran W, Cheng Z, Feng Y, Rong S (2024) *Chemical Engineering Journal* 500.
- [20]. Cui H-f, Liu X-j, Liu C, Zhu H-w, Liu M-y, Guo R-t (2026) *Fuel* 403.
- [21]. Wang F-F, Sun W-Y (2024) *ACS Sustainable Chemistry & Engineering* 12:15651-15658.
- [22]. Wang Y, Wang H, Kang Z, Long Z, Zhou G, Fu Q, Zhu X, Liao Q (2025) *Chemical Engineering Journal* 520.
- [23]. Zhang Y, Sun W-Y (2024) *Chemical Communications* 60:8824-8839.
- [24]. Zhiyun H, Liangai H, Jianchuan L, Wenwu Z (2024) *Surfaces and Interfaces* 49.
- [25]. Zhu Y, Li P, Yang X, Wang M, Zhang Y, Gao P, Huang Q, Wei Y, Yang X, Wang D, Shen Y, Wang M (2023) *Advanced Energy Materials* 13.

- [26]. Ma J, Huang F, Xu A, Wei D, Chen X, Zhao W, Chen Z, Yin X, Zhu J, He H, Xu J (2024) *Advanced Science* 11.
- [27]. Mu W-L, Li L, Cong X-Z, Chen X, Xia P, Liu Q, Wang L, Yan J, Liu C (2024) *Journal of the American Chemical Society*.
- [28]. Chang F, Zhu K, Liu C, Wei J, Yang S, Zhang Q, Yang L, Wang X, Bai Z (2024) *Advanced Functional Materials* 34.
- [29]. Ren Y, Bai Y, Wang G, Liu Y, Mou C, Chen J, Wei B, Wang H, Sun Y (2023) *Energy & Fuels* 37:9289-9296.
- [30]. Sun T, Wu J, Lu X, Tang X (2024) *Langmuir* 40:9289-9298.
- [31]. Cheng B, Shu M, Chi B, Yuan H, Feng S, Liu Z, Peng S, Ge S, Yu Q, Wang H (2025) *Chemical Engineering Journal* 515.
- [32]. Wu W, Zhou H, Liu Y, Pan Y, Chen Q, Zhang Y, Mao J, Ma W, Yu P (2025) *Nano Research* 18.
- [33]. Yun R, Zhang B, Shi C, Xu R, Suo T (2023) *Inorganic Chemistry* 62:15790-15796.
- [34]. Cao Z, Li J, Zhang X, Zhang B, Li J, Zhang Y, Zhang Q, Zhang P, Song Y (2023) *Journal of Alloys and Compounds* 968.
- [35]. Momin S, Mahmood T, Ullah A, Naeem A, Khan A (2023) *Arabian Journal for Science and Engineering* 49:9269-9290.
- [36]. Liu D, Yang X, Han Z, Wu X, Zhou Z, Zhang M, Song A, Ma D (2025) *Journal of Environmental Chemical Engineering* 13.
- [37]. Gao X, Jiang Y, Liu J, Shi G, Yang C, Xu Q, Yun Y, Shen Y, Chang M, Zhu C, Lu T, Wang Y, Du G, Li S, Dai S, Zhang L (2024) *Nature Communications* 15.
- [38]. Pan W, Wang P, Fan L, Chen K, Yi L, Huang J, Cai P, Liu X, Chen Q, Wang G, Wen Z (2023) *Inorganic Chemistry Frontiers* 10:2276-2284.

- [39]. Zhang F, Cao N, Wang C, Wang S, He Y, Shi Y, Yan M, Bao Y, Li Z, Xie P (2025) *Nature Communications* 16.
- [40]. Eziz A, Wang Y, Abulizi A, Ren T, Nulahong A, Mamat A, Okitsu K (2025) *Journal of Alloys and Compounds* 1010.
- [41]. Yuan L, Zhang L, Li X-X, Liu J, Liu J-J, Dong L-Z, Li D-S, Li S-L, Lan Y-Q (2023) *Chinese Chemical Letters* 34.
- [42]. Huang L, Liu Z, Gao G, Chen C, Xue Y, Zhao J, Lei Q, Jin M, Zhu C, Han Y, Francisco JS, Lu X (2023) *Journal of the American Chemical Society* 145:26444-26451.
- [43]. Meng DL, Zhang MD, Si DH, Mao MJ, Hou Y, Huang YB, Cao R (2021) *Angewandte Chemie International Edition* 60:25485-25492.
- [44]. Pérez-Gallent E, Figueiredo MC, Calle-Vallejo F, Koper MTM (2017) *Angewandte Chemie International Edition* 56:3621-3624.
- [45]. Qiu X-F, Zhu H-L, Huang J-R, Liao P-Q, Chen X-M (2021) *Journal of the American Chemical Society* 143:7242-7246.
- [46]. Xiao D, Bao X, Zhang M, Li Z, Wang Z, Gao Y, Zheng Z, Wang P, Cheng H, Liu Y, Dai Y, Huang B (2023) *Chemical Engineering Journal* 452.
- [47]. Zhang Y, Wang X, Zheng S, Yang B, Li Z, Lu J, Zhang Q, Adli NM, Lei L, Wu G, Hou Y (2021) *Advanced Functional Materials* 31.
- [48]. Yang Q, Wang X, Zhang J, Mao Y, Xi S, Liu Y-C, Hsu Y-H, Zhang L, Bin Dolmanan S, Wang M, Wang B, Zang Y, Zhang M, Leow WR, Hung S-F, Wang Z, Lum Y (2025) *Nature Synthesis* 4:1396-1407.
- [49]. Xie L, Cai Y, Jiang Y, Shen M, Lam JC-H, Zhu J-j, Zhu W (2024) *Nature Communications* 15.
- [50]. Chen Z, zhang H, Yin Y, Cao S, Yang C, Liu S, Wang Z, Chen H, Lu X (2025) *Applied Surface Science* 709.

- [51]. Hao J, Zhuang Z, Hao J, Wang C, Lu S, Duan F, Xu F, Du M, Zhu H (2022) *Advanced Energy Materials* 12.
- [52]. Calle-Vallejo F, Koper MTM (2013) *Angewandte Chemie International Edition* 52:7282-7285.
- [53]. Liu H, Yang C, Bian T, Yu H, Zhou Y, Zhang Y (2024) *Angewandte Chemie International Edition* 63.
- [54]. Ding X, Pan B, Fan B, Yu Q, Xu J, Yan Y, Luo Y, Wang L, Li Y (2025) *Nature Energy*.
- [55]. He A, Yang Y, Zhang Q, Yang M, Zou Q, Du J, Tao C, Liu Z (2022) *Chemical Engineering Journal* 450.
- [56]. Li H, Duan Y, Feng Q, Wei L, Zeng J, Chen Z, Zhang Q, Chen Y, Yan Z (2026) *Langmuir* 42:12166-12175.

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