1 Intermediate Binding Control Using Metal–Organic Frameworks 2 Enhances Electrochemical CO₂ Reduction

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5 **ABSTRACT:** In the electrochemical CO₂ reduction reaction
6 (CO₂RR), control over the binding of intermediates is key to
7 tuning product selectivity and catalytic activity. Here we report the
8 use of reticular chemistry to control the binding of CO₂RR
9 intermediates to metal catalysts encapsulated inside metal–organic
10 frameworks (MOFs), thereby allowing us to improve CO₂RR
11 electrocatalysis. By varying systematically both the organic linker
12 and the metal node in a face-centered cubic (*fcu*) MOF, we tune
13 the adsorption of CO₂, pore openness, and Lewis acidity of the
14 MOFs. Using *operando* X-ray absorption spectroscopy (XAS) and
15 *in situ* Raman spectroscopy, we reveal that the MOFs are stable
16 under operating conditions and that this tuning plays the role of
17 optimizing the *CO binding mode on the surface of Ag nanoparticles incorporated inside the MOFs with the increase of local CO₂
18 concentration. As a result, we improve the CO selectivity from 74% for Ag/Zr-*fcu*-MOF-1,4-benzenedicarboxylic acid (BDC) to
19 94% for Ag/Zr-*fcu*-MOF-1,4-naphthalenedicarboxylic acid (NDC). The work offers a further avenue to utilize MOFs in the pursuit
20 of materials design for CO₂RR.

21 ■ INTRODUCTION

22 The utilization of carbon dioxide (CO₂) is gaining interest in
23 carbon capture and management.^{1–3} The electrochemical CO₂
24 reduction reaction (CO₂RR) offers a pathway to its efficient
25 utilization as feedstock for renewable electricity storage and
26 conversion.³ CO₂RR suffers from poor product selectivity and
27 mixed products such as carbon monoxide (CO),⁴ methane
28 (CH₄),⁵ methanol (CH₃OH),⁶ formate (HCOO[−]),⁷ ethanol
29 (C₂H₅OH),⁸ and ethylene (C₂H₄),^{9,10} widely reported in
30 literature.¹¹

31 Control over the binding of CO₂RR intermediates on the
32 surface of an electrocatalyst can increase the Faradaic efficiency
33 (FE), and decrease the overpotential, toward a desired
34 product. Alloying,^{12–14} doping,¹⁵ metal/metal oxide inter-
35 faces,^{16,17} grain boundaries,¹⁸ and facets¹⁹ have been used to
36 achieve this control. However, currently, the CO₂RR perform-
37 ances such as selectivity to a desired product are still low,
38 increasing cost for separation steps.

39 Metal–organic frameworks (MOFs), composed of organic
40 linkers and metal nodes, have porous structures with spatially
41 distributed metal atomic centers, and these interact efficiently
42 with gaseous species and can be applied to selective gas
43 adsorption/diffusion/storage.^{20–23} For CO₂RR electrocata-
44 lysts, the metal atomic centers in the MOFs have been applied
45 mostly as an active material.^{24–29} For example, Co-porphyrin-
46 based MOFs exhibited a high selectivity for CO production.³⁰

Also, the coordination number of Cu clusters formed from
HKUST-1 was engineered for highly selective C₂H₄
production.³¹ Despite these advances, the abundant reticular
chemistry of MOFs offered by their great chemical flexibility of
both organic linkers and metal nodes has not been explored yet
in the electrochemical CO₂RR.

Here, we apply isorecticular MOFs to control reaction
intermediate binding for efficient CO₂RR with high product
selectivity. By functionalizing organic linkers with amine
groups, directly changing the linkers, and altering the metal
nodes, we tuned the CO₂ adsorption, pore openness, and
Lewis acidity of a model Zr-face-centered cubic (*fcu*)-MOF
and evaluated resulting impact on the CO₂RR properties of Ag
nanoparticles encapsulated inside the MOF pores. We found
that MOFs, chemically stable confirmed by *operando* X-ray
absorption spectroscopy (XAS), promote product selectivity
and decrease overpotential of the CO₂RR on Ag. Using *in situ*
Raman spectroscopy, we found that the promoted stronger
interaction by NH₂ and enhanced physisorption by pore size-

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Figure 1. MOF design strategies to enhance the CO₂RR activity of Ag nanoparticles. (a) On the basis of the basic matrix of Zr-*fcu*-MOF-BDC, the MOFs are controlled by adding amine functional group (–NH₂) to organic linker, changing the organic linker to naphthalenedicarboxylic acid, and changing the element in metal node site from Zr to Y. The crystalline structures and functional groups in As-synthesized MOFs are investigated by XRD and FT-IR: (b, c) Zr-*fcu*-MOF-BDC, (d, e) Zr-*fcu*-MOF-NH₂BDC, (f, g) Zr-*fcu*-MOF-NDC, and (h, i) Y-*fcu*-MOF-NDC.

66 confinement of the MOFs can induce the promoted binding of
 67 *CO in atop or bridge modes. Levering the gas-phase species
 68 control in electrocatalysts with the aid of MOFs can help to
 69 steer the CO₂RR pathway toward desired products and add a
 70 degree of freedom in the design of next-generation of CO₂RR
 71 cathodes.

72 ■ RESULTS AND DISCUSSION

73 **MOF Design Strategy and Fabrication.** Zr-*fcu*-MOF-
 74 BDC (UiO-66), a starting material, is synthesized via reaction
 75 between zirconium chloride (ZrCl₄) and 1,4-benzene-
 76 dicarboxylic acid (1,4-BDC). In the unit cell of Zr-*fcu*-MOF-
 77 BDC, Zr ion-based hexanuclear clusters, which act as
 78 secondary building unit (SBU), are located at the face-
 79 centered cubic position of the MOF (Figure 1a). The
 80 connection between the SBU and organic linkers forms the
 81 pore sites at tetrahedral (blue) and octahedral (cyan) cages. To
 82 enhance CO₂ capture/interaction, the BDC organic linker of
 83 Zr-*fcu*-MOF-BDC was functionalized with an amine (NH₂–)

group, which can provide stronger interaction with CO₂ (Zr-
 84 *fcu*-MOF-NH₂BDC). We changed 1,4-BDC to 1,4-
 85 naphthalenedicarboxylic acid (1,4-NDC) to enhance CO₂
 86 capture via physisorption by decreasing the size of pore and
 87 pore-aperture size (Zr-*fcu*-MOF-NDC). The effect of Lewis
 88 acidity on CO₂RR activity was studied by changing the Zr-ion
 89 to a Y-ion in the hexanuclear cluster (Y-*fcu*-MOF-NDC).
 90

Although these four types of MOFs share the same motif
 91 structure (*fcu*-MOF), we simulated each MOF structure,
 92 which can quantify the pore-aperture size and cage diameter, to
 93 find the effect of organic linker transition from 1,4-BDC to 1,4-
 94 NDC on the pore size confinement. Since the benzene rings of
 95 1,4-BDC and 1,4-NDC can be rotated (Figure S1), the
 96 tetrahedral and octahedral cage diameters were calculated by
 97 averaging the cage diameters in both 0° and 90° rotated
 98 benzene ring positions (Figures S2–S5, Tables S1 and S2). Zr-
 99 *fcu*-MOF-BDC exhibited the highest porosity. Through amine
 100 group functionalization (Zr-*fcu*-MOF-NH₂BDC), the porosity
 101 decreased compared to Zr-*fcu*-MOF-BDC. When 1,4-BDC was
 102

Figure 2. Metal nanoparticle incorporation at the pore site of MOFs. (a) Schematic for Ag nanoparticle incorporated MOF structure. The structure of encapsulated Ag nanoparticles in the pore of Zr-*fcu*-MOF-BDC is confirmed by (b) FE-SEM, (c) TEM BF, (d) STEM HAADF, and (e) STEM EDS images. Ag nanoparticles are incorporated by soaking the Zr-*fcu*-MOF-BDC with Ag⁺ ions and reducing with using NaBH₄. The material status at each process is analyzed by (f) EPR, (g) FT-IR, and (h) XRD.

substituted by 1,4-NDC (Zr-*fcu*-MOF-NDC), the maximum pore-aperture size and average tetrahedral, octahedral cage diameters were calculated as 5.0, 4.5, and 8.6 Å, respectively, which were lowest among the four MOF species. The porosity of Y-*fcu*-MOF-NDC was similar to that of Zr-*fcu*-MOF-NDC. The crystallinity and chemical status of organic linkers in the synthesized MOFs were verified by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) (Figure 1b–i). The XRD patterns of the MOFs coincided with previous reports and simulation results, thus confirming the successful synthesis of each MOF in this work.^{32–34} In the FT-IR of Zr-*fcu*-MOF-BDC, we observed the major peaks around 1660, 1656, 1583, 1506, 1395, 745, and 664 cm^{−1}, which indicate the C=O stretching vibration, carboxyl group coordinated with Zr⁴⁺, O–C–O asymmetric stretching vibration, C=C vibration of benzene ring, O–C–O symmetric stretching vibration, O–H vibration, and C–H vibration in 1,4-BDC ligands, respectively (Figure 1c).³⁵ Similarities between Zr-*fcu*-MOF-BDC and Zr-*fcu*-MOF-NH₂BDC were verified by the XRD patterns and FT-IR peaks for 1,4-BDC ligands. However, the C=N peak at 1257 cm^{−1} and –NH₂ peak at 1618 cm^{−1} in the FT-IR of Zr-*fcu*-MOF-NH₂BDC differentiated it from Zr-*fcu*-MOF-BDC (Figure 1e).^{36,37} The existence of 1,4-NDC in Zr-*fcu*-MOF-NDC and Y-*fcu*-MOF-

NDC was confirmed by the relevant FT-IR peaks (Figure 1g,i).³⁸

Active Material Incorporation into MOF. Using the electrochemical CO₂ conversion to CO as a model to understand the role of MOF supporter during CO₂RR, we fabricated Ag-incorporated MOFs (Figure 2a). We selected Ag for the model study since it is known to produce CO with high selectivity, and since it has weak binding with *CO, enabling study of the effect of MOF on intermediate binding control.³⁹ Ag is readily reduced selectively in MOFs that incorporate Ag compared to Zn. Ag nanoparticles were grown inside the pore sites of MOFs by a solution impregnation (soaking the MOFs with Ag⁺ containing solution, and then reducing the Ag⁺ with NaBH₄).⁴⁰ We incorporated Ag nanoparticles in all MOFs using the same methodology.

The size and distribution of incorporated Ag nanoparticles were analyzed with field-emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The spatial distribution of uniformly sized Ag nanoparticles (~5 nm) reveals the successful Ag incorporation because the nucleation and growth of Ag nuclei are confined by the dimensions of the MOF pore (Figure 2b–e). Ag nanoparticles formed not only in the interior pores but also on the exterior surfaces of the MOFs. Ag nanoparticles on the

Figure 3. Operando XAS analysis to investigate the MOF status during the electrochemical CO₂RR. At the constant applied potential of -2.0 V versus Ag/AgCl in 0.5 M KHCO₃, the Zr K-edge (a) XANES and (b) EXAFS of Ag/Zr-*fcu*-MOF-BDC, and the Y K-edge (a) XANES and (b) EXAFS of Ag/Y-*fcu*-MOF-NDC were analyzed according to the catalytic reaction time. Oxidation states and coordinative structure information, investigated by XANES and EXAFS, reveal the stable MOF status during the CO₂RR.

Figure 4. In situ Raman spectroscopy to investigate the status of MOF functional group evolution and *CO binding mode during CO₂RR. Raman spectra from 400 to 2200 cm⁻¹ reveals the stability of MOF functional groups in (a) Ag/Zr-*fcu*-MOF-BDC, (b) Ag/Zr-*fcu*-MOF-NH₂BDC, and (c) Ag/Zr-*fcu*-MOF-NDC according to the reaction potentials. Magnified Raman spectra from 1800 to 2200 cm⁻¹ show the CO intermediate binding mode at the catalysts of (d) Ag/Zr-*fcu*-MOF-BDC, (e) Ag/Zr-*fcu*-MOF-NH₂BDC, and (f) Ag/Zr-*fcu*-MOF-NDC.

151 exterior surface may contribute to enhance electrical
152 conduction of the MOFs on the gas diffusion electrode

(GDE).⁴¹ The structures of the Ag nanoparticles were similar 153
in both Zr- and Y-based MOFs (Figures S6–S8). The MOF 154

Figure 5. CO₂RR catalytic activity of Ag-incorporated MOFs. Electrochemical CO₂RR products of (a) Ag/Zr-*fcu*-MOF-BDC, (b) Ag/Zr-*fcu*-MOF-NH₂BDC, (c) Ag/Zr-*fcu*-MOF-NDC, and (d) Ag/Y-*fcu*-MOF-NDC were investigated according to the potential in the flow cell electrolyzer with the electrolyte of 0.5 M KHCO₃.

control will mainly affect the CO₂RR behavior of the interior Ag nanoparticles that exhibit higher surface to volume ratio and number of nanoparticles compared to exterior one. The outer morphology of the MOFs that incorporate Ag was affected by the type of organic linkers (Figure S9).⁴² Furthermore, X-ray photoelectron spectroscopy (XPS) exhibited identical oxidation states of Ag and other elements in all MOFs studied herein (Figure S10).

The reduction of Ag⁺ and the material stability of MOF during the fabrication were investigated using electron paramagnetic resonance (EPR), FT-IR, and XRD. Unlike the bare MOF, Ag⁺-soaked Zr-*fcu*-MOF-BDC exhibited a clear EPR signal. We confirmed the reduction of Ag⁺ to metallic Ag during solution impregnation by the increased EPR peak intensity (Figure 2f).⁴³ The major FT-IR peaks of Zr-*fcu*-MOF-BDC (C=O, O-C-O, C=C, O-H, and C-H) were maintained during the sequential Ag⁺ incorporation and reduction process (Figure 2g). Additionally, the formation of Ag nanoparticles and the MOF stability during the fabrication have been confirmed through XRD, which indicates the existence of (111) main peak for Ag (Figure 2h).

MOF Stability during CO₂RR. We investigated the stability of Ag-incorporated MOFs during CO₂RR by *operando* XAS at an applied potential of −2.0 versus Ag/AgCl (Figure 3) in 0.5 M KHCO₃. We tracked the oxidation states and atomic structures (coordination number and atomic distance) of the elements in the metal node of MOFs with X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). There was no observed difference between the “before reaction” and “during reaction” states in both XANES and EXAFS of the Zr K-edge in Ag/Zr-*fcu*-MOF-BDC (Figure 3a,b). This was confirmed clearly when we

compared XANES spectra with standard metal and metal oxide (Figure S11a,c). Combined with the identical peak position of derivative normalized $\chi\mu(E)$, these results indicated a constant Zr oxidation state, coordination number, and atomic distance around the Zr atoms in Zr-based MOFs during the reaction (Figure S12). This trend was similar in the Y K-edge XANES and EXAFS of Ag/Y-*fcu*-MOF-NDC (Figure 3c,d). If MOFs were changed by the reduction of metal node in SBU of MOFs during CO₂RR, there should be an increase of *operando* EXAFS peak intensity for metal–metal bonding and a suppression of *operando* EXAFS peak intensity for metal–oxygen bonding.³¹ However, in this work, there was no remarkable increase of *operando* EXAFS peak intensity for metal–metal bonding and suppression of *operando* EXAFS peak intensity for metal–oxygen bonding in Ag/Zr-*fcu*-MOF-BDC and Ag/Y-*fcu*-MOF-NDC (Figure S11b,d). These observations suggest that the Zr- and Y-based MOFs in this work are stable during CO₂RR.

Intermediates Binding Control by MOF. To identify the function of the MOF supporter on the cathode, we used *in situ* Raman spectroscopy to track, in real time, the binding of intermediates on the catalyst surface (Figure 4). Raman spectra were collected before and during the reaction according to a series of applied potentials. As the reference, the Raman spectra of Zr-*fcu*-MOF-BDC, Zr-*fcu*-MOF-NH₂BDC, Zr-*fcu*-MOF-NDC, and Y-*fcu*-MOF-NDC were measured without Ag species (Figure S13). Matching it with the Raman spectra in Figure 4a–c, the Raman peaks from MOFs can be distinguished with those from Ag species. In all cases, there was no difference in the Raman peak according to the applied potential in 0.5 M KHCO₃, and this also supports the superior MOF stability during CO₂RR.

The clear difference between MOF species was observed at the Raman shift from 1800 to 2200 cm^{-1} , which corresponds to the $\ast\text{CO}$ binding mode. In the bare Ag/Zr-*fcu*-MOF-BDC, there was no peak in this range (Figure 4d). This phenomenon can be interpreted as $\ast\text{CO}$ desorption during CO_2RR .⁴⁴ Indeed, in general, the binding energy between Ag and CO is low, and this has been observed in *in situ* Raman of Ag/Zr-*fcu*-MOF-BDC.^{39,45} However, in the NH_2 -functionalized Ag/Zr-*fcu*-MOF- NH_2BDC , the broad peaks were observed in the region around 2100 cm^{-1} , which indicates the $\text{C}\equiv\text{O}$ stretching mode of CO_{atop} molecules (Figure 4e).^{46,47} In the *in situ* Raman of pore size-confined Ag/Zr-*fcu*-MOF-NDC, narrow peaks were observed at 1950 cm^{-1} , which indicates the $\text{C}\equiv\text{O}$ stretching mode of $\text{CO}_{\text{bridge}}$ molecules (Figure 4f).^{46,47} The existence of $\ast\text{CO}$ Raman peaks in both Ag/Zr-*fcu*-MOF- NH_2BDC and Ag/Zr-*fcu*-MOF-NDC can be interpreted as the increased local CO_2 concentration near active materials by the NH_2 -functionalization and pore size confinement of the MOF. In the case of Ag/Y-*fcu*-MOF-NDC with decreased Lewis acidity compared to Zr-based MOFs, the Raman peaks for CO intermediates were not observed (Figure S14). This shows that the binding mode control of the intermediates is effective when the Lewis acidity environment is well-prepared for CO_2RR .

As the local CO_2 concentration is increased via the action of the MOFs, the local pH in KHCO_3 can be decreased.⁴⁸ There is also a possibility that the $\ast\text{CO}$ binding mode can be controlled by the local pH change; the increase of local pH can increase the $\text{CO}_{\text{bridge}}$ population on Ni, Co, Pt, and Cu electrodes.⁴⁷ Reticular chemistry-based $\ast\text{CO}$ binding mode control can potentially be extended further by varying electrolytes and active materials with systematic MOF design.

CO_2RR of Active Material-Incorporated MOFs. The electrochemical CO_2RR performance of Ag nanoparticle-incorporated MOFs was investigated using a GDE where CO_2 is supplied directly to the catalyst. The gaseous products were analyzed under chronoamperometric operation and in a neutral electrolyte of 0.5 M KHCO_3 (Figure S15). We confirm that Ag is the active material for CO_2RR of Ag-incorporated MOFs because H_2 was major products upon using bare MOFs without Ag (Figure S16).

In the bare MOF (Ag/Zr-*fcu*-MOF-BDC), main CO_2RR products were identified as CO and hydrogen (H_2), as is typical of Ag active materials (Figure 5a). The CO FE was mostly lower than 74% and H_2 FE increased from 13% to 29% as the potential increased toward the range enabling high current densities around 40 mA/cm^2 . In the NH_2 -functionalized MOFs (Ag/Zr-*fcu*-MOF- NH_2BDC) and pore size-confined MOFs (Ag/Zr-*fcu*-MOF-NDC), the overall CO_2RR activities were enhanced compared to the bare MOF. The overpotentials decreased, and the CO_2RR were more dominant than the hydrogen evolution reaction (HER). In the Ag/Zr-*fcu*-MOF- NH_2BDC , the CO FE increased to over 80%, and H_2 FE decreased to lower than 8% (Figure 5b). Especially, the H_2 FE was extremely low in the potential range lower than -1.0 V versus RHE. The amine group in Ag/Zr-*fcu*-MOF- NH_2BDC can induce the formation of carbamate intermediate, promoting CO_2RR activity.⁴⁹ The enhanced CO FE can be explained by the increase of local CO_2 concentration and the formation of carbamate.^{42,49} In the Ag/Zr-*fcu*-MOF-NDC, the enhanced CO_2RR performance in terms of CO and H_2 FE was similar to that of Ag/Zr-*fcu*-MOF- NH_2BDC , which was lower than 8% (Figure 5c). In the potential range for CO_2RR of Ag/Zr-*fcu*-MOF-NDC more negative than -1.0 V versus RHE, the

CO FE increased to 94% and H_2 FE decreased to 1%. This indicates higher CO selectivity than that of Ag/Zr-*fcu*-MOF- NH_2BDC . Recently, it was reported that $\text{CO}_{\text{bridge}}$ are inert and do not participate in the reaction, unlike CO_{atop} .⁴⁷ The inertness of $\text{CO}_{\text{bridge}}$ in Ag/Zr-*fcu*-MOF-NDC may enhanced the CO selectivity in the CO_2RR of Ag active materials compared to CO_{atop} in Ag/Zr-*fcu*-MOF- NH_2BDC . The difference in CO binding modes, specifically between CO_{atop} and $\text{CO}_{\text{bridge}}$, controlled by modifying the MOF functional group and porosity, might affect the CO selectivity of Ag nanoparticles located at the pore site of the Zr-based MOFs. When the metal node was changed from Zr to Y, the CO_2RR performance of Ag/Y-*fcu*-MOF-NDC was lower even in the similar pore structure with Ag/Zr-*fcu*-MOF-NDC (Figure 5d). This is due to the decrease in Lewis acidity and the change in the framework overall charge from neutral (Zr-*fcu*-MOF-NDC) to cationic (Y-*fcu*-MOF-NDC).

The TEM images of MOFs that incorporate Ag indicate the coexistence of Ag nanoparticles in the interior pores and on the exterior surface of the MOFs. We observed more interior Ag than exterior Ag. The surface to volume ratio of interior Ag is higher in view of its size and number. Therefore, we expect that the effect of MOFs will be dominated by the effect of interior Ag.

We investigated the structures of Ag nanoparticles in Ag-incorporated MOFs by TEM after 1 h CO_2RR at -2.4 V versus Ag/AgCl. Ag/Zr-*fcu*-MOF- NH_2BDC and Ag/Zr-*fcu*-MOF-NDC exhibited good stability by suppressing HER (Figure S17). We found that interior Ag nanoparticles maintain their structure, a finding we associate with the confinement effect of the MOF pores. In the case of exterior Ag nanoparticles, we found that reconstruction of Ag nanoparticles occurs during CO_2RR (Figure S18).

CONCLUSION

We present a new approach to utilize MOF materials to control the binding mode of CO_2RR intermediates, thus modulating the product selectivity and activity of the reaction. Starting from a material design with reticular chemistry, we studied the effect of capturing CO_2 near the active site and modifying Lewis acidity on CO_2RR performance by utilizing isorecticular MOFs as a support. This was enabled by adding amine functional group (Zr-*fcu*-MOF- NH_2BDC), and changing the organic linker (Zr-*fcu*-MOF-NDC) and metal node (Y-*fcu*-MOF-NDC) from the bare Zr-*fcu*-MOF-BDC. The increase of local CO_2 concentration near the Ag nanoparticles by MOF supporters enhanced CO_2RR while it suppressed HER. Furthermore, we found that atop and bridge binding modes of CO intermediates can be modulated by the NH_2 -functionalized and pore size-confined MOF species; CO_{atop} / $\text{CO}_{\text{bridge}}$ control is crucial for determining the product selectivity. Away from the conventional approach to controlling the binding energy between active materials and CO_2RR intermediates, this work paves the way for improving CO_2RR activity and product selectivity by directly interacting with the gaseous intermediates and controlling their binding mode.

EXPERIMENTAL SECTION

Synthesis of Isorecticular MOFs. *Synthesis of Zr-*fcu*-MOF-BDC.* Zr-*fcu*-MOF-BDC was synthesized by dissolving ZrCl_4 (0.053 g, 0.227 mmol) and 1,4-benzene-dicarboxylic acid (H_2BDC) (0.034 g, 0.227 mmol) in 6 mL DMF at room temperature in a 15 mL glass vial. Then 1 mL of acetic acid was added to the resulting mixture, and

343 it was placed in a preheated oven at 120 °C for 24 h. After the
344 reaction mixture was cooled in air to room temperature, the resulting
345 solid was filtered, repeatedly washed with DMF, and dried at room
346 temperature.

347 **Synthesis of Zr-fcu-MOF-NH₂BDC.** Synthesis of Zr-fcu-MOF-
348 NH₂BDC was performed by dissolving ZrCl₄ (1.50 g, 6.4 mmol),
349 2-amino-1,4-benzenedicarboxylic acid (H₂N-BDC) (1.5 g, 6.4
350 mmol), and 5 mL of acetic acid in DMF (150 mL) at room
351 temperature in a 500 mL volumetric flask. The resulting mixture was
352 placed in a preheated oven at 120 °C for 24 h. After the solution was
353 cooled to room temperature in air, the resulting solid was filtered and
354 repeatedly washed with absolute hot ethanol (~60 °C) for 3 days.
355 The resulting yellow powder was filtered and dried under vacuum at
356 ambient temperature.

357 **Synthesis of Zr-fcu-MOF-NDC.** Synthesis of Zr-fcu-MOF-NDC
358 was performed by dissolving ZrCl₄ (0.053 g, 0.227 mmol) and
359 naphthalene 1,4-dicarboxylic acid (50 mg, 0.231 mmol) mixed in 10
360 mL of DMF. Then 2 mL of acetic acid was added to the mixture and
361 heated for 24 h at 120 °C in a preheated oven. After that, the white
362 ppt was centrifuged and washed thrice with DMF and after 1 day
363 three times with acetone. Then it was dried and used for the next
364 purpose.

365 **Synthesis of Y-fcu-MOF-NDC.** The 1,4-H₂NDC (9.41 mg, 0.0435
366 mmol), Y(NO₃)₃·5H₂O (19.15 mg, 0.0515 mmol), 2-fluorobenzoic
367 acid (48.7 mg, 0.348 mmol), DMF (2.2 mL), H₂O (0.5 mL), and
368 HNO₃ (0.3 mL, 3.5 M in DMF) were combined in a 20 mL
369 scintillation vial, sealed, and heated to 115 °C for 60 h and cooled to
370 room temperature. The polyhedral crystals were collected and air-
371 dried. The as-synthesized sample of Y-fcu-MOF-NDC was washed
372 with 10 mL of anhydrous DMF and immersed in 10 mL of ethanol for
373 7 days, during which time the ethanol was replaced three times per
374 day.

375 **Metal Incorporation at the MOF Pore Site.** Silver nitrate
376 (AgNO₃, 100 mg) was dissolved in the 2 mL acetonitrile solution.
377 Then 100 mg of powders of each MOF (Zr-fcu-MOF-BDC, Zr-fcu-
378 MOF-NH₂BDC, Zr-fcu-MOF-NDC, Y-fcu-MOF-NDC) was im-
379 mersed in the AgNO₃ containing acetonitrile solution and stirred at
380 the room temperature for 12 h. After centrifuging, Ag⁺-soaked MOF
381 was dried in the vacuum oven overnight. Ag⁺-soaked MOF was
382 dispersed and stirred in 0.6 mmol/mL NaBH₄ containing ethanol
383 solution for the reduction of Ag⁺. After centrifuging, Ag incorporated
384 MOF was dried in the vacuum overnight.

385 **Material Characterization.** Powder X-ray diffraction (PXRD)
386 measurements were carried out at room temperature on a PANalytical
387 X'Pert PRO diffractometer 45 kV, 40 mA for Cu Kα (λ = 1.5418 Å),
388 with a scan speed of 1.0° min⁻¹ and a step size of 0.02° in 2θ. Also,
389 Rigaku MiniFlex 600 diffractometer with Copper Kα radiation (λ =
390 1.5406 Å) was applied for PXRD. FT-IR was carried out by Thermo
391 Scientific iS50 with the spectral range of 4600–50 cm⁻¹. XPS for
392 investigating the Ag, Zr, Y, and O oxidation status was carried out by
393 Thermo Scientific Al Kα source XPS system with a spot size of 400
394 μm. SEM and TEM analyses for structure characterization were
395 carried out by a Hitachi FE-SEM S-5200 and Hitachi CFE-TEM
396 HF3300. The local atomic structure was measured by EPR. It was
397 carried out by a Bruker ECS-EMX X-band EPR spectrometer at the
398 room temperature of 300 K. DPPH (2,2-diphenyl-1-picrylhydrazyl)
399 was used for standardization of the peak position and intensity of EPR
400 signal.

401 **Electrochemical CO₂ Reduction.** CO₂RR performance of Ag
402 incorporated MOF was evaluated in a flow cell. It was composed of
403 Ag-incorporated MOF on gas diffusion layer (GDL) as a cathode, Ni
404 foam as an anode, and Ag/AgCl (3 M KCl) as a reference electrode.
405 The cathode was made by spray coating the Ag-incorporated MOF
406 containing ink (nafion + methanol). In the flow cell, 0.5 M KHCO₃
407 electrolyte was flowed in cathode and anode independently separated
408 by anion exchange membrane. CO₂ gas flowed with a rate of 50 sccm.
409 Chronoamperometry at the constant potential was performed by
410 electrochemical station (Autolab). The electrode potentials were
411 converted to RHE based on the following equation: E_{RHE} = E_{Ag/AgCl} +
412 0.210 V + 0.059 × pH + iR (with iR-correction) The collected

gaseous products during CO₂RR were analyzed in 1 mL volumes by a
gas chromatograph (PerkinElmer Clarus 600) with a thermal
conductivity detector (TCD) and a flame ionization detector (FID).

In Situ/Operando Spectroscopy. XAS measurements at the Cu
K-edge were performed at 9-BM beamline of the Advanced Photon
Source (APS, Argonne National laboratory, IL). *Operando* XAS
measurements were performed by using a custom flow cell in 0.5 M
KHCO₃ electrolyte with CO₂ gas flowing from the backside of a gas
diffusion layer. *Operando* XANES and EXAFS scan data were
collected during the cell operation mode of chronoamperometry at
the potential of -2.0 V versus Ag/AgCl, same with the CO₂RR
activity measurement condition. *In situ* Raman was carried out by a
Renishaw inVia Raman Microscope (objective lense: 63×, 785 nm
laser) with the liquid-electrolyte gas flow cell.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
<https://pubs.acs.org/doi/10.1021/jacs.0c10774>.

Detailed information on simulation of pore structures of
MOFs, structure investigation, XPS analysis, XAS
analysis, Raman spectra, chronoamperometry, stability,
liquid product analysis for CO₂RR performance
measurement (PDF)

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511 ■ REFERENCES

- 512 (1) De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S. A.; Jaramillo, T. F.;
513 Sargent, E. H. What Would It Take for Renewably Powered
514 Electrosynthesis to Displace Petrochemical Processes? *Science* **2019**,
515 *364* (6438), No. eaav3506.
516 (2) Birdja, Y. Y.; Pérez-Gallent, E.; Figueiredo, M. C.; Göttle, A. J.;
517 Calle-Vallejo, F.; Koper, M. T. M. Advances and Challenges in
518 Understanding the Electrocatalytic Conversion of Carbon Dioxide to
519 Fuels. *Nat. Energy* **2019**, *4* (9), 732–745.
520 (3) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.;
521 Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Nørskov,
522 J. K.; Jaramillo, T. F.; Chorkendorff, I. Progress and Perspectives of
523 Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte.
524 *Chem. Rev.* **2019**, *119* (12), 7610–7672.
525 (4) Liu, M.; Pang, Y.; Zhang, B.; De Luna, P.; Voznyy, O.; Xu, J.;
526 Zheng, X.; Dinh, C.-T.; Fan, F.; Cao, C.; García de Arquer, F. P.;
527 Safaei, T. S.; Mepham, A.; Klinkova, A.; Kumacheva, E.; Filletier, T.;
528 Sinton, D.; Kelley, S. O.; Sargent, E. H. Enhanced Electrocatalytic
529 CO₂ Reduction via Field-Induced Reagent Concentration. *Nature*
530 **2016**, *537*, 382–386.
531 (5) Li, Y.; Cui, F.; Ross, M. B.; Kim, D.; Sun, Y.; Yang, P. Structure-
532 Sensitive CO₂ Electroreduction to Hydrocarbons on Ultrathin 5-Fold
533 Twinned Copper Nanowires. *Nano Lett.* **2017**, *17* (2), 1312–1317.

- (6) Yang, H.; Wu, Y.; Li, G.; Lin, Q.; Hu, Q.; Zhang, Q.; Liu, J.; He, S.
C. Scalable Production of Efficient Single-Atom Copper Decorated
Carbon Membranes for CO₂ Electroreduction to Methanol. *J. Am. Chem. Soc.* **2019**, *141* (32), 12717–12723.
(7) Klinkova, A.; De Luna, P.; Dinh, C.-T.; Voznyy, O.; Larin, E. M.;
Kumacheva, E.; Sargent, E. H. Rational Design of Efficient Palladium
Catalysts for Electroreduction of Carbon Dioxide to Formate. *ACS Catal.* **2016**, *6* (12), 8115–8120.
(8) Li, Y. C.; Wang, Z.; Yuan, T.; Nam, D.-H.; Luo, M.; Wicks, J.;
Chen, B.; Li, J.; Li, F.; de Arquer, F. P. G.; Wang, Y.; Dinh, C.-T.;
Voznyy, O.; Sinton, D.; Sargent, E. H. Binding Site Diversity
Promotes CO₂ Electroreduction to Ethanol. *J. Am. Chem. Soc.* **2019**,
141 (21), 8584–8591.
(9) Dinh, C.-T.; Burdyny, T.; Kibria, M. G.; Seifitokaldani, A.;
Gabardo, C. M.; García de Arquer, F. P.; Kiani, A.; Edwards, J. P.; De
Luna, P.; Bushuyev, O. S.; Zou, C.; Quintero-Bermudez, R.; Pang, Y.;
Sinton, D.; Sargent, E. H. CO₂ Electroreduction to Ethylene via
Hydroxide-Mediated Copper Catalysis at an Abrupt Interface. *Science*
2018, *360* (6390), 783–787.
(10) Li, F.; Thevenon, A.; Rosas-Hernández, A.; Wang, Z.; Li, Y.;
Gabardo, C. M.; Ozden, A.; Dinh, C. T.; Li, J.; Wang, Y.; Edwards, J.
P.; Xu, Y.; McCallum, C.; Tao, L.; Liang, Z.-Q.; Luo, M.; Wang, X.;
Li, H.; O'Brien, C. P.; Tan, C.-S.; Nam, D.-H.; Quintero-Bermudez,
R.; Zhuang, T.-T.; Li, Y. C.; Han, Z.; Britt, R. D.; Sinton, D.; Agapie,
T.; Peters, J. C.; Sargent, E. H. Molecular Tuning of CO₂-to-Ethylene
Conversion. *Nature* **2020**, *577*, 509–513.
(11) Hori, Y. Electrochemical CO₂ Reduction on Metal Electrodes
BT - Modern Aspects of Electrochemistry; Vayenas, C. G., White, R.
E., Gamboa-Aldeco, M. E., Eds.; Springer New York: New York,
2008; pp 89–189.
(12) Wang, X.; Wang, Z.; Zhuang, T.-T.; Dinh, C.-T.; Li, J.; Nam,
D.-H.; Li, F.; Huang, C.-W.; Tan, C.-S.; Chen, Z.; Chi, M.; Gabardo,
C. M.; Seifitokaldani, A.; Todorović, P.; Proppe, A.; Pang, Y.;
Kirmani, A. R.; Wang, Y.; Ip, A. H.; Richter, L. J.; Scheffel, B.; Xu, A.;
Lo, S.-C.; Kelley, S. O.; Sinton, D.; Sargent, E. H. Efficient Upgrading
of CO to C₃ Fuel Using Asymmetric C-C Coupling Active Sites. *Nat. Commun.* **2019**, *10* (1), 5186.
(13) Ma, S.; Sadakiyo, M.; Heima, M.; Luo, R.; Haasch, R. T.; Gold,
J. I.; Yamauchi, M.; Kenis, P. J. A. Electroreduction of Carbon Dioxide
to Hydrocarbons Using Bimetallic Cu-Pd Catalysts with Different
Mixing Patterns. *J. Am. Chem. Soc.* **2017**, *139* (1), 47–50.
(14) Kim, D.; Resasco, J.; Yu, Y.; Asiri, A. M.; Yang, P. Synergistic
Geometric and Electronic Effects for Electrochemical Reduction of
Carbon Dioxide Using Gold-Copper Bimetallic Nanoparticles. *Nat. Commun.* **2014**, *5* (1), 4948.
(15) Zhou, Y.; Che, F.; Liu, M.; Zou, C.; Liang, Z.; De Luna, P.;
Yuan, H.; Li, J.; Wang, Z.; Xie, H.; Li, H.; Chen, P.; Bladt, E.;
Quintero-Bermudez, R.; Sham, T.-K.; Bals, S.; Hofkens, J.; Sinton, D.;
Chen, G.; Sargent, E. H. Dopant-Induced Electron Localization
Drives CO₂ Reduction to C₂ Hydrocarbons. *Nat. Chem.* **2018**, *10* (9),
974–980.
(16) Li, C. W.; Ciston, J.; Kanan, M. W. Electroreduction of Carbon
Monoxide to Liquid Fuel on Oxide-Derived Nanocrystalline Copper.
Nature **2014**, *508* (7497), 504–507.
(17) Xiao, H.; Goddard, W. A.; Cheng, T.; Liu, Y. Cu Metal
Embedded in Oxidized Matrix Catalyst to Promote CO₂ Activation
and CO Dimerization for Electrochemical Reduction of CO₂. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (26), 6685–6688.
(18) Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W.
Selective Increase in CO₂ Electroreduction Activity at Grain-
Boundary Surface Terminations. *Science* **2017**, *358* (6367), 1187–
1192.
(19) Wang, Y.; Wang, Z.; Dinh, C.-T.; Li, J.; Ozden, A.; Golam
Kibria, M.; Seifitokaldani, A.; Tan, C.-S.; Gabardo, C. M.; Luo, M.;
Zhou, H.; Li, F.; Lum, Y.; McCallum, C.; Xu, Y.; Liu, M.; Proppe, A.;
Johnston, A.; Todorovic, P.; Zhuang, T.-T.; Sinton, D.; Kelley, S. O.;
Sargent, E. H. Catalyst Synthesis under CO₂ Electroreduction Favours
Faceting and Promotes Renewable Fuels Electrosynthesis. *Nat. Catal.* **2020**, *3*, 98–106.

- (20) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* **2002**, 295 (5554), 469–472.
- (21) Jiang, J.; Furukawa, H.; Zhang, Y.-B.; Yaghi, O. M. High Methane Storage Working Capacity in Metal-Organic Frameworks with Acrylate Links. *J. Am. Chem. Soc.* **2016**, 138 (32), 10244–10251.
- (22) Millward, A. R.; Yaghi, O. M. Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *J. Am. Chem. Soc.* **2005**, 127 (51), 17998–17999.
- (23) Guntern, Y. T.; Pankhurst, J. R.; Vávra, J.; Mensi, M.; Mantella, V.; Schouwink, P.; Buonsanti, R. Nanocrystal/Metal-Organic Framework Hybrids as Electrocatalytic Platforms for CO₂ Conversion. *Angew. Chem., Int. Ed.* **2019**, 58 (36), 12632–12639.
- (24) Diercks, C. S.; Liu, Y.; Cordova, K. E.; Yaghi, O. M. The Role of Reticular Chemistry in the Design of CO₂ Reduction Catalysts. *Nat. Mater.* **2018**, 17 (4), 301–307.
- (25) Jiao, L.; Wang, Y.; Jiang, H.-L.; Xu, Q. Metal-Organic Frameworks as Platforms for Catalytic Applications. *Adv. Mater.* **2018**, 30 (37), 1703663.
- (26) Nam, D.-H.; De Luna, P.; Rosas-Hernández, A.; Thevenon, A.; Li, F.; Agapie, T.; Peters, J. C.; Shekhah, O.; Eddaoudi, M.; Sargent, E. H. Molecular Enhancement of Heterogeneous CO₂ Reduction. *Nat. Mater.* **2020**, 19 (3), 266–276.
- (27) Hou, S.-L.; Dong, J.; Zhao, B. Formation of C-X Bonds in CO₂ Chemical Fixation Catalyzed by Metal-Organic Frameworks. *Adv. Mater.* **2020**, 32 (3), 1806163.
- (28) Albo, J.; Vallejo, D.; Beobide, G.; Castillo, O.; Castaño, P.; Irabien, A. Copper-Based Metal-Organic Porous Materials for CO₂ Electrocatalytic Reduction to Alcohols. *ChemSusChem* **2017**, 10 (6), 1100–1109.
- (29) Albo, J.; Perfecto-Irigaray, M.; Beobide, G.; Irabien, A. Cu/Bi Metal-Organic Framework-Based Systems for an Enhanced Electrochemical Transformation of CO₂ to Alcohols. *J. CO₂ Util.* **2019**, 33, 157–165.
- (30) Kornienko, N.; Zhao, Y.; Kley, C. S.; Zhu, C.; Kim, D.; Lin, S.; Chang, C. J.; Yaghi, O. M.; Yang, P. Metal-Organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **2015**, 137 (44), 14129–14135.
- (31) Nam, D.-H.; Bushuyev, O. S.; Li, J.; De Luna, P.; Seifitokaldani, A.; Dinh, C.-T.; Garcia de Arquer, F. P.; Wang, Y.; Liang, Z.; Proppe, A. H.; Tan, C. S.; Todorovic, P.; Shekhah, O.; Gabardo, C. M.; Jo, J. W.; Choi, J.; Choi, M.-J.; Baek, S.-W.; Kim, J.; Sinton, D.; Kelley, S. O.; Eddaoudi, M.; Sargent, E. H. Metal-Organic Frameworks Mediate Cu Coordination for Selective CO₂ Electroreduction. *J. Am. Chem. Soc.* **2018**, 140 (36), 11378–11386.
- (32) Luan, Y.; Qi, Y.; Gao, H.; Andriamantsoa, R. S.; Zheng, N.; Wang, G. A General Post-Synthetic Modification Approach of Amino-Tagged Metal-Organic Frameworks to Access Efficient Catalysts for the Knoevenagel Condensation Reaction. *J. Mater. Chem. A* **2015**, 3 (33), 17320–17331.
- (33) Butova, V. V.; Budnyk, A. P.; Guda, A. A.; Lomachenko, K. A.; Bugaev, A. L.; Soldatov, A. V.; Chavan, S. M.; Øien-Ødegaard, S.; Olsbye, U.; Lillerud, K. P.; Atzori, C.; Bordiga, S.; Lamberti, C. Modulator Effect in UiO-66-NDC (1,4-Naphthalenedicarboxylic Acid) Synthesis and Comparison with UiO-67-NDC Isoreticular Metal-Organic Frameworks. *Cryst. Growth Des.* **2017**, 17 (10), 5422–5431.
- (34) Xue, D.-X.; Belmabkhout, Y.; Shekhah, O.; Jiang, H.; Adil, K.; Cairns, A. J.; Eddaoudi, M. Tunable Rare Earth Fcu-MOF Platform: Access to Adsorption Kinetics Driven Gas/Vapor Separations via Pore Size Contraction. *J. Am. Chem. Soc.* **2015**, 137 (15), 5034–5040.
- (35) Cao, Y.; Zhao, Y.; Lv, Z.; Song, F.; Zhong, Q. Preparation and Enhanced CO₂ Adsorption Capacity of UiO-66/Graphene Oxide Composites. *J. Ind. Eng. Chem.* **2015**, 27, 102–107.
- (36) Hou, J.; Luan, Y.; Tang, J.; Wensley, A. M.; Yang, M.; Lu, Y. Synthesis of UiO-66-NH₂ Derived Heterogeneous Copper (II) Catalyst and Study of Its Application in the Selective Aerobic Oxidation of Alcohols. *J. Mol. Catal. A: Chem.* **2015**, 407, 53–59.
- (37) Tang, J.; Dong, W.; Wang, G.; Yao, Y.; Cai, L.; Liu, Y.; Zhao, 672 X.; Xu, J.; Tan, L. Efficient Molybdenum(vi) Modified Zr-MOF 673 Catalysts for Epoxidation of Olefins. *RSC Adv.* **2014**, 4 (81), 42977– 674 42982. 675
- (38) NIST. *NIST Chemistry WebBook*, SRD 69; NIST, 2018. 676
- (39) Kuhl, K. P.; Hatsukade, T.; Cave, E. R.; Abram, D. N.; 677 Kibsgaard, J.; Jaramillo, T. F. Electrocatalytic Conversion of Carbon 678 Dioxide to Methane and Methanol on Transition Metal Surfaces. *J.* 679 *Am. Chem. Soc.* **2014**, 136 (40), 14107–14113. 680
- (40) Yang, Q.; Xu, Q.; Jiang, H.-L. Metal-Organic Frameworks Meet 681 Metal Nanoparticles: Synergistic Effect for Enhanced Catalysis. *Chem.* 682 *Soc. Rev.* **2017**, 46 (15), 4774–4808. 683
- (41) Kung, C.-W.; Audu, C. O.; Peters, A. W.; Noh, H.; Farha, O. 684 K.; Hupp, J. T. Copper Nanoparticles Installed in Metal-Organic 685 Framework Thin Films Are Electrocatalytically Competent for CO₂ 686 Reduction. *ACS Energy Lett.* **2017**, 2 (10), 2394–2401. 687
- (42) Ghalei, B.; Wakimoto, K.; Wu, C. Y.; Isfahani, A. P.; 688 Yamamoto, T.; Sakurai, K.; Higuchi, M.; Chang, B. K.; Kitagawa, 689 S.; Sivaniah, E. Rational Tuning of Zirconium Metal-Organic 690 Framework Membranes for Hydrogen Purification. *Angew. Chem.,* 691 *Int. Ed.* **2019**, 58 (52), 19034–19040. 692
- (43) Popovych, N.; Kyriienko, P.; Soloviev, S.; Baran, R.; Millot, Y.; 693 Dzwigaj, S. Identification of the Silver State in the Framework of Ag- 694 Containing Zeolite by XRD, FTIR, Photoluminescence, ¹⁰⁹Ag NMR, 695 EPR, DR UV-Vis, TEM and XPS Investigations. *Phys. Chem. Chem.* 696 *Phys.* **2016**, 18 (42), 29458–29465. 697
- (44) Schmitt, K. G.; Gewirth, A. A. In Situ Surface-Enhanced Raman 698 Spectroscopy of the Electrochemical Reduction of Carbon Dioxide on 699 Silver with 3,5-Diamino-1,2,4-Triazole. *J. Phys. Chem. C* **2014**, 118 700 (31), 17567–17576. 701
- (45) Gao, J.; Zhang, H.; Guo, X.; Luo, J.; Zakeeruddin, S. M.; Ren, 702 D.; Grätzel, M. Selective C-C Coupling in Carbon Dioxide 703 Electroreduction via Efficient Spillover of Intermediates As Supported 704 by Operando Raman Spectroscopy. *J. Am. Chem. Soc.* **2019**, 141 (47), 705 18704–18714. 706
- (46) Duan, S.; Fang, P.-P.; Fan, F.-R.; Broadwell, I.; Yang, F.-Z.; Wu, 707 D.-Y.; Ren, B.; Amatore, C.; Luo, Y.; Xu, X.; et al. A Density 708 Functional Theory Approach to Mushroom-like Platinum Clusters on 709 Palladium-Shell over Au Core Nanoparticles for High Electrocatalytic 710 Activity. *Phys. Chem. Chem. Phys.* **2011**, 13 (12), 5441–5449. 711
- (47) Gunathunge, C. M.; Ovalle, V. J.; Li, Y.; Janik, M. J.; Waegle, 712 M. M. Existence of an Electrochemically Inert CO Population on Cu 713 Electrodes in Alkaline PH. *ACS Catal.* **2018**, 8 (8), 7507–7516. 714
- (48) Kas, R.; Kortlever, R.; Yilmaz, H.; Koper, M. T. M.; Mul, G. 715 Manipulating the Hydrocarbon Selectivity of Copper Nanoparticles in 716 CO₂ Electroreduction by Process Conditions. *ChemElectroChem* 717 **2015**, 2, 354. 718
- (49) Liu, H.; Chu, J.; Yin, Z.; Cai, X.; Zhuang, L.; Deng, H. Covalent 719 Organic Frameworks Linked by Amine Bonding for Concerted 720 Electrochemical Reduction of CO₂. *Chem.* **2018**, 4 (7), 1696–1709. 721