Atomically Dispersed CuN_x Sites from Thermal Activation of Boron Imidazolate Cages for Electrocatalytic Methane Generation

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Abstract

Atomically dispersed heteroatom coordinated metal sites (ADMS) have been recognized as promising candidates for electrochemical conversion. Among a diverse range of molecular precursors for ADMS synthesis, framework materials are particularly interesting due to the presence of pre-formed heteroatoms coordinated active sites. Herein, we demonstrate that the copper boron imidazolate cage, BIF-29(Cu) can be an ideal precursor for nitrogen coordinated single site Cu catalyst for electrocatalytic carbon dioxide reduction (CO₂RR). Although the pristine material exhibited moderate methane selectivity over hydrogen evolution reaction (HER), the methane selectivity is significantly enhanced by 2 times (55 % CH₄ at -1.25 V vs. RHE) after mild thermal activation. Extensive characterization methods indicate the transformation of crystalline BIF-29(Cu) into an amorphous carbonaceous material comprising isolated CuN_x sites. Moreover, *in situ* X-ray absorbance spectroscopy further indicates stable CuN_x sites that are reduced during CO₂RR. This work encourages the discovery of single-site electrocatalytic systems through a rational selectivity.

Keywords

Single site catalyst, copper, boron, coordination cage, methane electrosynthesis, atomically dispersed metal sites, carbon conversion, electrocatalysis

Introduction

Electrochemical carbon dioxide reduction (CO₂RR) for fuel and other combustible material can be an effective strategy for solar energy conversion and closing the anthropogenic carbon cycle. An intense research effort has been dedicated to identifying promising electrode material¹⁻⁶ and electrolyte systems⁷⁻¹² for enhanced CO₂RR selectivity and activity. While CO and formate production can be achieved by many metal catalysts, copper is among the few metals that can achieve significant generation of hydrocarbon.^{1,3–5,13–16} However, the active sites of these metallic catalysts are not well-defined, which hinders efforts to establish robust structure-activity relationships and systematic catalyst development. Although molecular catalysts can mitigate these hurdles, coordination compounds can suffer from deactivation, sluggish heterogeneous electron transfer, incomplete utilization of all active sites, and challenging product isolation.^{17–19} Recently, several solid-state frameworks, coordination cages, and coordination polymers have been developed with discrete transition metal active sites.^{15,20–23} The active sites in these materials can either directly participate in catalysis^{24–29} or generate catalytically active species under electrochemical bias.^{30,31} For electrogenerated catalysts, the catalytic performance primarily depends on the coordination environment of the transition metal site in the pristine material.³² Such tunability makes framework materials an emerging candidate for electrocatalytic application.

Inspired by the distinctive hydrocarbon selectivity of copper catalysts and the tunability of frameworks, a number of Cu-based metal-organic frameworks (MOFs) has been developed for CO₂ reduction. For example, a Cu-based MOF constructed with a mixed porphyrin and carboxylate coordination environment was shown to produce a significant amount of CH₄ and C₂H₄ in an aqueous KHCO₃ electrolyte.³³ Similar systems have been reported to produce formate and acetate in nonaqueous conditions at relatively low overpotential.³¹ Moreover, single-site materials are also an emerging candidate for electrocatalytic application.³⁴⁻⁴⁰Among several reported synthetic pathways and precursors, framework materials are known to be one of the ideal precursor for thermally derived atomically dispersed metal sites (ADMS).⁴¹⁻⁴⁵The framework-derived ADMS are advantageous due to the presence of pre-formed isolated heteroatom coordinated metal sites, allowing a high degree of control and tunability. These systems can overcome the typically low conductivity of the parent framework and can improve

activity without altering selectivity. In a recent study, Sargent *et al.* utilized thermal activation to distort Cu dimers in a paddlewheel MOF system, HKUST- $1.^{30}$ The distorted coordination environment was observed to produce undercoordinated Cu clusters under an electrochemical bias and exhibited unprecedented C₂H₄ selectivity among MOF-based electrocatalytic systems. In addition, thermal activation has been used to promote mixed valency in a Cu-MOF system, which is beneficial for C-C coupling.⁴⁶

Cu ADMS systems are intriguing candidates for electrochemical CO₂ conversion to CH₄.^{32,38,47} It has been previously shown that Cu doped with p-block elements can suppress HER, leading to high CO₂RR selectivity.^{4,48,49} For instance, boron doping enhanced the CO₂RR selectivity on Cu by stabilizing sub-surface oxygen and altering the electronic structure.⁴ Bdoped CuO nanobundles⁵⁰ have also been utilized for electrocatalytic CO₂RR. Additionally, catalytic centers embedded in a partially oxidized matrix have been reported to promote CO₂RR⁵¹ and impact selectivity.⁵² The remarkable CO₂RR activity of these systems inspired us to use boron imidazolate cages (BIF)⁵³ that contain isolated square planar nitrogen coordinated Cu²⁺ sites as a precursor for a thermally derived solid-state ADMS catalyst. The isolated CuN₄ in pristine boron imidazolate, BIF-29(Cu), is an active site for photocatalytic CO₂ conversion to CO.⁵⁴ However, to the best of our knowledge, the electrochemical property of this material is still underexplored. In this work, we discovered that BIF-29(Cu) can electrochemically catalyze the conversion of CO₂ to CH₄ with high selectivity and activity. Importantly, this catalytic performance is further enhanced by mild thermal activation of BIF-29(Cu), achieving 55% selectivity for CH₄. This selectivity is remarkable as there are only a few pristine frameworks and framework-derived ADMS electrocatalysts that exhibit hydrocarbon selectivity. Our spectroscopic investigation suggests the emergence of undercoordinated CuN_x sites in a Bcontaining carbonaceous matrix due to partial decomposition of the primary coordination sphere. Moreover, we demonstrate that controlled heat treatment at relatively low temperatures can prevent single site agglomeration and loss of molecular active sites, as demonstrated by in situ X-ray absorption spectroscopy (XAS). Overall, we hypothesize that the formation of an undercoordinated CuNx (x < 4) sites and the improved charge transport and substrate availability contribute to the observed catalytic enhancement in the BIF-29(Cu)-200C. Our work demonstrates the potential of coordination cage materials for the synthesis of single-site metal catalysts and avails new opportunities for rational materials design.

Experimental section

Materials and general instrumentation

Sodium borohydride (96 %), imidazole (99 %), and 1,2,3-triazole (97%) were purchased from Sigma Aldrich. N, N – Dimethylacetamide (DMA, 99 %, Sigma-Aldrich), acetone (ACS grade, Sigma-Aldrich), and methanol (ACS grade, Sigma-Aldrich) were used without any further purification. Copper nitrate pentahydrate (\geq 99.99 %, trace metal basis) was purchased from Thomas Scientific and Sigma-Aldrich. The organic linker, Na[HB(Im)₃] (Im = imidazole), and BIF-29(Cu) was synthesized according to literature procedures (see **Supporting Information**).⁵⁴

The powder diffraction XRD (PXRD) measurements were performed with a Bruker D8 Focus diffractometer (Cu K α , LynxEye detector). Scanning electron microscopy experiments were conducted using a JEOL JSM-IT100 scanning electron microscope. All electrochemical measurements were performed using an Ivium n-STAT multichannel electrochemical analyzer and the gaseous product was detected using an Agilent Micro GC 490 equipped with a PoraPlot (U) column and a Molsieve 5A column. A Bruker Avance 400 MHz FT NMR instrument was used to analyze the liquid product. The solid-state EPR experiments were conducted in a Bruker X-band EPR spectrometer. Raman spectra were measured using a micro-Raman setup and Horiba JY T64000 spectrometer with liquid nitrogen-cooled CCD. The laser probe is 2 micrometers in diameter. Spectra are excited with a 514.5 nm line of Ar-Kr laser using a power of 0.5 mW. Single crystal X-ray data (Table S1) were collected on a Rigaku Oxford Diffraction SuperNova diffractometer (equipped with Atlas detector) with Mo K α radiation ($\lambda = 0.71073$ Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.39.29c, Rigaku OD, 2017). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2018/3 (Sheldrick, 2018) and was refined on F^2 with SHELXL-2018/3 (Sheldrick, 2018). Numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 43 (imidazole) or AFIX 133 (disordered lattice methanol molecule) with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms. The H atoms attached to B1 and O1W (coordinated water molecule) were found from difference

Fourier maps, and the coordinates for H1B (attached to B1) were refined pseudofreely using the DFIX instruction in order to keep the B–H distance within an acceptable range. The H atoms attached to O1W must be disordered as the coordinated water is found at one site of fourfold axial symmetry. The H atom attached to O1S (lattice methanol molecule) could not be retrieved from the difference Fourier map. The cage structure is ordered. Within the cavity of the cage structure, there seems to be some amount of very disordered lattice methanol molecules. It is estimated there is 0.226(11) lattice methanol solvent molecule per asymmetric unit [occupancy factor: 0.226(11)], and hence atoms from the lattice methanol molecules were refined isotropically. The absolute configuration has been established by anomalous-dispersion effects in diffraction measurements on the crystal, and the Flack parameter refines to -0.01(2). The crystal that was mounted on the diffractometer was a composite of two crystal components (one major and one minor components), and the two components are related by a 123.83° rotation along the 0.6088**a*** + 0.5733**b*** – 0.5483**c*** reciprocal direction. The BASF scale factor refines to 0.010(3).

Solid-state nuclear magnetic spectroscopy

Solid-state ¹¹B nuclear magnetic resonance (NMR) spectroscopy experiments were performed on an 11.7 T wide-bore Bruker Avance III NMR spectrometer, operating at Larmor frequencies of 500.13 MHz and 160.46 MHz for ¹H and ¹¹B. A Bruker multinuclear HX 4.0 mm magic angle spinning (MAS) probe was used. ¹¹B NMR spectra were acquired at 25 °C and vr = 10 kHz or 12 kHz. A broad ¹¹B background signal from the MAS stator materials was removed using a DEPTH pulse sequence⁵⁵ with a small tip angle θ corresponding to an rf pulse length of 1.5 µs. 75 kHz ¹H decoupling was applied during acquisition. A 2 s recycle delay was used.

X-Ray photoelectron spectroscopy

BIF-29 powder samples were prepared on double-sided copper tape, which was attached to a gold-plated Si wafer. After the samples were prepared, they were loaded onto a sample bar and pumped down in an introductory chamber in preparation for data collection. X-ray photoelectron spectroscopy was conducted on an Axis Ultra DLD acquired from Kratos Analytical (Chestnut Ridge, NY). The base pressure of the analysis chamber was approximately 5×10^{-10} torr. Additional XPS experimental parameters can be found in **Tables S2-S5**.

X-ray absorption spectroscopy

Cu K-edge XAS measurements were performed at the 10-ID-B beamline of the Advanced Photon Source, Argonne National Laboratory. For ex situ analysis, powders were spread across polyimide tape and measured in a fluorescence geometry. For *in situ* electrocatalysis, the catalyst ink was deposited on carbon fiber electrodes and placed within an electrochemical cell consisting of X-ray transparent Kapton windows. The catalyst working electrode was connected to the exterior of the cell using at Ti wire, which also consisted of a graphite counter electrode and Ag/AgCl reference electrode. XAS was performed under steady state conditions at (0 V vs. RHE to -1.35 V vs. RHE) under the same fluorescence geometry used for *ex situ* experiments. Data were collected from ≈ 200 eV below the Cu K-edge to ≈ 700 eV above the edge. All data reduction, analysis, and modeling were performed using the Demeter XAS software package.⁵⁶ EXAFS modeling was performed using Cu-N, Cu-O, and Cu-C backscattering paths generated from the crystal structure of the BIF-29(Cu), where Cu-N and Cu-C paths originate from the imidazole and Cu-O from the bound water molecule. The uncertainty from least squares fitting is shown (**Table S6**). A value of S_0^2 of 0.941 was obtained by modeling a reference Cu foil.

High energy X-ray diffraction (HE-XRD) & atomic pair distribution functional (PDF) analysis

HE-XRD measurements were performed at the 11-ID-C beamline of the Advanced Photon Source, Argonne National Laboratory using an X-ray wavelength of 0.1173 Å. Sample powders were loaded into 1 mm OD Kapton capillaries and sample to detector distance of ~375 mm was used to obtain a Q_{max} of ≈ 35 Å⁻¹. The HE-XRD patterns were background corrected, transformed into reduced structure factors, and Fourier transformed into atomic PDFs using the program PDFGetX3.⁵⁷

Electrode preparation

A square piece of carbon paper (Toray 120, Fuel Cell Store) was wrapped with a thin silver wire (99.9 %, trace metal, Alfa Aesar). The exposed wire was masked with polyimide tape (McMaster – Carr). The sides of the electrode were also masked with the polyimide tape to expose a 1 cm² geometric area. Fresh catalyst inks were prepared right before electrolysis. To

prepare the ink, 10 mg of BIF-29(Cu) or, BIF-29(Cu)-200C was mixed with 2 mL 4:1 (v/v) water: ethanol with an agate mortar and pestle. The mixture was transferred to a 10 mL vial and was sonicated for 30 min to ensure complete dispersion. 100 μ l of the suspension was drop-casted on the exposed 1 cm² area of the carbon paper and dried under an infrared lamp to promote even drying.

GC calibration

All calibrations were conducted by injecting a known volume of analytically pure gas (H₂, CO, CH₄, C₂H₄) into our sealed electrolysis cell containing CO₂ and electrolyte. The H-cell was stirred for 15 minutes before a sample of the headspace was injected into the GC. The procedure was repeated with different volume of the calibrating gas to achieve a linear fit between GC peak area and gas volume. The calibration plot was used to estimate an unknown amount of gas generated during the electrolysis.

Controlled potential electrolysis

The electrolyte was prepared by dissolving K₂CO₃ (99.997 %, Sigma-Aldrich) to a measured volume of "Type 1" purified water (18.2 M Ω , Milli-Q) to yield a concentration of 0.05 M. The pH of the electrolyte solution was measured using a METTLER TOLEDO FiveEasy Plus pH meter. The controlled potential electrolysis (CPE) experiments were performed in a twocompartment glass cell (Adams and Chittenden) where each 70 mL compartment was separated by a glass frit. Both chambers were filled with 40 mL electrolyte solution before electrolysis. The working electrode (framework material supported on carbon paper) and the reference electrode (Ag/AgCl, 3 M NaCl, BASI) were placed together in a compartment and a graphite rod counter electrode (99.9995 %, Alfa Aesar) was placed in the other compartment. Both compartments were purged with CO₂ (99.99%, Airgas) for 15 minutes. After CO₂ saturation, the measured electrolyte pH was 6.8 and the cell was sealed for the duration of the electrolysis. Electrochemical impedance spectroscopy (EIS) was performed before the electrolysis to measure the solution resistance. At 10⁴ Hz, the real component of the Nyquist plot was used as solution resistance and 85 % of that resistance was compensated using the software. The remaining 15 % resistance was compensated manually after electrolysis. Electrolysis experiments at each potential were repeated at least 3 times with separately prepared electrodes and the average and standard deviation are shown.

Cyclic voltammetry

Similar to CPE experiments, the cyclic voltammetry (CV) experiments were performed in an H-type cell with the pristine or calcined BIF-29 coated on a carbon paper electrode. 80 mL (40 mL each side) 0.05 M K₂CO₃ or, 0.1 M potassium phosphate buffer was employed as an electrolyte. The electrolyte was purged with N₂ or CO₂ gas for at least 15 minutes before the experiments. After that, the purging needles were lifted above the solution and maintained at a constant flow. All voltammograms were taken in quiescent solution. All data collection was started from open circuit potential. Before the final data collection, the electrodes were cycled between -0.9 V to 0.5V vs. Ag/AgCl (3 M NaCl) 50 times at 500 mV s⁻¹ to achieve a stable surface. The final data were collected between desired potential range and at specific scan rates. The potentials were reported without the Ohmic loss compensation and converted to reverse hydrogen electrode (RHE) using the following equation:

E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 + 0.059 pH

Results and discussions

Inspired by the unique electrocatalytic CO₂RR activity of single-site nitrogen coordinated copper systems, we explore the catalytic performance of isolated Cu sites in boron imidazolate cages (**Scheme 1**) and the corresponding thermally activated ADMS catalyst. The pristine coordination cage, BIF-29(Cu), was synthesized solvothermally in a solution containing Cu(NO₃)₂ and a tripodal boron imidazolate ligand, Na[HB(Im)₃] (Im = imidazole). The structure and phase purity of the powder were characterized by powder X-ray diffraction (PXRD) (**Figure S1**), which matches previously reported diffraction patterns.^{53,54} The solid-state structure from single-crystal X-ray diffraction showed the BIF-29(Cu) is composed of dodecahedron boron imidazolate cages (**Scheme 1**), Cu₆[HB(Im)₃]₈(H₂O)₆(NO₃)₄ with each Cu²⁺ ion in a square pyramidal coordination environment. In these cages, the square planes of Cu ions are coordinated with four imidazole nitrogen atoms from four surrounding boron imidazolate ligands, and the fifth coordination is occupied by a water molecule.



Scheme 1. Schematic representation of the self-assembly of BIF-29(Cu) and CuN₄ site containing isolated boron imidazolate cage

To synthesize the atomically dispersed metal sites in this material, thermogravimetric analysis (TGA) was performed to determine a calcination temperature that would preserve the atomically dispersed copper sites and molecular primary coordination sphere (**Figure S2a**). The percent weight loss versus temperature graph shows a ≈ 5 % weight loss until 210 °C followed by a sharp decomposition. Accordingly, the BIF-29(Cu) powder was calcined in a tube furnace at 200 °C for 1 h under a continuous Ar flow to prevent oxidation of the material. The TGA of BIF-29(Cu)-200C is similar to that of BIF-29(Cu), which confirms there is no significant mass loss after the thermal treatment (**Figure S2b**). A dramatic color change was observed from a purple BIF-29(Cu) (**Figure S2c,i**) to a green-brown BIF-29(Cu)-200C, **Figure S2c,ii**). In the PXRD of BIF-29(Cu)-200C, a decrease in intensity at all 2 Θ values suggest a loss of long-range order (**Figure 1a**).

The IR spectrum of pristine material shows a broad band at $\approx 3500 \text{ cm}^{-1}$ (Figure 1b, black), which corresponds to the O-H stretch of the axially coordinated water molecule. This feature disappeared after thermal treatment (Figure 1b, red). Similar IR bands in the fingerprint region (800 cm⁻¹ to 1800 cm⁻¹) of BIF-29(Cu) and BIF-29(Cu)-200C suggest the retention of the organic ligand environment in the calcined material (Figure 1b). While the IR spectra of BIF-29(Cu) and BIF-29(Cu)-200C are similar, the Raman spectra of those materials are strikingly different. The calcined BIF exhibits broad features (Figure 1c, red) centered at $\approx 1500 \text{ cm}^{-1}$ instead of sharp Raman bands seen in the pristine material (Figure S3, black). A previous report

for another calcined Cu-based framework, Cu-BTC (BTC = 1,3,5-benzene tricarboxylate), suggests the features centered at \approx 1370 cm⁻¹ and 1550 cm⁻¹ correspond to dangling carbon bonds and amorphous sp² carbon / CuN_x species, respectively.³⁸ In the case of BIF-29(Cu)-200C, these strong Raman features imply partial carbonization of the BIF, which obscures the expected bands from the intact molecular boron imidazolate cages observed in IR spectroscopy.

To probe structural changes at the boron imidazolate sites, solid-state ¹H (**Figure S4**) and ¹¹B (**Figure 1d**) magic angle spinning (MAS) NMR spectra of the pristine and calcined materials were acquired. In pristine BIF-29(Cu), the ¹¹B peak (**Figure 1d**, black) is centered at \approx 50 ppm, which is expected for a boron hydride. In the calcined material, the peak (**Figure 1d**, red) is shifted up-field, indicating a more electronegative coordination environment around B.⁵⁸ A more electronegative linker backbone has been previously shown to improve CO₂RR selectivity of Coporphyrin catalytic sites in an oriented COF thin film electrocatalyst by means of inductive effect.²⁵ Furthermore, as observed in the scanning electron micrographs, the calcined BIF-29(Cu) particles retain the polyhedral morphology of pristine material (**Figure 1e, f**). No metallic particle formation is observed unlike other MOF-derived materials,³⁸ which suggests the Cu sites remain isolated in the calcined material.



Figure 1. (a) PXRD comparison between pristine BIF-29(Cu) (black), BIF-29(Cu)-200C (red), (b) infrared spectra of BIF-29(Cu) (black) and BIF-29(Cu)-200C (red), (c) Raman scattering of BIF-29(Cu)-200C (red), (d) solid state ¹¹B MAS NMR of BIF-29(Cu) (black) and BIF-29(Cu)-200C (red), and scanning electron micrograph of (e) BIF-29(Cu) and (f) BIF-29(Cu)-200C. The cylindrical morphology in e) represents carbon fibers of the carbon paper electrode.

We next investigated the impact of the thermal treatment on the local coordination environment and oxidation state of Cu using X-ray absorption spectroscopy (XAS). The Cu Kedge of the pristine BIF-29(Cu) in the X-ray near-edge spectrum (XANES) has an E₀ position consistent with Cu²⁺ and exhibits a profile similar to other Cu-based MOF structures,^{30,32,59} including minimal pre-edge features coupled with modest white line intensity (Figure 2a, black). Clear changes are observed in XANES after calcination (Figure 2a, red). The calcined sample exhibits a lower white line intensity, suggesting the partial removal of electron-withdrawing functionalities around the Cu atoms, such as the axial water and N functionalities in the imidazole (Figure 2a, red). The first derivative of the XANES (Figure 2b) further indicates a small decrease in E₀, suggesting a partial reduction in the Cu oxidation state relative to pristine BIF-29(Cu). A large pre-edge feature emerges upon calcination, corresponding to $1s \rightarrow 4p$ dipolar shakedown transition that is often found in CuN_x catalysts.^{38,60} The extended X-ray absorption fine structure (EXAFS) obtained from both pristine and calcined material were compared (Figure 2c, d, S5). The EXAFS show that the sharp feature centered at \approx 1.5 Å corresponding to the Cu-N coordination environment is partially preserved in the calcined material (uncorrected for phase shift, Figure 2c, d). The pristine MOF exhibits features at longer distances as compared to the calcined material (Figure 2c, d, S5), showcasing the lack of ordered node structure. Furthermore, the absence of characteristic metallic Cu scattering features centered at ≈ 2.2 Å also further rules out the possibility of site agglomeration in BIF-29(Cu)-200C to metallic Cu (Figure 2c, d, S6).

The EXAFS for each material was then modeled using backscattering paths taken from atomic positions discovered from single-crystal XRD experiments (see experimental section). A summary of the modeling results is shown in **Table S6**. Modeling of the pristine BIF-29(Cu) MOF results in coordination numbers (CNs) of 4.67 +/- 0.31 for Cu-N, 0.72 +/- 0.57 for Cu-O_w (from bound water), and 8.25 +/- 0.73 for Cu-C, which are all consistent with expected values of 4.0, 1.0 and 8.0 for the crystalline MOF. Upon calcination, the local Cu coordination is partially decreases, with a Cu-N CN of 2.20 +/- 0.20 and a Cu-O_w CN of 0.39 +/- 0.28, indicating that a Cu-N₂ motif is formed.⁶⁰ The undercoordination was also accompanied by a partial decrease of Cu-N bond lengths, with modeled distances of 1.98 ± 0.01 and 1.926 ± 0.006 Å for the pristine and calcined BIF-29(Cu) respectively. The longer-range Cu-C cannot be modeled, likely due to imidazole decomposition during calcination. Importantly, the XAS analysis reveals key

structural changes upon calcination, notably the most likely catalytic motif of a Cu-N₂ unit in the calcined MOF.

In addition, we applied high energy X-ray diffraction (HE-XRD) measurements coupled to atomic pair distribution function (PDF) analysis to elucidate the effect of the thermal activation in the atomic-scale structure of BIF-29(Cu). PDF is a powerful approach to complement EXAFS studies, capable of accessing atomic-scale structure across lengths scales exceeding those obtained by EXAFS.^{61–63} HE-XRD patterns are shown in Figure S7a, where pristine BIF-29(Cu) exhibits well-defined Bragg peaks and the calcined BIF-29(Cu) exhibits a lack of diffraction patterns, consistent with PXRD data shown in PXRD (Figure 1a). Conversion of the HE-XRD data to their structure functions, F(Q) (Figure S7b), and Fourier transformation to atomic PDFs (Figure 2e) clearly demonstrate structural variations in atomic structure upon thermal activation. The pristine MOF exhibit atomic pairs at 0.95, 1.33, 1.69, 1.98, and 2.88 Å corresponding to the first coordination spheres of C-H, C-N, B-N, Cu-N, and Cu-Cu, respectively. Compared to the pristine material, BIF-29(Cu)-200 show absence of C-H (0.95 Å) correlations pairs, suggesting the release of H species, which can contribute to the carbonaceous nature of the calcined system. The C-N correlation (1.33 Å) is retained in the calcinated material, suggesting a partial network N-C groups commonly seen in ADMS materials. Changes in Cu-N pairs were also observed to a decreased distance, which agrees with EXAFS modelling. The large feature at 2.3 Å is likely due to the second coordination sphere of graphitic carbon, strongly indicating a loss of the MOF framework. Furthermore, thermal activation has shifted the correlations of the pairs B-N from 1.69 to 1.87 Å, which likely corresponds to the local environment changes observed in the solid-state ¹¹B MAS NMR spectroscopy (Figure 1d).

The Cu oxidation state in the pristine and calcined BIF materials is further probed by Xray photoelectron spectroscopy (XPS). The Cu 2p spectra show the dominant features (>94.9%) of Cu²⁺ state at 935.0 eV +/- 0.0 eV along with the characteristic broad shakeup feature at higher binding energies (942.9 eV +/- 0.0 eV) (**Figure 2f**) (all positions reflect the average +/- the standard deviation of 30 fitted spectra from the two materials (2 spots for BIF-29(Cu); 3 spots for BIF-29(Cu)-200C) rounded to the nearest 0.1eV; see the SI for more details).⁶⁴ While modeling suggests that the distribution of Cu oxidation states are comparable before and after calcination, there is the presence of a small peak at 932.3 +/- 0.1 eV, attributed to reduced Cu, and is slightly higher for the BIF-29(Cu)-200C sample. Because Cu^0 is also observed in the pristine sample, we conclude that this peak was in part the result of X-ray exposure. Although we cannot eliminate the possibility that some of the observed signal for Cu^0 may be due to the calcination process, it is notable that PXRD, SEM, and EXAFS did not show detectable site agglomeration and Cu particle formation in BIF-29(Cu)-200C. X-ray-induced artifacts and other XPS data acquisition/analysis details are discussed in the SI (**Figure S8**). A sharp EPR signal (**Figure S9**, red) at similar field strength as the pristine material (**Figure S9**, black) further indicates dominance of Cu^{2+} oxidation state in the calcined material.



Figure 2. (a) Cu K-edge XANES spectra BIF-29(Cu) (black), BIF-29(Cu)-200C (red) and Cu foil (brown), (b) first derivative of Cu K -edge XANES for BIF-29(Cu) (black), BIF-29(Cu)-200C (red) and Cu foil (brown), experimental EXAFS data (solid line) and fitting (dashed line) of (c) BIF-29(Cu) (black) and (d) BIF-29(Cu)-200C (red), (e) atomic pair distribution function (PDF) analysis of BIF-29(Cu) (black) and BIF-29(Cu)-200C (Red) (f) Cu 2p XPS spectrum for BIF-29(Cu) (black) and BIF-29(Cu)-200C (red)

After evaluating the chemical and structural changes in BIF-29(Cu) following thermal treatment, we explored the electrochemical behavior of these materials. The catalyst powder was dispersed into a water-ethanol solution and the ink was drop-cast onto a carbon paper to prepare the BIF-based working electrode (See Experimental section for detailed procedure). SEM images of the electrodes at low magnification (Figure S10) show a homogeneous dispersion of BIF microcrystals on the carbon paper. Cyclic voltammograms of both pristine (Figure 3a, black) and calcined BIF-29(Cu) (Figure 3a, red) showed a quasi-reversible feature centered at 0.64 V vs. RHE, which is attributed to the reduction of Cu²⁺ to Cu⁺. At potentials more cathodic than -0.2 V, we observe a catalytic current enhancement for both catalyst (Figure S11). The splitting of the anodic feature at 0.87 V vs. RHE is may be due to the presence of defective sites such as undercoordinated Cu sites. Additionally, a non-zero peak separation qualitatively indicates a diffusion-limited redox hopping.^{65,66} In scan rate dependence experiments, the slope of log (peak current) vs. log (scan rate) plot provides quantitative insights into the nature of redox hopping. Such analysis has been performed in our catalytic system by plotting the cathodic peak current (centered at ~ 0.37 V vs RHE) with respect to scan rate. A slope ≈ 0.5 indicates a diffusion-limited redox event, while a slope ≈ 1 indicates a redox event due to surface-confined species.⁶⁵ A slope ≈ 0.68 (Figure S12a, b) was obtained for the pristine BIF, indicating a mixed behavior. On the other hand, a slope ≈ 0.54 (Figure S12c, d) for the calcined material suggests a diffusion-limited hopping event. Moreover, the calcined BIF-29(Cu)-200C exhibited a smaller charge transfer resistance (Figure 3b, S13, 14, Table S7, S8) compared to the pristine BIF. We attribute this improvement to the enhanced redox hopping in the calcined material, which has been noted in oriented MOF thin films⁶⁶ and carbonaceous materials.⁶⁷

To obtain preliminary insight into the catalysis, cyclic voltammetry experiments were performed at catalytically relevant potentials. Both materials exhibit lower catalytic current in CO₂-saturated 0.05 M K₂CO₃ (pH 6.8) compared to the N₂-saturated solutions (pH 10.9, **Figure S15**). CV experiments were also conducted in 0.1 M potassium phosphate buffer (pH 6.56) to compare reactivity under N₂ and CO₂ in similar pH (**Figure S15**). An analogous trend was observed, which suggests the decreased current under CO₂ conditions is due to HER suppression.



Figure 3. (a) CV of pristine BIF-29(Cu) (black) and calcined BIF-29(Cu)-200C (red) in CO₂saturated 0.05 M K₂CO₃ (pH 6.8) at a scan rate of 500 mV s⁻¹, (b) Nyquist plot of BIF-29(Cu) (black) and BIF-29(Cu)-200C (red) from EIS conducted in CO₂-saturated 0.05 M K₂CO₃

Next, a series of controlled potential electrolysis was performed in an H-cell at different cathodic biases using CO₂-saturated 0.05 M K₂CO₃ as an electrolyte. In pristine BIF-29(Cu), CH₄ Faradaic efficiency reaches an average selectivity of 32.2 % at -1.25 V vs. RHE, with some selectivity for ethylene and CO (**Figure 4a, b**). As most framework materials can only convert CO₂ to CO, the methane selectivity and activity of BIF-29(Cu) stand out from other MOFs and coordination cages (**Table S9**). Among the few frameworks that can generate CH₄, HKUST-1,³² BIF-103 nanosheet,⁶⁸ and an adenine-based Cu MOF⁶⁹ exhibited a CH₄ selectivity of 20% (-1.06 V vs. RHE), 4% (-1.0 V vs. RHE), and 8% (-1.3 V vs. RHE), respectively. A Cu coordination polymer²⁹ was shown to be 82% selective for CH₄ at -0.9 V vs. RHE. Nonetheless, the low overpotential and high CH₄ selectivity of BIF-29(Cu) are notable.

Unlike traditional heterogeneous catalysts, a unique aspect of BIF-29(Cu) is its ability to be solubilize in organic solvents as intact molecular cages (**Scheme S3**). To demonstrate the molecular Cu cluster is responsible for CO₂RR, acetonitrile solutions of varying concentrations of soluble BIF-29(Cu) was injected into a CO₂-saturated solution of K₂CO₃ and a colloidal suspension was observed. Characterization of the dried solution showed identical PXRD and IR spectrum as BIF-29(Cu) (**Figure S16**). Controlled potential electrolysis at -1.2 V vs. RHE showed comparable CH₄ selectivity and activity as the electrode-deposited catalyst, particularly for 5 mg of BIF-29(Cu). The high activity is unexpected due to limited electrochemical contact between the suspended catalyst and the carbon paper electrode. These results further validate the electrochemical performance of BIF-29(Cu). Moreover, the solution processability of BIF-29(Cu) is noteworthy from a scale-up perspective.

The CO₂RR selectivity and activity are greatly improved after thermal activation (**Figure 4c, d**). A significant enhancement in CH₄ activity and selectivity was observed, particularly at more cathodic potentials (**Figure 4c, d**). In BIF-29(Cu)-200C electrodes, an average CH₄ selectivity of 55 % was achieved at -1.25 V vs. RHE, surpassing that of other framework-derived ADMS catalysts (**Table S9**).^{30,38} For comparison, CO₂RR electrolysis using a polycrystalline Cu working electrode showed H₂ is the major product under analogous conditions (**Figure S18**).



Figure 4. HER and CO₂RR (a) partial current density and (b) Faradaic efficiency for bulk electrolysis conducted with BIF-29(Cu), (c) partial current density, and (d) Faradaic efficiency for bulk electrolysis conducted with BIF-29(Cu)-200C. All values are representative of the

average +/- one standard deviation of at least 3 measurements on 3 individual cathodes with similar material.

The effect of calcination temperature on the catalytic sites was also probed. The pristine BIF-29 was calcined at 500 °C for 1 h under continuous Ar flow and the resulting material, BIF-29(Cu)-500C, was characterized by PXRD, IR, and SEM. The broadening of the IR spectrum (**Figure 5a**, green) at the fingerprint region (700 to 1700) cm⁻¹ indicates the decomposition of the boron imidazolate ligand. The disintegration of the molecular active sites is also demonstrated by the emergence of crystalline metallic Cu peaks in the PXRD spectrum (**Figure 5b**, green). SEM micrographs (**Figure 5c**, **d**) confirm the formation of metallic Cu particles. Furthermore, BIF-29(Cu)-500C showed lower activity and selectivity for CH4 compared to BIF-29(Cu)-200C during constant potential electrolysis at -1.2 V vs. RHE (**Figure 5e**, **f**). We attribute this decrease in the catalytic performance of material calcined at 500 °C to the loss of discrete molecular Cu sites. These results highlight the importance of the rational selection of calcination parameters for optimum catalytic activity.



Figure 5. (a) Comparison of IR spectral feature between pristine BIF-29(Cu) (black) and BIF-29(Cu)-500C (green), (b) comparison of PXRD feature of pristine BIF-29(Cu) (black), Cu nano powder (brown) and BIF-29(Cu)-500C (green), (c, d) scanning electron micrograph of the BIF-29(Cu)-500C at different magnification, (e) CO₂RR current density and (f) Faradaic efficiency for electrolysis carried out with BIF-29(Cu), BIF-29(Cu)-200C and BIF-29(Cu)-500C.

To explore the fate of the BIF catalysts, cyclic voltammetry experiments were performed after 1-h electrolysis at -1.2 V vs. RHE for BIF-29(Cu) and BIF-29(Cu)-200C (**Figure S19**). The ratio between cathodic current and the anodic current is \approx 1 for the pre-electrolysis CVs (**Figure S19**). Post-electrolysis CVs show a larger anodic current in the reverse cycle, which indicates the accumulation of reduced Cu species during electrolysis. The post-electrolysis voltammograms are different than those of bulk Cu powder and electrodeposited Cu (**Figure S19**). SEM images showed the morphology of the material did not evolve after electrolysis, and no particle formation was observed on the surface of the microcrystals (**Figure 6a-d**). Comparison of preand post-electrolysis PXRD of both catalysts suggest minimal formation of metallic Cu⁰ (**Figure S20a, b**).

In situ electrochemical XAS measurements was then performed to probe changes to the Cu active site during CO₂RR (Figure 6e, f, S21, S22). The XANES for the pristine BIF-29(Cu) is shown in Figure 6e. At open-circuit voltage (OCV), the BIF-29(Cu) exhibits similar XANES as the solid powder (Figure 2a), which demonstrates MOF stability in the electrolyte. With increasing applied reducing bias, E_0 is commensurately reduced to lower energy and is indicative of a partial reduction of Cu^{2+} during CO_2RR . The white line intensity also increases when an applied voltage of -1.05 V vs RHE, suggesting that electron density is being pulled away from the Cu atoms, likely due to the imidazolate ligands around the Cu atoms. After increasing the cathodic potential to -1.15 V and -1.25 V, the white line intensity decreases along with some perturbations to the XANES profile as compared to BIF-29(Cu) at OCV. These changes occur at the onset of enhanced hydrocarbon conversion and likely corresponds to the activation of Cu species responsible for methane production. At -1.35 V, the white line intensity again increases coupled with a significant change to the XANES profile, indicating that at highly reducing potentials, the Cu speciation is again changed from the original BIF-29(Cu) coordination. At higher reducing potentials, the profile of the XANES exhibit increased number of features, suggesting a superposition of multiple Cu sites.

By comparison, BIF-29(Cu)-200C (**Figure 6f**) demonstrates some similar trends vs. applied potential, but with a few key differences. Shifts to lower E_0 as a function of applied reducing potential are again observed, indicating that the isolated Cu sites undergo similar redox chemistry between the two catalysts. A similar trend in white line intensity is also observed,

with the exception that a lower relative white line intensity is maintained at the high cathodic potentials, potentially indicating that the Cu active site of BIF-29(Cu)-200C is structural more robust at higher operating potentials. The profile of the XANES for BIF-29(Cu)-200C does not change as drastically as BIF-29(Cu), further showcasing the stability of the calcined material. The pre-edge feature of the BIF-29(Cu)-200C substantially increases with increasingly negative voltage, especially past -1.05 V. Similar potential dependent enhancement of pre-edge feature was noticed in a previously reported single site $Cu^{2+}N_4$ electrocatalyst.⁷⁰ Such a trend was indicative of electrochemically mediated undercoordination under oxygen reduction reaction condition. A similar XANES feature in our BIF-29(Cu)-200C suggests a voltage-driven symmetry breaking (or reconfiguration of the Cu-N sites) at potentials relevant to CO₂RR. These reconfigured Cu sites are likely responsible for improved efficiency for CH₄.

Importantly, the *in situ* XAS data of pristine and calcined BIF-29(Cu) differ significantly from that of Cu foil and suggest Cu⁰ formation during catalysis is unlikely. The lack of Cu⁰ formation is further confirmed by the *in situ* EXAFS data (**Figures S21-S22**). The Cu-N peak at ~ 1.5 Å in pristine and calcined BIF-29(Cu), respectively, are largely preserved at all cathodic potentials, albeit with some changes to intensity and relative peak position. There is also no new feature associated with a Cu-Cu metallic bond during catalysis for both samples. These results illustrate BIF-29(Cu) systems are remarkably stable ADMS materials as previous catalysts based on MOFs and molecular precursors have shown ready formation of Cu⁰ under catalytic conditions.^{30, 32} Importantly, the *in situ* EXAFS data confirm that the Cu sites in BIF-29(Cu) and BIF-29(Cu)-200C are different, despite the similar valence state observed in XPS.



Figure 6. SEM images of pristine BIF-29(Cu) electrode (a) before (b) after constant potential electrolysis (-1.2 V vs. RHE, 1 h) and BIF-29(Cu)-200C (c) before and (d) after constant potential electrolysis (-1.2 V vs. RHE, 1 h), (e) *in situ* Cu *K*-edge XANES results in for (e) BIF-29(Cu) and (f) BIF-29(Cu)-200C for chronoamperometry carried out in CO₂-saturated 0.05 M K_2CO_3 .

We also investigated the stability of pristine and calcined BIF-29(Cu) using chronoamperometry. In the case of BIF-29(Cu), the specific current density is stable over the 8-h experiment (**Figure 7a** and **S23a**), suggesting the catalyst largely remains intact. For calcined BIF-29(Cu)-200C, a decline in CH₄ current density is observed (**Figure 7b and FigureS23b**). To test if the origin of this decline is due to dissolution and re-deposition of Cu,⁵² we electrodeposited Cu particles onto a carbon paper electrode from a solution of Cu(NO₃)₂ in CO₂-saturated 0.05 M K₂CO₃ at -1.2 V vs. RHE. After 10 minutes of deposition, the solution was purged with CO₂, and controlled potential electrolysis was initiated. The electrodeposited Cu exhibits a strikingly different HER and CO₂RR product distribution compared to the BIF and BIF-derived catalysts (**Figure S24**). We hypothesize the decline in activity for BIF-29(Cu)-200C may be due to catalyst detachment from the carbon paper electrode over extended electrolysis. Nonetheless, our results suggest the unique coordination environment of BIF-29(Cu) is critical for enhanced electrocatalytic CO₂RR.



Figure 7. HER and CO₂RR partial current density long term electrolysis conducted at -1.2 V vs. RHE with (a) BIF-29(Cu), and (b) BIF-29(Cu)-200C. Solution was re-saturated with CO₂ every 2 h.

Conclusion

Herein, we utilized a bottom-up synthetic strategy to assemble CuN₄ molecular cages followed by a controlled thermal treatment to generate atomically dispersed nitrogen coordinated Cu sites for CO₂RR. A key difference in this work compared to other framework-derived ADMS

is the use of low temperature activation that allows the preservation of existing CuN_x sites in BIF-29(Cu). The careful temperature selection avoided the formation of metallic Cu, which was observed in a previous report.³⁸ We discovered that the electrocatalytic CO₂RR activity and selectivity in the calcined system surpassed that of the pristine material as well as other relevant Cu ADMS catalysts (Table S9). Our combined electrochemical and spectroscopic results strongly suggest the formation of single-site metal sites and an improved redox conductivity in the calcined BIF-29(Cu) dramatically enhances the electrocatalytic reduction of CO₂. Raman spectroscopy suggests that the calcination of BIF-29(Cu) leads to the formation of a partially carbonized material, while XAS indicates a formation of coordinatively unsaturated CuN₂ sites. The local environment changes are supported by solid-state ¹¹B NMR spectroscopy, which indicates proximal changes to the boron site upon thermal treatment. In situ XAS further illustrated the Cu centers remain isolated single atom sites throughout catalysis, a stark difference amongst other Cu-based ADMS materials. 30,32 We hypothesize the improved electrocatalytic CO₂RR performance in the calcined material is likely due to undercoordination at the Cu center and improved charge transfer processes imparted by the carbonaceous material. This work adds to the growing body of literature in ADMS materials and paves the path towards the systematic discovery of framework-derived single-site electrocatalytic systems.

Supporting information

Additional experimental details, synthetic procedure and electrochemical data

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