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Published in:
Angewandte Chemie International Edition

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202111700

Link to VoR: https://doi.org/10.1002/anie.202111700
Highly ethylene-selective electrocatalytic CO₂ reduction enabled by isolated Cu-S motifs in metal-organic framework-based precatalysts


Abstract: Copper-based material is an efficient electrocatalyst for CO₂ conversion to C₂ products, most of which will reconstruct to in-situ regenerate active species. It is a challenge to precisely design precatalyst to obtain active sites for CO₂ reduction reaction (CO₂RR). Herein, we develop a local sulfur doping strategy over the Cu-based metal-organic frameworks precatalyst that disperses stable Cu-S motif in the framework of HKUST-1 (S-HKUST-1). The precatalyst exhibits a high ethylene selectivity in H-type cell with maximum faradaic efficiency (FE) of 60.0%, and delivers a current density of 400 mA cm⁻² with ethylene FE to 57.2% in a flow cell. Operando X-ray absorption results demonstrate that Cu²⁺ species stabilized by Cu-S motif exist in S-HKUST-1 during CO₂RR. Density functional theory calculations indicate the partially oxidized Cu²⁺ at Cu/Cu,S₂ interface is favorable for CO intermediate coupling due to the modest distance of coupling sites and optimized adsorption energy.

Introduction

The electrochemical reduction of carbon dioxide (CO₂) into value-added feedstocks is a desirable route to mitigate the depletion of fossil fuels and alleviate the greenhouse gas emissions[10]. The high-value multi-carbon (C₂⁺) hydrocarbons products via CO₂ reduction reaction (CO₂RR) are highly attractive due to their practical applications[2]; however, their selectivity and activity are severely limited by multi-step hydrogenation steps and competitive reactions[3]. Copper-based material is the most efficient electrocatalyst for selectively convert CO₂ to C₂ products[4], and its performance can be further influenced via modulating oxidation states[5], grain boundaries[6] and unsaturated sites[7]. It's worth noting that these structural features of copper-based material can be in-situ changed due to the precatalyst reconstruction under CO₂RR conditions. Taken copper oxides as a classic example, they usually act as CO₂RR precatalysts, which can be partially reduced to regenerate biphasic copper/copper oxide, coupled with abundant grain boundaries and unsaturated sites as active CO₂RR species, exhibiting significantly increased CO₂RR performance than the pure copper[8, 9].

Besides the widely reported copper oxides-based precatalysts[9], other copper-based compounds[10] have also been chosen as efficient precatalysts to introduce stable oxidized Cu²⁺ species for C₂⁺ production, due to the more stable Cu(X) (X means the B, N or other heteroatoms) species than the Cu(O) matrix under CO₂RR condition[10]. Unfortunately, these copper-based compounds could not elaborately regenerate abundant biphasic Cu²⁺ species which features isolated Cu(X) species in the...

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reconstructed catalyst. It still remains as a big challenge to precisely control the local structure of precatalysts to regenerate stable and active sites under CO2/RR condition, especially for Cu2+, products. Unlike metal compounds, metal-organic frameworks-based (MOFs-based) material is an ideal precatalyst due to its controllable size/shape, high surface area, chemical tunability and the open metal sites\textsuperscript{[13]}, which affords a platform for incorporating isolated active species at atomic level. Therefore, we anticipate isolating stable Cu(X) species into the Cu-based MOFs precatalyst might regenerate homogeneously dispersed active sites under CO2/RR condition.

Herein, we rationally constructed isolated Cu-S motif on HKUST-1 precatalyst by a local sulfur doping strategy (S-HKUST-1). Although Cu(S)-based materials can electrochemically reduce CO2 to major products of formate\textsuperscript{[12]}, some Cu(S) catalysts have recently been reported with enhanced CO2 reduction selectivity to C2 products\textsuperscript{[7]}, because of the local modification of geometric and electronic structure of Cu sites, which would influence its activity and selectivity. In this work, the S-HKUST-1 can be in-situ reconstructed to give Cu(S) matrix with abundant and active biphassic copper/copper sulfide (Cu/CuS\textsubscript{x}) interfaces, which can obtain a high ethylene (C\textsubscript{2}H\textsubscript{4}) selectivity in the H-type cell with the maximum faradaic efficiency (FE) of 60.0\%, and delivers a current density of 400 mA cm\textsuperscript{-2} with FE\textsubscript{C2H4} reaching up to 57.2\% and FE\textsubscript{C2} (FE of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{5}OH and CH\textsubscript{3}COOH) of 84.8\% in the flow cell configuration. The systematic characterizations demonstrate the stable existence of Cu-S motif before and after CO2/RR.

Density functional theory (DFT) calculations further reveal that the electronic structure of Cu sites, which would influence its activity and selectivity. FE\textsuperscript{C2H4} shows that the weight fractions of S elements in S-HKUST-1 is nearly similar to that of HKUST-1, which is consistent with Cu-S bonding\textsuperscript{[12a, 17]} (Figure 1d). This result unambiguously confirms the successful incorporation of S element in HKUST-1. In the XPS spectra of Cu 2p\textsubscript{3/2} region, both S-HKUST-1 and HKUST-1 precatalysts possess a peak centered at the binding energy of 934.7 eV, which is attributed to Cu\textsuperscript{2+} species, demonstrating that partial Cu centers of the S-HKUST-1 still maintain coordination with trimesic acid. The peak at 932.4 eV associated with Cu\textsuperscript{2+} species were partially reduced after S incorporation to form Cu-S coordinated species. The Cu LMM\textsubscript{3/2} Auger spectra of HKUST-1 and S-HKUST-1 were measured for the further clarification of Cu valency (Figure S8). Compared with HKUST-1, S-HKUST-1 exhibits a broad peak at the binding energy of 570.0 and 567.9 eV, which indicates the presence of Cu\textsuperscript{2+} and Cu\textsuperscript{0} \textsuperscript{[19]}. Sulfor is lower electronegative than oxygen, so that the attract-electrons ability of S atoms is weak, which might lead to a relatively low valence of Cu. We speculate that the local Cu-O bond in HKUST-1 might be broken by the treatment of thioacetamide molecules for construction of Cu-S motif.

The surface composition and elemental states of S-HKUST-1 and controlled sample were further characterized by X-ray photoelectron spectroscopy (XPS). Compared with that of HKUST-1, a broad S 2p peak is visible at 162.5 eV in S-HKUST-1, which is consistent with Cu-S bonding\textsuperscript{[12a, 17]} (Figure 1d). This result unambiguously confirms the successful incorporation of S element in HKUST-1. In the XPS spectra of Cu 2p\textsubscript{3/2} region, both S-HKUST-1 and HKUST-1 precatalysts possess a peak centered at the binding energy of 934.7 eV, which is attributed to Cu\textsuperscript{2+} species, demonstrating that partial Cu centers of the S-HKUST-1 still maintain coordination with trimesic acid. The peak at 932.4 eV associated with Cu\textsuperscript{2+} species were partially reduced after S incorporation to form Cu-S coordinated species. The Cu LMM\textsubscript{3/2} Auger spectra of HKUST-1 and S-HKUST-1 were measured for the further clarification of Cu valency (Figure S8). Compared with HKUST-1, S-HKUST-1 exhibits a broad peak at the binding energy of 570.0 and 567.9 eV, which indicates the presence of Cu\textsuperscript{2+} and Cu\textsuperscript{0} \textsuperscript{[19]}. Sulfor is lower electronegative than oxygen, so that the attract-electrons ability of S atoms is weak, which might lead to a relatively low valence of Cu. We speculate that the local Cu-O bond in HKUST-1 might be broken by the treatment of thioacetamide molecules for construction of Cu-S motif.

To confirm the transformation process from HKUST-1 to S-HKUST-1 proposed, the changes of oxidation states and local coordination environments of Cu atoms were investigated by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses, respectively. Figure S9 shows the high-quality k-space (k\textsuperscript{\*}-weighted) Cu K-edge EXAFS spectra of HKUST-1, S-HKUST-1 and controlled Cu foil,
CuO, Cu2S and Cu2O samples, which can support the reliability of Fourier transformation (FT) of the EXAFS spectra\(^\text{[20]}\). The FT of EXAFS spectra for S-HKUST-1 and original HKUST-1 exhibit similar curves featuring a main peak at approximately 1.53 Å (without phase correction if not mentioned) arising from Cu-O bond (Figure 1f), suggesting that the main structure of HKUST-1 is maintained. When incorporating S elements into HKUST-1 to form S-HKUST-1, the Cu-O peak exhibits a remarkable intensity decrease, which is consistent with those reported in literatures\(^\text{[21]}\), indicating that the water molecule directly linked with the Cu atoms are partially lost. Furthermore, the main Cu-O peak for S-HKUST-1 shifts to longer lengths, suggesting the expansion of the Cu-O bond due to the S incorporation to construct local Cu-S motif. From the XANES spectra of HKUST-1 and S-HKUST-1 (Figure 1g), two peaks were observed, including a pre-edge peak at 8981 eV corresponding to 1s\(\rightarrow\)3d transition and a white-line peak at 8997 eV\(^\text{[21]}\). When S incorporated into the HKUST-1, the decreased intensity for the white line peak and the increased intensity for the 1s\(\rightarrow\)3d peak indicate a change in the coordination of Cu centers, which is resulted from the removal of water molecule\(^\text{[22]}\). The obtained precatalysts with different S contents also exhibit the similar phenomena, indicating the increased intensity of Cu-O peak, the decreased intensity of white line peak and the increased intensity of the 1s\(\rightarrow\)3d peak (Figure S10). The electron paramagnetic resonance (EPR) signal intensity of S-HKUST-1 also increases and the peak becomes sharper compared to the HKUST-1, indicating that the Cu microstructure has changed\(^\text{[16]}\) (Figure 1h). As shown in Figure S11, the BET surface area of S-HKUST-1 was determined to be 816.54 m\(^2\) g\(^{-1}\), which is lower than that of HKUST-1 (855.52 m\(^2\) g\(^{-1}\)). This may be due to the fact that part of the thioacetamide molecules entered the cavity of MOF, forming Cu-S species and reducing its pore cage, which eventually leads to a slight decrease in the BET surface area\(^\text{[13]}\). Above characterization results have clearly shown the existence of the isolated Cu-S motif in HKUST-1 precatalyst. We speculate that the S heteroatoms generated from the thioacetamide might locally replace the flanking water molecule (\(\text{O}_\text{w}\)) attached to the Cu atoms and break the Cu-O\(_\text{w}\) bonds without destroying the long-range order of HKUST-1\(^\text{[22]}\).

**Figure 1.** (a) Schematic illustration of the preparation of S-HKUST-1, which indicates the local \(\text{H}_2\text{O}\) molecule might be replaced by S heteroatoms. (b) XRD patterns of the prepared S-HKUST-1 and HKUST-1 precatalysts, which are well indexed to the simulated HKUST-1. The insets are digital photos of S-HKUST-1 (dark green) and HKUST-1 (blue). (c) FTIR spectra of S-HKUST-1 and HKUST-1 precatalysts, indicating negligible difference. The XRD and FTIR results prove that the long-range ordered structure has not been destroyed after S incorporation. (d, e) High-resolution XPS spectra of S-HKUST-1 and HKUST-1 precatalysts in (d) \(\text{S}_\text{2p}\) region, showing the characteristic Cu-S bonds in the S-HKUST-1 precatalyst and (e) Cu-O region, showing the increased content of Cu\(_\text{S}\) or Cu\(_\text{2}\) species. (f) FT of the EXAFS spectra and (g) Cu K-edge XANES spectra of HKUST-1 and S-HKUST-1 precatalysts. The inset of (g) is the magnified image. The XAFS results in (f, g) prove the successful incorporation of local heteroatoms, which might be bonded to Cu atoms in MOFs. (h) EPR spectra of the samples measured at 300 K.

**Electrocatalytic activity and selectivity evaluation of CO\(_2\)-RR**

The electrochemical CO\(_2\)-RR performance was firstly evaluated using a gas-tight H-type cell, with S-HKUST-1 or HKUST-1 samples decorated glassy carbon electrode, Ag/AgCl and Pt mesh as working electrode, reference electrode and counter electrode, respectively (see more details in the Methods). We firstly studied the effects of different incorporated S contents, and their corresponding electrocatalytic CO\(_2\)-RR selectivity results (biased at -1.22 to -1.52 V vs. RHE, potentials were referenced to RHE if not mentioned, and all potentials were not iR-corrected) illustrate that as the incorporated S contents increase, the \(\text{FE}_{\text{CO}_2}\) gradually increases; however, when the S content further increases, the \(\text{FE}_{\text{CO}_2}\) is significantly reduced (Figure S12). In addition, the excess S incorporated sample of CuS obtained from
vulcanization shows a poor selectivity towards CO₂RR (Figures S12c and S12d), which proves the critical role of isolated Cu-S motif in the S-HKUST-1 precatalyst. The CO₂RR activities of the optimized S-HKUST-1 and pristine HKUST-1 were summarized in Figure 2. Linear sweep voltammetry (LSV) curves for S-HKUST-1 and HKUST-1 were conducted in a CO₂-saturated 0.1 M KHCO₃ aqueous solution (Figure 2a). The S-HKUST-1 shows higher reduction current densities relative to HKUST-1. The liquid products were collected and analyzed by using ¹H nuclear magnetic resonance (NMR) spectroscopy. As shown in Figure S13, no obvious detectable liquid products were produced, which might be attributed to ultralow content of liquid products in the H-type cell. Figure S14 exhibits the distribution of CO₂RR gas products at different applied potentials on S-HKUST-1. For S-HKUST-1, the FE₃CH₄ maintains values of above 50.0% in a range of potentials from -1.22 to -1.42 V, and are higher than that of HKUST-1 (Figure 2b and Table S7). A maximum FE₃CH₄ of 60.0±2.0% can be reached at -1.32 V, while this value of HKUST-1 is only 24.4±2.1% (Figure 2b). The electrochemical active surface area (ECSA) for S-HKUST-1 and HKUST-1 were measured (Figure S15). To compare the intrinsic activity for CO₂RR, the ECSA-normalized j of C₂H₄ was obtained (Figure 2c). It reveals that the higher activity for ethylene production on S-HKUST-1 than HKUST-1. The Nyquist plots in Figure S16 reveal that S-HKUST-1 is characterized with a lower interfacial charge-transfer resistance (Rₛ) than HKUST-1, evidencing a faster electron transfer from the electrodes to CO₂ during CO₂RR process[10b, 23], which may also contribute to the higher catalytic j of S-HKUST-1 than the HKUST-1 control (Figures 2a and 2c).

The reaction rate of CO₂RR might be limited by mass transport due to the low solubility of CO₂ in the H-type cell[24]. Thus, we further evaluated the CO₂RR performance of S-HKUST-1 in a flow cell system with 1.0 M KOH as electrolyte (Figure 2d, digital photos were shown in Figure S17). H₂, C₂, and C₃ products were formed on bare copper and HKUST-1 controls, and the FE₃H₂ and C₁ products decreased and C₂ products increased over S-HKUST-1 (Figure 2e and Tables S8-S10). The C₂ products include ethylene, ethanol, acetic acid, and among them, ethylene is the major product (Figure S18). For comparison, the FE₃CH₄ on bare Cu and HKUST-1 electrodes are generally below 40% over the current densities from 100 to 500 mA cm⁻² (Figure S19 and Tables S8-S10). The FE₃CH₄ on S-HKUST-1 is obviously higher than that of HKUST-1 across the j range from 100 to 500 mA cm⁻². At the j of 400 mA cm⁻², H₂ selectivity remains below 20% FE, whereas the FE towards C₂H₄ surpasses 57.2% with the C₂H₄ partial j of 228 mA cm⁻² (Figures 2e and S20). This is the highest selectivity of C₂H₄ and the highest C₂H₄ partial j among the Cu-based organometallic catalysts and MOFs; furthermore, the S-HKUST-1 also shows comparable C₂H₄ selectivity and activity among the reported Cu-based electrocatalysts (Table S11). When we used the S-HKUST-1 precatalyst, the Faradaic efficiency of overall C₂ product is 70.0–88.4% from 100 to 500 mA cm⁻², with peak selectivity of C₂ products towards FE of 88.4% at 400 mA cm⁻², which is higher than those of the bare Cu and HKUST-1 electrodes (Figure S21). Noteworthy, the S-HKUST-1 also demonstrates good electrocatalytic stability, retaining nearly unchanged FE of C₂H₄ (~50%) at an applied j of 150 mA cm⁻² in a flow cell reactor (Figure 2f). Taken together, we demonstrate that isolating Cu-S motif in the HKUST-1 precatalyst could subtly activate the C₂H₄ performance.

![Figure 2](image)

**Figure 2.** (a) LSV curves in the CO₂-saturated 0.1 M KHCO₃ aqueous solution at a scan rate of 10 mV s⁻¹ for S-HKUST-1 and HKUST-1. The S-HKUST-1 shows larger catalytic current density relative to HKUST-1. (b) FE of C₂H₄ and (c) ECSA-normalized j of C₂H₄ for S-HKUST-1 and HKUST-1 in the CO₂-saturated 0.1 M KHCO₃ at various applied potentials. (d) Schematic illustration of the flow cell reactor. (e) FE of products with S-HKUST-1 precatalysts at various applied j ranging from 100 to 500 mA cm⁻² in liquid-electrolyte flow cell reactor. FE of CH₄ is below 1% at all applied j and was not plotted. (f) Long-time stability of S-HKUST-1 in 1.0 M KOH at an applied j of 150 mA cm⁻² in a flow cell reactor, showing stable activity and selectivity for C₂H₄ over 480 min.

**Structural evolution of the precatalyst**

We firstly conducted *ex-situ* characterizations to study the structural evolution before and after CO₂RR (after reacting in CO₂-saturated 0.1 M KHCO₃ at a potential of -1.32 V for 1 h) over the precatalysts. In order to avoid the oxidation of copper as much as possible, the entire cell was transferred to the nitrogen glove box immediately after CO₂RR (Figure S22). The XPS spectra of the S-HKUST-1 precatalyst given in Figure S23a shows that the peak of Cu²⁺ species centered at 934.7 eV was disappeared, which indicates that the valence states of Cu changed from Cu²⁺ to Cu⁺/Cu²⁺ after CO₂RR[25]. Further surface state analysis was performed with a Cu LMM auger peak, which shows the Cu⁺ auger peak at 570.0 eV and Cu²⁺ peaks at 567.9 eV (Figure S23b)[19]. It is obvious that both Cu²⁺ and Cu⁺ states are present on the surface of the catalyst after the CO₂RR. In the XRD pattern, the S-HKUST-1 precatalyst has lost the characteristic diffraction peaks of original MOFs, but exhibits typical diffraction peaks of Cu(111) and Cu(200) at 43.3° and 50.4° (PDF 04-0836), which is consistent with the XPS results (Figure S24). Concomitantly, the morphological changes are revealed by the TEM images of S-HKUST-1 and HKUST-1 precatalysts after CO₂RR, which indicates that both samples have changed from the initial micron sized octahedral particles to the final dendritic morphologies (Figures 3a, S25a and S26a), which is consistent with the SEM results (Figures S27). Moreover, the high-resolution transmission electron microscopy (HRTEM) images (Figures 3b, S25 and S26) display the lattice fringes with a spacing distance of 2.08 Å, which is corresponding to the Cu(111) crystal planes, also demonstrating that the Cu ion in precatalysts have been reduced.
to metallic Cu during CO$_2$RR process. The HAADF-STEM and corresponding EDS elemental maps show that Cu and S elements distributed homogeneously throughout the whole catalyst structure (Figures 3c and S26d-S26e). We further replaced the Nafion solution with an anion solution (Sustainion® XA9 ionomer solution), which doesn’t contain the sulfur element. The EDS analysis revealed that sulfur also exist in the catalyst after CO$_2$RR, indicating that S element is derived from the S-HKUST-1 catalyst (Figure S28). The XPS result of S-HKUST-1 after CO$_2$RR also indicates the existence of S element, which is consistent with the above-mentioned characterizations (Figure S29 and S30). We speculate that the regenerative Cu(S) matrix during CO$_2$RR might give abundant Cu/CuS$_x$ interfaces on the atomic level local structure.

HKUST-1 catalysts with the reference samples suggests that the average oxidation states of Cu in S-HKUST-1 and HKUST-1 derived catalysts lie between 0 and +1 after 15 minutes of reaction at -1.30 V (Figure 3f). Furthermore, the absorption edge of S-HKUST-1 is on the higher energy side than that of HKUST-1, implying the higher Cu oxidation state[26]. The result show that the regenerative Cu(S) matrix derived from predesign S-HKUST-1 features more oxidized Cu$^{3+}$ species than the HKUST-1 control, which might give abundant active sites for C$_2$ products generation.

In-situ Raman measurement was carried out to further investigate the origins of the excellent CO$_2$RR performance of S-HKUST-1. A custom-built Raman setup was used to probe the surface of S-HKUST-1 and HKUST-1 during CO$_2$RR at different potentials in CO$_2$-saturated 0.1 M KHCO$_3$ (Figure S32). The vibration of C-H on S-HKUST-1 and HKUST-1 was observed in the area at 2700-3000 cm$^{-1}$ (Figures 3g and S33)[28]. The peaks are more obvious on S-HKUST-1 than that on HKUST-1, indicating that more reaction intermediates containing C-H bonds are produced on S-HKUST-1. Remarkably, S-HKUST-1 catalyst significantly improved the formation of key hydrocarbon intermediates, which might promote the subsequent C-C coupling step and thus the production of hydrocarbons.

Theoretical studies of biphasic Cu/Cu$_x$S$_y$ interface

To elucidate the superior selectivity of Cu(S) matrix on catalyzing CO$_2$RR into C$_2$ products, we further performed the density functional theory (DFT) calculations to reveal the inherent mechanism (see the calculation details in the Methods). Essentially, it has been widely regarded that the bound ‘CO intermediate (‘ denotes an adsorption site) is the key species in the formation of both C$_1$ and C$_2$ products[30], and the ‘CO hydrogenation (‘CO + H $\rightarrow$ ‘CHOH) versus the dimerization process (‘CO $\rightarrow$ ‘OCCO +’ ) as the rate-limiting steps (RLS) largely limits the selectivity of Cu formation[31], which is confirmed by the thermodynamic energy profiles for these two processes computed over the Cu(111) surface (Figure 4a; see more details in Figure S34 and Table S12). Thus, we focused on these two elementary steps for comparison to understand the CO$_2$RR activity and selectivity on Cu(S) matrix. Regarding the construction of Cu(S) matrix, the possible structures are diverse including stoichiometric and non-stoichiometric sulfide phases. However, because of the experimental characterization on the valence states of surface and bulk Cu (around 0 ~ 1), the stoichiometric Cu(S) systems are ruled out (i.e., CuS and Cu$_2$S). Estimated from the thermodynamic phase diagrams in Figure S35, the binary Cu/Cu$_2$S interface structure can be expected to dominantly exist, and thus we constructed the Cu/Cu$_2$S interface for modelling the realistic active site eventually (Figure S36, see more details in the Methods). Notably, the average charge of Cu atoms near the optimized Cu/Cu$_2$S interface is 0.14 |e| from the Bader charge analysis, indicating that these Cu sites are in the form of partially oxidized Cu$^{3+}$, which is in line with the experimental observation.

The ‘CO dimerization step was calculated at the Cu/Cu$_2$S interface (Figure 4c). The effect of realistic solution environment is considered in the calculation, in which explicit water layers are introduced over the catalyst to simulate the liquid/solid interface by invoking the ab initio molecular dynamics (AIMD) simulations.
widely accepted precursor prior to creating C\textsubscript{2} formation from atoms. Specifically, we calculated the progress of into Cu/Cu\textsubscript{2} structure on reaction products. The CO\textsubscript{2} adsorption via the carbon atom interacts with three Cu\textsuperscript{0} sites at Cu/Cu\textsubscript{2} interface, which conduces to the easy 'CO dimerization geometrically. Moreover, as illustrated in Figure S38, 'CO occupies the hollow-site and interacts with three Cu atoms (i.e., two Cu\textsuperscript{0} and one Cu\textsuperscript{2+}) at the Cu/Cu\textsubscript{2} interface, in which the interface Cu\textsuperscript{2+} takes a Bader charge 0.14 [e]. Based on the crystal orbital Hamilton populations (-COHP) and integrated -ICOHP (-ICOHP) analysis (Figure 4b), the -ICOHP of Cu\textsuperscript{2+}-CO bond at the Cu/Cu\textsubscript{2} interface rises continuously and reaches a relatively steady value (~1.55 eV) at the Fermi level, which is smaller than that of Cu\textsuperscript{2+}-CO bond (1.61 eV) on Cu(111) surface. The smaller -ICOHP value demonstrates a weaker interaction between 'CO species and Cu\textsuperscript{2+} in comparison with the metallic Cu\textsuperscript{0} site. Quantitatively, the adsorption energy at the Cu/Cu\textsubscript{2} interface is -1.12 eV (-0.51 eV considering temperature effect at 298 K), which is weaker by 0.29 eV than that on Cu(111) surface. In other word, the presence of partially oxidized Cu\textsuperscript{2+} at the Cu/Cu\textsubscript{2} interface weakens the 'CO adsorption and thus facilitates the CO dimerization to C\textsubscript{2} products.

In addition, regarding previous studies reported S-modified copper catalyst for formate product, we also did some first-principles calculations to verify the peculiarity of our catalyst structure on reaction products. The CO\textsubscript{2} adsorption via the carbon atom instead of di-oxygen generally serves as a key precursor for 'COOH formation\textsuperscript{32}, and it tends to be further hydrogenated into 'CO intermediate rather than the formate product. For our catalyst, it mainly comprises of a majority of metallic Cu\textsuperscript{0} with abundant Cu/Cu\textsubscript{2} interfaces, which might be different from the S-modified catalysts reported in previous studies\textsuperscript{33}. At the interface Cu region, the computational result shows that CO\textsubscript{2} tends to adsorb into 'CO\textsubscript{2} species via carbon atom rather than the di-oxygen atoms. Specifically, we calculated the progress of 'COOH formation from 'CO\textsubscript{2} species, and the reaction barrier is only 0.10 eV with an enthalpy change of -0.66 eV (Figure S39). These 'COOH intermediates can be further hydrogenated into 'CO, a widely accepted precursor prior to creating C\textsubscript{2} products\textsuperscript{34}. On the contrary, S-modified copper will weaken the CO\textsubscript{2} adsorption and suppress the formation of 'CO intermediate. Also, previous studies suggested that the sulfur doping on the copper surface could suppress the HER owing to the slower combined desorption rate of H\textsubscript{2}\textsuperscript{33}, accordingly, the formate production competes with HER for surface accumulated H\textsuperscript{+}, possibly via a Heyrovsky-like mechanism into HCOO\textsuperscript{-} product\textsuperscript{35}.

In light of these analysis above, the superior selectivity of S-HKUST-1 precatalyst on catalyzing CO\textsubscript{2}RR into C\textsubscript{2} product, compared with copper or copper sulfide, can be rationalized: benefited from the approximate Cu\textsuperscript{2+}-Cu\textsuperscript{2+} distance, 'CO dimerization step can easily occur at the Cu/Cu\textsubscript{2} interface, and excessively high S-content catalysts (i.e., Cu/S) features with the long Cu-Cu distance, geometrically hindering the 'CO dimerization; the Cu/Cu\textsubscript{2} interface presents a weakened binding energy to 'CO species, which prompts the 'CO dimerization than pure metallic Cu catalyst.

Figure 4. (a) Calculated free energy profiles for CO\textsubscript{2}RR to CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} over pure Cu(111) surface, indicating the initial 'CO hydrogenation and dimerization steps basically determine the CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} products distribution. Detailed geometries and energetic information are listed in Figure S35 and Table S12. (b) Integrated crystal orbital Hamilton populations (-ICOHP) curves for Cu\textsuperscript{2+}-CO and Cu\textsuperscript{2+}-CO bonds. (c) The reaction barriers together with enthalpies, and (d) corresponding transition states configuration for 'CO dimerization and hydrogenation over Cu(111) and Cu/CuS surfaces, respectively. Yellow, red, gray, white, orange and blue balls refer to S, O, C, H, Cu\textsuperscript{2+} and Cu\textsuperscript{0} atoms, respectively. (e) Surface configuration (top view) of Cu-based structures with different degrees of Vulcanization. The distances between two neighboring Cu atoms on different surfaces are labeled, respectively (in Å).
Conclusion

In this work, we develop a rational predesign strategy to isolate stable Cu-S motif into the HKUST-1 precatalyst. The regenerative Cu(S) matrix exhibits a high CO₂H₄ selectivity up to 57.2% at the operated a j of 400 mA cm⁻². This is the best selectivity and activity value for CO₂H₄ among the Cu-based metalorganic and MOFs for CO₂RR electrocatalysts. The operando XAFS analysis along with systematic characterizations demonstrate the stable Cu-S motif during CO₂RR, which can be stabilize more active Cu₄S₄ species. The theoretical results further illustrate the significant importance of the S stabilized Cu₄S₄ at the Cu/Cu₅S₄ interface with optimized geometric and electronic structures for CO dimerization. We believe this work opens up a new avenue to finely predesign precatalysts with stable and active species for CO₂ products-selective electrocatalysts.

Acknowledgements

This work was financially supported by the International (Regional) Cooperation and Exchange Projects of the National Natural Science Foundation of China (51920105003), the National Natural Science Funds for Distinguished Young Scholars (51725201), the Innovation Program of Shanghai Municipal Education Commission (E00014), the National Natural Science Foundation of China (51902105, 21873028, 22072045), the Shanghai Engineering Research Center of Hierarchical Nanomaterials (18DZZ252400) and the Shanghai Sailing Program (19YF1411600). The authors acknowledge the support from National Natural Science Funds for Distinguished Young Scholars (51922001), the Funds for the Central Universities (JKD01211519, JKVJ1211022). The authors also thank the crew of the BL14W1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF) and the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) for their construction. The authors also thank the Shanghai Sailing Foundation of China, the Regional Cooperation and Exchange Projects of the National Natural Science Foundation of China (51922001), the Funds for the Central Universities (JKD01211519, JKVJ1211022). Additional support was provided by the Ferring Nobel Prize Scientist Joint Research Center. The authors also thank the Funders Science Center for Matieriology, and Dynamic Chemistry. The authors also thank the crew of the BL14W1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF) and the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) for their constructive advice with the XAFS measurements and data analyses.

Keywords: CO₂ electrocatalysis; ethylene-selective; isolated Cu-S motif; operando XAFS; precatalyst


The S-HKUST-1 precatalyst with a stable isolated Cu-S motif was prepared by local sulfur doping strategy, which can be in-situ reconstructed to obtain Cu(S) matrix with active biphasic copper/copper sulfide interfaces, delivering a current density of 400 mA cm$^{-2}$ with Faradaic efficiency of ethylene to 57.2% in the flow cell.