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Highly Selective CO₂ Electroreduction to C₂H₄ Using a Metal– Organic Framework with Dual Active Sites

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Cite This: J. Am. Chem. Soc. 2021, 143, 7242–7246



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ABSTRACT: Conversion from CO₂ to C₂H₄ is important for the development of energy and the environment, but the high energy barrier of hydrogenation of the *CO intermediate and C–C coupling step tend to result in C₁ compounds as the main product and thus restrict the generation of C₂H₄. Here, we report a metal–organic framework (denoted as **PcCu-Cu-O**), composed of 2,3,9,10,16,17,23,24-octahydroxyphthalo-cyaninato)copper(II) (PcCu-(OH)₈) ligands and the square-planar CuO₄ nodes, as the electrocatalyst for CO₂ to C₂H₄. Compared with the discrete molecular copper-phthalocyanine (Faradaic efficiency (FE) of C₂H₄ = 25%), **PcCu-Cu-O** exhibits much higher performance for electrocatalytic reduction of CO₂ to C₂H₄ with a FE of 50(1)% and a current density of 7.3 mA cm⁻² at the potential of -1.2 V vs RHE in 0.1 M KHCO₃ solution, representing the best performance reported to date. *In-situ* infrared spectroscopy and control experiments suggested that the enhanced electrochemical performance may be ascribed to the synergistic effect between the CuPc unit and the CuO₄ unit, namely the CO on the CO-producing site (CuO₄ site) can efficiently migrate and dimerize with the *CO intermediate adsorbed on the C₂H₄-producing site (CuPc), giving a lower C–C dimerization energy barrier.

n recent years, electrocatalytic carbon dioxide reduction reaction (CO_2RR) has attracted extensive attention from researchers due to its potential application on the mitigation of the greenhouse gas effect and energy crisis.¹⁻⁴ Currently, HCOOH and CO account for the majority of reduction products in electrochemical CO2RR;⁵ on the other hand, hydrocarbons are rare, especially for C_2H_4 . As the petrochemical capturing the largest volume among other petrochemicals, C₂H₄ is mainly obtained industrially by the cracking reaction of naphtha and the distillation of cracking gas.^{6,7} In this regard, employing electrochemistry for the efficient reduction of CO₂ to C₂H₄ could be meaningful for the C_2H_4 industry. However, the high overpotential (almost 0.6– 1.0 V for yielding $C_2H_4^{8,9}$ while a low value of 0.016 V yields CO¹⁰) and the multielectron transfer processes (12 electrons for yielding C₂H₄ compared to 2 for yielding CO or HCOOH and 8 for yielding CH₄) in CO₂RR encumber the electroconversion of CO_2 to C_2H_4 .¹¹ Therefore, the development of efficient electrocatalysts to achieve the electroreduction of CO₂ to C₂H₄ is a very significant and challenging task.

Metal-phthalocyanine compounds have been proved to be efficient for electrochemical CO_2RR .^{11–15} For instance, discrete molecular cobalt-phthalocyanine (CoPc) exhibits high activity for the electroreduction of CO_2 to CO^{16} with a current density of 54.1 mA cm⁻² at a potential of -1.71 V vs RHE. Recently, researchers achieved improved electrochemical performances for CO_2RR by constructing metal–organic frameworks (MOFs) or covalent organic frameworks (COFs) with metal-phthalocyanine as secondary building units.^{12,13} This improvement could be attributed to the highly ordered framework structure, strong designability of active sites, and high crystallinity of MOFs and COFs. However, most metal-phthalocyanine compounds for electrochemical $\rm CO_2RR$ tend to yield CO as the main product.^{17–19} Among all metal-phthalocyanine compounds, only discrete molecular copper-phthalocyanine (CuPc) exhibit electrochemical activity for yielding C₂H₄, but the selectivity (FE(C₂H₄) = 25%, FE(CH₄) = ~5\%, FE(CO) = ~4.5%) needs to be improved.¹¹

It is widely accepted that the C-C dimerization is an important step during the reduction of CO2 to C2H4, and optimizing the energy barrier of the dimerization should be beneficial for yielding C2H4. As a catalyst with one type of catalytically active site (Scheme 1a), when the distance between a pair of active sites is suitable, it is easy for the *CO intermediate to dimerize with the *CHO intermediate adsorbed on the adjacent active site to generate the *OCCOH intermediate.²⁰ And, further hydrogenation of *OCCOH intermediate can yield C2H4 as the final product. When the distance is unsuitable, it is needed for one of the two *CO intermediates to be desorbed and migrate to the *CHO intermediate for C-C dimerization (Scheme 1b).⁴ However, the formation of the *CHO intermediate from the *CO intermediate needs high adsorption enthalpy, which goes against desorption of CO, resulting in a high C-C dimerization energy barrier.²¹ Combining a CO-producing site with a C₂H₄-producing site might be feasible to balance the desorption and hydrogenation of CO. As shown in Scheme 1c, such a catalyst with dual active sites may be beneficial for

Received: February 6, 2021 Published: May 6, 2021



Scheme 1. Illustration of the C-C Dimerization Pathways and Corresponding Energy Barriers^a



 a M represents one type of catalytically active site; M₁ and M₂ represent two different active sites, respectively.

the *CO on the CO-producing site (M_1) to desorb, migrate, and then dimerize with the *CO intermediate on the C_2H_4 producing site (M_2) , thus resulting in a lower C–C dimerization energy barrier. Nevertheless, to be our best knowledge, such a catalyst possessing dual active sites has not been investigated for electrochemical CO₂ reduction to C_2H_4 .

The metallo-ligand (2,3,9,10,16,17,23,24-octahydroxyphthalo-cyaninato)copper(II) (PcCu-(OH)₈) is very similar to CuPc and should be able to serve as a single active site for C_2H_4 production. Compared to CuPc, it should be noted that the electron donating effect of eight hydroxyl groups on the ligand PcCu-(OH)₈ should be able to enhance the coordination ability of the nitrogen atoms, as a result of enhancing the Cu–N interaction.^{14,22} Therefore, we anticipate that the combination of PcCu-(OH)₈ with a CO-producing site will be promising to achieve high selectivity and durability for CO₂RR to C_2H_4 . **PcCu-Cu-O** is a two-dimensional MOF constructed by PcCu-(OH)₈ ligands and the square-planar CuO₄ nodes (Figure 1). Since the CuO₄ nodes of MOFs have



Figure 1. Illustration of the structure of PcCu-Cu-O.

been proven to be active for the electroreduction of CO_2 to $CO_1^{10,23,24}$ such a two-dimensional structure is beneficial for an electrocatalyst with high activity and high selectivity for CO_2RR to C_2H_4 . In this work, **PcCu-Cu-O** was employed to investigate the structure and performance for selective conversion of CO_2 . Interestingly, with the help of the active site CuO_4 , the $FE(C_2H_4)$ given by **PcCu-Cu-O** was significantly enhanced compared to that of discrete molecular CuPc.

The PcCu- $(OH)_8$ ligand was obtained by the solvothermal reaction of 1,2-dicyano-4,5-dimethoxybenzene and CuCl₂, and

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its proposed structure was confirmed by its mass spectrum (Figure S1a). Solvothermal reaction of PcCu-(OH)₈ and copper(II) acetylacetonate at 85 °C could give a microcrystalline powder of **PcCu-Cu-O**. In view of the potential effect of the particle size on reaction activity, exfoliation was performed by ultrasonic treatment to obtain a **PcCu-Cu-O** sample with smaller particle size.^{25–28} Powder X-ray diffraction peaks at 5.2° , 7.2° , 10.1° , and 27.5° are ascribed to the (100), (110), (200), and (001) facets of **PcCu-Cu-O**, respectively (Figure S2). Electrochemical impedance spectroscopy measurement of **PcCu-Cu-O** revealed an impressive conductivity (5 S m⁻¹) (Figure S3). Such a high conductivity is beneficial for efficient electron transfer in electrocatalysis and yielding hydrocarbons with a high current density.

In order to verify our conjecture, we carried out electrocatalytic performance measurement of **PcCu-Cu-O**. The microcrystalline powder of **PcCu-Cu-O** was coated on a glassy carbon electrode (GCE) with Nafion binder to prepare the working electrode for measurement of the electrochemical CO_2RR activity in an H-type cell with two compartments. Cyclic voltammetry (CV) measurements were carried out in 0.1 M KHCO₃ aqueous solution saturated with CO_2/Ar . In the Ar atmosphere, the reduction of the compound were observed at the potentials of -1.0 to -1.3 V vs RHE (Figure 2a), which



Figure 2. (a) CV curves of PcCu-Cu-O. (b) FEs of C_2H_4 , CH₄, CO, and H₂ for PcCu-Cu-O. (c) Comparisons of $FE(C_2H_4)$ obtained under neutral condition between PcCu-Cu-O and some previously reported electrocatalysts. (d) Durability of PcCu-Cu-O in the electrocatalysis at the potential of -1.2 V vs RHE.

can be ascribed the reduction of Cu(II) to Cu(I) ion. The current density was enhanced in the CO₂ saturated electrolyte, indicative of the process of CO₂RR. The FEs of different reduced products at different potentials were tested (Figure 2b). Gas chromatography (GC) revealed the generation of C₂H₄, CH₄, CO, and H₂ (Figure S4). The **PcCu-Cu-O** exhibited high selectivity toward C₂H₄ (FE(C₂H₄) = 50%) and current density of 7.3 mA cm⁻² at -1.2 V vs RHE (Figure 2b), and no liquid phase product was observed in the ¹H nuclear magnetic resonance (¹H NMR) spectra (Figure S5). The measurements of FE(C₂H₄) of S0(1)% was obtained, indicative of good repeatability. Compared to the exfoliated sample, the as-

synthesized bulk sample exhibited poor performance (FE- $(C_2H_4) = 43\%$, current density = 4.2 mA cm⁻²) under the same conditions (Figure S6c and d), indicative of the potential effect of particle size on electrochemical activity. In order to further increase the conductivity of the catalyst, we deposited PcCu-Cu-O on carbon nanotubes (CNTs) with weight ratios of 2:1. However, PcCu-Cu-O/CNT just gave H₂ as the main reduction production at all applied potential ranges (-1.0 to)-1.6 V vs RHE) and yielded no C₂H₄ (Figure S7a), which might be ascribed to the high catalytic activity for hydrogen evolution reaction of CNT (Figure S7b). Importantly, the performance of PcCu-Cu-O is not only much higher than those of discrete molecular PcCu with a $FE(C_2H_4)$ of 25%¹¹ and all reported MOFs and MOF derivatives (Table S1)²⁹⁻³¹ but also higher than those of most copper salts, copper nanoparticles, and copper alloys (Figure 2c), such as CuOHFCl ($FE(C_2H_4)$ of 36.3%),³² CuPd ($FE(C_2H_4)$ of 48%),³³ and Cu nanocube-O ($FE(C_2H_4)$ of 45%)³⁴ under similar conditions. Actually, to our best knowledge, only a reconstructed nanocopper electrocatalyst exhibited a higher $FE(C_2H_4)$ than that of PcCu-Cu-O in neutral electrolyte,³⁵ but the high selectivity was obtained at a higher potential of about -2.0 V vs RHE, indicative of a higher energy consumption (Figure 2c and Table S1).

To evaluate the durability, PcCu-Cu-O was treated with continuous electroreduction of CO₂ at -1.2 V. The *i*-*t* curve indicates that the performance of PcCu-Cu-O is durable for at least 4 h (Figure 2d). According to PXRD patterns, scanning electron microscope (SEM), and transmission electron microscope (TEM) images, no Cu or Cu₂O clusters were generated during electrocatalysis (Figures S2, S8, and S9). The X-ray photoelectron spectroscopy (XPS) pattern revealed negligible changes during the electrocatalysis (Figure S10). Most importantly, in-situ operando X-ray absorption spectroscopy (XAS) experiments of PcCu-Cu-O indicated that no significant change in Cu K-edges, or no visible metallic Cu (0) signals, could be observed in the X-ray absorption nearedge structure (XANES) profiles of PcCu-Cu-O during the catalytic process (Figure S11a), and no Cu-Cu bond was observed in the extended X-ray absorption fine structure (EXAFS) spectrum. Therefore, PcCu-Cu-O has sufficient durability for electroconversion of CO2 to C2H4. In the literature,4,14 during the electrocatalytic CO2RR process, the Cu-N interaction in the discrete molecular CuPc catalyst is not strong enough to stabilize the copper ion centers, and the aggregation of these atomically dispersed Cu atoms leads to the generation of Cu clusters and nanoparticles. By comparison, as for PcCu-Cu-O, on the one hand, the electron donating effect of the oxygen atoms in PcCu-Cu-O can enhance the coordination ability of nitrogen atoms, thus enhancing the Cu-N interactions; on the other hand, we think that the high crystallinity and the strong $\pi - \pi$ interaction between MOF layers can limit the distortion of Cu ions from tetragonal to tetrahedral. Therefore, CuPc based MOFs with high crystallinity exhibit high stability during electrocatalysis without distortion of Cu ions.

Aspired by XANES and EXAFS results, we think that no aggregated Cu(0) atoms exist during the catalytic process, and thus the excellent electrochemical performance should not be ascribed to the aggregated sites which has been illustrated in many literature works.^{14,36} As shown in Figure 1, PcCu-Cu-O possesses two types of potential Cu-based active sites, namely CuPc and CuO₄ units. In order to clarify the electrocatalytic

activity, PcCo-Cu-O and CuHHTP (HHTP = 2,3,6,7,10,11hexahydroxytriphenylene) (Figure S12) were selected as comparative materials. PcCo-Cu-O and CuHHTP were prepared according to the previous reports,^{12,37} and their purities were confirmed by PXRD patterns (Figure S13). PcCo-Cu-O is isostructural to PcCu-Cu-O, being constructed by the PcCo- $(OH)_8$ ligands and the square-planar CuO₄ nodes. CuHHTP is constructed by tripodal bridging HHTP ligands and CuO₄ nodes. The electrocatalytic activities for CO₂RR of PcCo-Cu-O and CuHHTP were examined under the same conditions. Similar to the reported performances,^{12,37} both of PcCo-Cu-O and CuHHTP just gave CO as the main reduction production at all applied potential ranges (-1.0 to)-1.6 V vs RHE) and yielded no C₂H₄ (Figure S6c and d), suggesting that the CuPc unit should serve as the C2H4producing active site and both the CoPc and CuO₄ units should serve as the CO-producing active sites. On the other hand, the performance of PcCu-Cu-O (FE(C_2H_4) of 50%) is much higher than that of PcCu (FE(C_2H_4) of 25%),¹¹ thus the enhanced electrochemical performance of PcCu-Cu-O may be ascribed to the synergistic effect between CuPc and CuO4 units.

To understand the synergistic effect between CuPc and CuO₄ units in PcCu-Cu-O during electrocatalytic CO₂RR, the adsorption energies of *CO intermediates adsorbed on them were calculated by the periodic density functional theory (PDFT). The two *CO intermediates adsorbed on the CuPc and CuO₄ units are separated by 8.95 Å, obviously not suitable for direct C-C dimerization into the *OCCOH intermediate. Thus, one of the *CO intermediates needs to be desorbed before the C-C dimerization. For the CuPc unit, the *CO adsorption energy is about 48 kJ mol⁻¹, being much higher than that of the CuO_4 unit (16 kJ mol⁻¹), which can be ascribed to the different coordination fields around the metal ions. Since the CuO₄ unit has a high activity for reduction of CO_2 to CO_1^{10} the lower *CO adsorption energy of the CuO_4 unit implies that it could serve as the ideal CO source for C-Cdimerization on CuPc during electrocatalytic CO₂RR. On the other hand, the higher *CO adsorption energy of the CuPc site is beneficial for the hydrogenation of CO into *CHO before the C-C dimerization. Therefore, the combination of CuPc and CuO₄ units in PcCu-Cu-O significantly reduces the energy barrier of C-C dimerization, compared with those of the discrete molecular PcCu and PcCu- $(OH)_8$ in the catalysis, leading to a much better performance. In other words, the CO molecule desorbed on the CuO₄ unit can easily migrate to dimerize with the *CHO intermediate adsorbed on CuPc unit, forming the *OCCHO intermediate, as shown in the proposed mechanism of CO_2RR to C_2H_4 depicted in Figure 3a. A similar mechanism of C-C dimerization on a catalyst with a single active site has been documented previously.²¹

In order to verify this mechanism, *in-situ* ATR-FTIR measurements were performed (Figure S14). In the spectra (Figure 3b and c), the absorption peaks at 1253 and 1396 cm⁻¹ could be attributed to the C–O stretch and symmetric vibration (vibration of O–C=O) of the *COOH intermediate, respectively,³⁷ and the peak at 1575 and 1713 cm⁻¹ could be attributed to the asymmetric vibration of *COCHO and C=O stretching of carbonyl intermediates, respectively. Additionally, the peak at 1031 cm⁻¹ could be ascribed to the nonplanar vibration (O=C-H) of the *CHO intermediate.^{37,38} Most importantly, the absorption peaks of the *CH₂= intermediate (894 cm⁻¹ for C–H bending vibration

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Figure 3. (a) Proposed CO_2RR mechanism of PcCu-Cu-O. Color codes: carbon (gray), nitrogen (blue), oxygen (red), hydrogen (white), copper (orange). (b, c) *In-situ* ATR-FTIR spectra of PcCu-Cu-O during the electrochemical CO_2RR .

and 3108 cm⁻¹ for C–H stretch) were observed, indicative of a good agreement with the previously reported mechanism of yielding C_2H_4 .²¹

In summary, the MOF **PcCu-Cu-O** with dual active sites (*i.e.*, both C_2H_4 -producing and CO-producing sites) exhibits an impressive performance for electroreduction of CO₂ to C_2H_4 . As revealed by the mechanism study, such high performance may be ascribed to the synergistic effect of the dual active sites that can reduce the energy barrier in the C–C dimerization. Therefore, this work may provide a new strategy to design and utilize electrocatalysts with multiple catalytic active sites for conversion CO₂ into high-valued C₂₊ chemicals.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01466.

Detailed information regarding the characterization analysis, electrochemical measurement, DFT calculation, and intermediate illustration (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSFC (21890380 and 21821003), Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01C161), and Guangdong Natural Science Funds for Distinguished Young Scholar (2018B030306009).

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NOTE ADDED AFTER ASAP PUBLICATION

This communication published ASAP on May 6, 2021. Figure 2d has been updated and the corrected version was reposted on May 7, 2021.

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