

Integrated CO₂ Capture and Conversion by a Robust Cu(I)-Based Metal–Organic Framework

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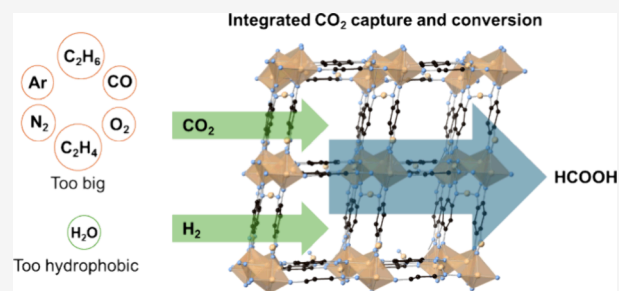


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ABSTRACT: Metal–organic frameworks (MOFs) have shown promise in both capturing CO₂ under flue gas conditions and converting it into valuable chemicals. However, the development of a single MOF capable of capturing and selectively converting CO₂ has remained elusive due to a lack of a harmonious combination of selectivity, water stability, and reactivity. For example, Cu(I)-based MOFs are particularly effective for CO₂ conversion, but they do not typically exhibit selective CO₂ adsorption and often suffer from instability in the presence of air and moisture. Developing a Cu(I) MOF that is stable under flue gas conditions while also capturing CO₂ from this mixture would likely afford a material capable of selectively capturing and converting CO₂ in an integrated pathway, which would represent a significant advancement in this field. In this study, we introduce NU-2100, an ultramicroporous Cu(I) MOF, which exhibits both selectivity for CO₂ adsorption and great stability even in the presence of moisture and air. Comprehensive evaluations involving exposure to air, oxygen, water, and varying temperatures reveal that NU-2100 demonstrates superior stability compared to other known Cu(I) MOFs. Utilizing adsorption isotherms and thermogravimetric analysis coupled with gas chromatography–mass spectrometry (TGA-GCMS), we establish the high selectivity of NU-2100 for CO₂ over common flue gas components, including water, nitrogen, and oxygen. Additionally, under mild reaction conditions (50 °C and H₂:CO₂ = 3:1), NU-2100 exhibits CO₂ capture and catalytic conversion to formic acid with 100% selectivity. This study marks an important step toward the design of next-generation MOFs capable of integrated carbon capture and utilization (iCCU) under industrial conditions.



INTRODUCTION

The world currently relies heavily on burning fossil fuels like coal, petroleum, and natural gas to meet its energy needs. Unfortunately, this method also leads to the production of significant amounts of carbon dioxide (CO₂), a greenhouse gas that contributes to environmental problems such as global warming, ocean acidification, extreme weather, and loss of species diversity.^{1–4} Therefore, reducing emissions and mitigating atmospheric CO₂ concentrations are crucial tasks that require immediate and drastic attention. The primary sources of CO₂ emissions are transportation, electricity, and industry.⁵ While several alternative approaches have been made to reduce carbon emissions from the transportation and electricity sectors, such as fuel switching and using renewable fuel, limited attempts have been made to reduce carbon emissions in the industry.

Among various industrial sectors, the cement industry is responsible for almost 8% of CO₂ emissions.⁶ Several strategies have been implemented to achieve carbon neutrality for this process, including increasing clinker substitution, using alternative fuels, and improving thermal energy efficiency. As a result, specific emissions per ton of cement are expected to

decrease from 730 kg CO₂ in 2009 to about 540–590 kg CO₂ by 2050.⁶ Lower CO₂ intensity cements have been suggested as a way to meet required targets, but they are not likely to be widely adopted. Several commercial technologies can separate CO₂ from a gas stream or air, such as amine scrubbing and calcium looping. However, these technologies have not been specifically developed for large-scale carbon sequestration operations that could be used in applications like the cement industry. Instead, they are designed to capture CO₂ and, upon regeneration, produce a high-purity CO₂ stream for commercial purposes, such as chemical manufacturing and food processing.^{1,7} According to various NGO-based analysts like the Intergovernmental Panel on Climate Change (IPCC) and International Energy Agency (IEA), the most effective technology group for achieving the necessary emission

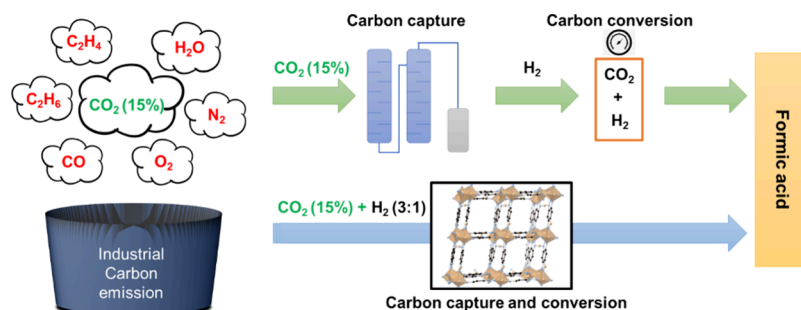
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Scheme 1. Reactive Capture of CO₂ by NU-2100 from a 15% CO₂ Stream^a

^aNU-2100 can convert selectively captured CO₂ to formic acid in the presence of hydrogen, which is expected to have more energy savings than the independent capture and conversion processes.¹⁵

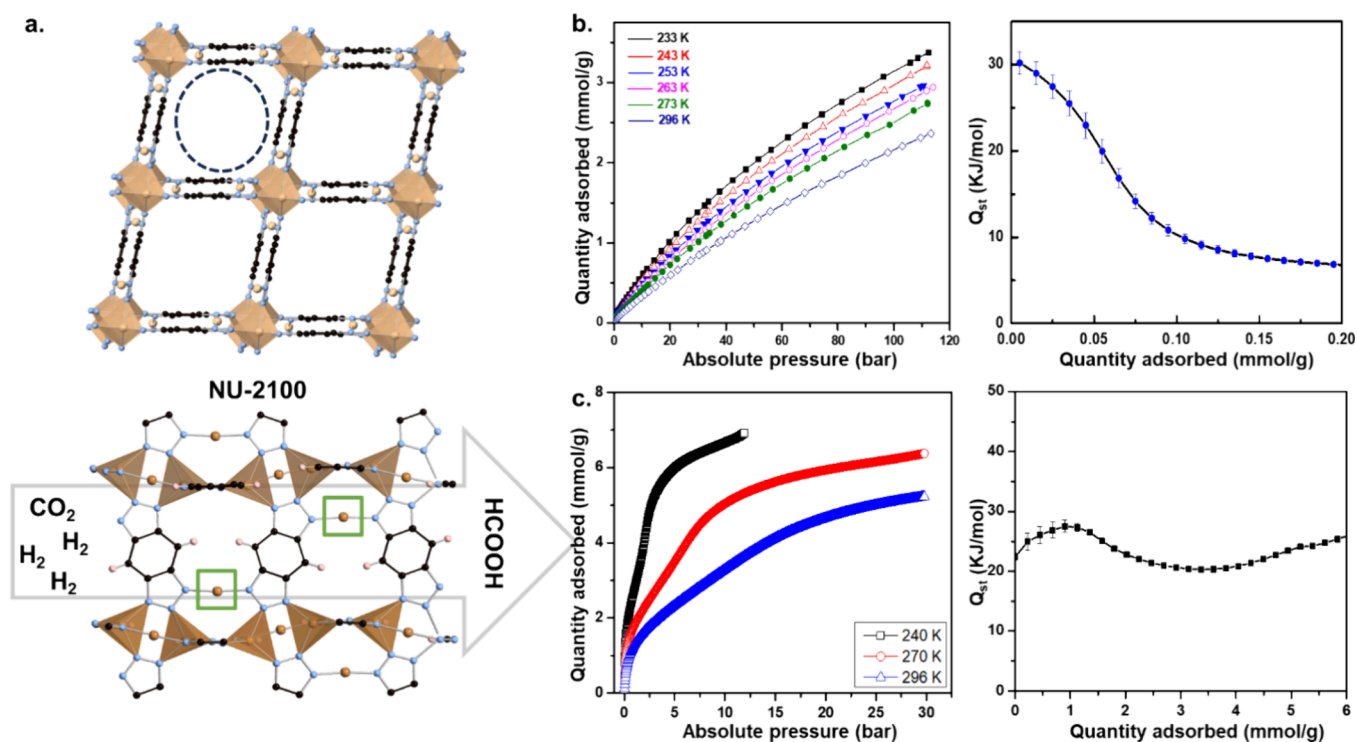


Figure 1. (a) Single crystal X-ray structure of NU-2100 highlighting the pore channel and the active sites. High-pressure isotherm and isosteric heats of adsorption (Q_{st}) of NU-2100 for (b) hydrogen (H₂)¹⁴ (Reproduced from [ref 14 Copyright [2023] American Chemical Society) and (c) carbon dioxide (CO₂).

reductions is integrated carbon capture and utilization (iCCU) from these large point source emitters.^{8–10} However, the development of materials capable of selectively capturing and converting CO₂ in an iCCU process has remained elusive.

Metal–organic frameworks (MOFs) have recently garnered attention as promising solutions to the challenges of both CO₂ capture and the catalytic conversion of CO₂.¹¹ Typically, CO₂ streams generated at various point sources are mixed with components like N₂, O₂, alkanes, alkenes, SO_x, NO_x, and water. Capturing CO₂ from mixed gases is challenging for both homogeneous and heterogeneous catalysts due to the need for precise separation from other gases. While CO₂ can be selectively captured using amine, hydroxide, or polarized bonds, converting CO₂ into value-added chemicals generally requires catalytic metal sites.¹⁰ Unfortunately, these catalytic sites often lose their reactivity in the presence of water. Therefore, creating an effective framework for integrated CO₂ capture necessitates the harmonious combination of selectivity,

water stability, and reactivity. Currently, MOFs are designed to selectively remove CO₂ from flue gas streams or convert dry CO₂ to value-added chemicals like methanol or ethanol.^{11,12} Despite their potential, no single MOF capable of synergistically capturing and converting CO₂ to value-added chemicals in the presence of hydrogen has been reported in the literature, to the best of our knowledge (Table S2).

To overcome the challenges associated with developing a MOF-based iCCU material for potential use in cement industry point sources, the ideal MOF should feature open metal sites (OMS) available for catalytic CO₂ conversion, demonstrate high temperature and moisture stability, and selectively capture CO₂ from other flue gas components. In this regard, Cu(I) MOFs are well-known for their catalytic CO₂ conversion capabilities, making them a promising class of MOFs for use in this application.^{12,13} However, the Cu(I) sites are typically rapidly oxidized upon exposure to humid air conditions. In contrast, our previously reported Cu(I) MOF

NU-2100 ($\text{Cu}_2(\text{BBTA})$, $\text{H}_2\text{BBTA} = 1,5\text{-Dihydrobenzo}[1,2\text{-d}:4,5\text{-d}']\text{bis}([1,2,3]\text{triazole})$) exhibits excellent thermal, moisture, and air stability,¹⁴ suggesting that it may meet the conditions required for an iCCU material. In this work, we investigated **NU-2100** for use in the integrated capture and conversion of CO_2 (Scheme 1). We found that this MOF displays excellent selectivity for CO_2 and H_2 over other gases such as methane, ethane, ethylene, nitrogen, carbon monoxide, and water. Due to both the high density of **NU-2100** and the hydrophobic nature of the H_2BBTA ligand, this MOF exhibits high CO_2 capture selectivity over water, and the open Cu(I) sites are available for catalysis, even under humid reaction conditions. Based on these combined properties, we found that upon exposure to 15% CO_2 and in the presence of 3 equiv H_2 (with respect to CO_2), **NU-2100** selectively captures and hydrogenates CO_2 to formic acid with 100% selectivity through an iCCU process. More broadly, this approach provides a new opportunity for the targeted capture and conversion of CO_2 , even in humid conditions.

RESULTS AND DISCUSSION

We recently synthesized a robust Cu(I) MOF, **NU-2100**, which was synthesized *de novo* upon heating a 2:3 ratio of ZnCl_2 and CuCl_2 with H_2BBTA in *N,N*-dimethylformamide (DMF) at 140 °C for 2 days.¹⁴ Notably, **NU-2100** features two types of open Cu(I) sites in distinct environments. While one Cu unit adopts a tetrahedral environment, the other unit resides in a nearly linear geometry (Figure 1a). Previously, we observed that **NU-2100** demonstrates one of the highest initial isosteric heats of adsorption for hydrogen ($Q_{\text{st}} = 32$ kJ/mol) (Figure 1b).¹⁴ We also collected CO_2 adsorption isotherms at 240, 270, and 296 K at the National Institute of Standards and Technology (NIST), which revealed good physisorption interactions between **NU-2100** and CO_2 ($Q_{\text{st}} = 22\text{--}28$ kJ/mol) (Figure 1c). The isosteric heat of adsorption for hydrogen gas is notably higher than that of CO_2 , which is a prerequisite for the CO_2 hydrogenation reaction.^{11,16} We hypothesize that **NU-2100**, due to its ability to interact with both CO_2 and H_2 , along with its excellent thermal and air stability and high density of open Cu(I) sites per cubic centimeter, might be a suitable candidate to carry out the Cu(I)-mediated hydrogenation of CO_2 .^{11,14}

Selectivity for Gases. An ideal iCCU material should selectively capture CO_2 from large point sources, such as industrial facilities, and subsequently convert it to chemical feedstocks, even with other contaminants present in the gas stream.⁷ Typically, postcombustion flue gas contains approximately 8–14% CO_2 , along with water, oxygen, and nitrogen as the major components, as shown in Table 1. It also includes minor components such as sulfur oxides (SO_x), nitrogen oxides (NO_x), and particulate matter. In contrast, cement kiln off-gas generally contains around 19% CO_2 , with the remaining

Table 1. Major Components of Various Post Combustion Flue and Cement Kiln Gases^{17,18}

Gas	Natural gas-fired power plants (v/v%)	Coal-fired power plants (v/v%)	Cement Kiln (v/v%)
CO_2	8–10%	12–14%	19%
H_2O	18–20%	8–10%	13%
O_2	2–3%	3–5%	8%
N_2	67–72%	72–77%	61%

composition including water vapor, oxygen, and nitrogen, along with SO_x and NO_x . Pollution control technologies can effectively remove SO_x and NO_x , but the selective capture and conversion of CO_2 from other major component gases remains challenging.¹⁷

Previously, we observed that **NU-2100** exhibits negligible uptake of either N_2 (77 K) or Ar (87 K).¹⁴ To further explore the adsorption properties of **NU-2100** toward other major components in flue gas mixtures, we collected both O_2 and H_2O adsorption isotherms. We found that **NU-2100** exhibits negligible O_2 uptake at both 195 and 298 K, which is expected since O_2 has a larger kinetic diameter (346 pm) compared to Argon (340 pm) (Figure 2a). Interestingly, **NU-2100** also displays very low water uptake at 298 K (Figure S1). To gain a better understanding of the selectivity of **NU-2100** for CO_2 over H_2O , we employed real-time thermogravimetric analysis coupled with a gas chromatography mass spectrometer (TGA-GCMS) (Figure 2b).¹⁹ In this experiment, **NU-2100** was first exposed to 1 bar CO_2 at a relative humidity (RH) of 50% at 298 K for 60 min. The sample was then heated at 120 °C and the adsorbed gases were identified using GCMS. Analysis of the TGA-GCMS results revealed that **NU-2100** adsorbs approximately 3 wt % of the gas mixture, and this mixture is comprised of almost entirely CO_2 and a negligible amount of H_2O (Figure 2b). The overall amount of adsorbed $\text{CO}_2 + \text{H}_2\text{O}$ is also consistent with the weight loss measured by TGA analysis (Figure S4). We plotted the integrated intensities of the chromatograms corresponding to CO_2 (m/z : 44) and H_2O (m/z : 18) against the retention time of GCMS (Figure 2b). The calibration curves for CO_2 and H_2O from standard calcium oxalate are shown in Figure S2. We believe that negligible water uptake by **NU-2100** is linked to the high crystal density and hydrophobic nature of the ligand, which helps maintain the +1 oxidation state of the Cu sites and preserves their reactivity properties.

One major concern with using a low-coordinated Cu(I) center for CO_2 reduction is carbon monoxide (CO) poisoning, which will coordinate with Cu sites and render them inactive.^{20–22} To investigate whether CO can access the internal Cu(I) sites within the pores of **NU-2100**, we collected CO adsorption isotherms for **NU-2100** at both 195 and 298 K. Interestingly, **NU-2100** exhibits very low CO uptake at these temperatures, which suggests the Cu(I) active sites should remain stable under a CO environment (Figure 2a). This result is consistent with the larger kinetic diameter of CO (376 pm) relative to that of CO_2 (330 pm) due to the polarized nature of CO .²³ We further explored the stability of **NU-2100** following exposure to CO (both at 25 and 50 °C) by collecting powder X-ray diffraction (PXRD) data, X-ray photoelectron spectroscopy (XPS) and CO_2 sorption isotherms, which are both comparable to those collected prior to CO exposure and confirm that the crystalline and porous nature of **NU-2100** remains intact, along with the oxidation state of the Cu(I) center (Figures S3 and S5). In addition to CO isotherms, we also collected ethane and ethylene adsorption isotherms at 298 K, as these gases are primary components found in point sources in the petrochemical industry.²⁴ Due to its limited pore size, **NU-2100** exhibits negligible ethane or ethylene uptake under these conditions, suggesting that it is also a viable adsorbent for selective CO_2 capture from other point sources as well (Figure 2a).

Stability in Air and Moisture. Next, we were interested in examining the durability of **NU-2100** when exposed to air and

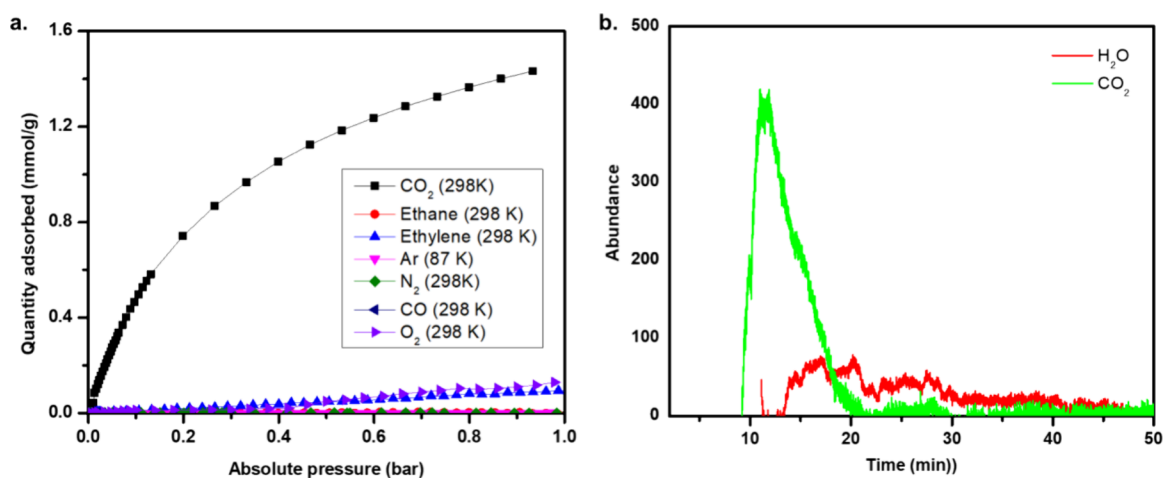


Figure 2. (a) Gas selectivity of NU-2100 over Ethane (red), Ethylene (blue), Argon (pink), Nitrogen (green), carbon monoxide (CO, dark blue) and oxygen (purple). (b) Integrated intensity of desorbed CO₂ (green) and H₂O (red) obtained from TGA-GCMS analysis.

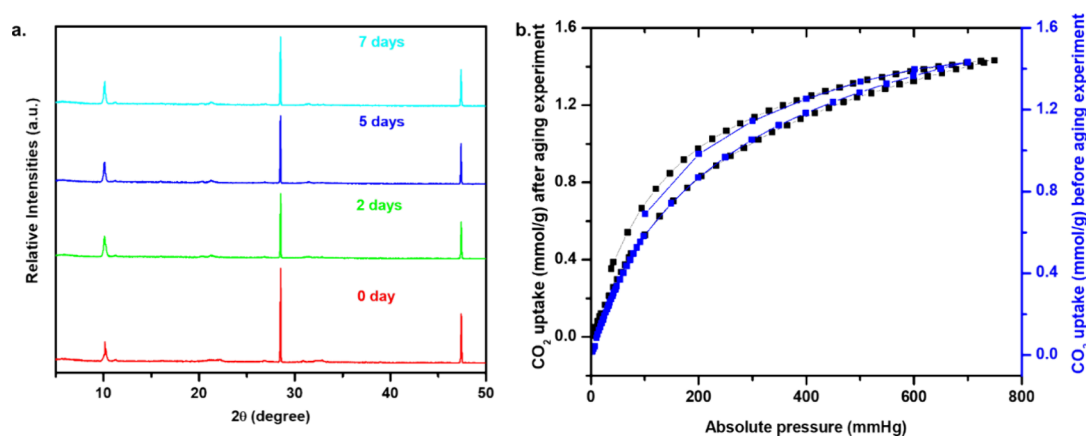


Figure 3. (a) Aging experiments on NU-2100. The sample was exposed to 80% RH at 50 °C and the PXRD was monitored with silica as an internal standard. Quantitative analysis was performed by comparing the area under the peaks of silica (peaks at 28.5° and 47.5°) and NU-2100 (10.0°). (b) CO₂ isotherm of before and after Aged (80% RH at 50 °C) sample for 7 days.

moisture, as this is crucial for industrial applications. Previously, we found that NU-2100 did not exhibit any oxidation after exposure to air for 7 days.¹⁴ The room-temperature O₂ adsorption isotherm (Figure 2) suggests limited diffusion of O₂ into the pores of NU-2100, which likely prevents the aerial oxidation of Cu(I) sites. To study the stability of NU-2100 upon exposure to moisture, we performed accelerated aging experiments in which we heated NU-2100 in a humidity oven at 50 °C and RH = 80% for 7 days. Quantitative PXRD analysis that employed silica as an internal standard indicates that NU-2100 maintains its crystallinity under these conditions (Figure 3a).²⁵ Furthermore, the CO₂ adsorption isotherm (298 K) collected following this accelerated aging experiment is almost identical to that of the pristine NU-2100 (Figure 3b), indicating excellent stability and no loss of porosity upon exposure to these harsh conditions. We attribute the negligible water uptake of NU-2100 to its high crystal density and the hydrophobic nature of the ligand. These factors contribute to maintaining the Cu sites in their +1 oxidation state, thereby preserving their reactivity.

Stability in SO_x and pH. We are also interested in evaluating the stability performance of NU-2100 under real flue gas conditions, which has 200–1000 ppm of SO_x

components depending on the source.²⁶ We exposed NU-2100 to 1000 ppm of SO₂ for 36 h and measured the PXRD, XPS and CO₂ isotherm to check the crystallinity and porosity, respectively. The CO₂ adsorption isotherm (298 K), XPS and PXRD analysis collected following this SO_x exposure experiment are almost identical to that of the pristine NU-2100, indicating robust stability under low-concentration (<1000 ppm) SO_x conditions (Figure S4–S5). We also evaluated the stability of NU-2100 across different pH levels. The sample was immersed in water for 10 h with pH values ranging from 1 to 14, adjusted using varying amounts of HCl and NaOH. Interestingly, NU-2100 demonstrated outstanding stability throughout this entire pH range, indicating its suitability for use under diverse conditions (Figure S6).

Recyclability in Air and Moisture. Since typical postcombustion flue gas mixtures contain approximately 8–14% CO₂, along with nitrogen and water as other major components (Table 1) and typical cement kiln gas contains 19% CO₂ along with the water and nitrogen, it is crucial to assess the material's recyclability under both humid CO₂ and a mixture of 15% CO₂ with 85% N₂. Therefore, we employed thermogravimetric analysis (TGA) to collect isobars at ambient pressure, beginning with a 15% CO₂ and 85% N₂ stream under dry conditions (Figure S7). After 4 h exposure to

this gas stream at 30 °C, the sample was heated to 120 °C for 1 h and found to lose 3.5% of its mass. After 10 cycles (adsorption: 30 °C, 60 min, desorption: 120 °C, 30 min) for 1300 min, no loss in capacity was observed (Figure S8). Next, we collected isobars using humid 100% CO₂ by first passing CO₂ through a water bubbler at room temperature before it enters the sample chamber. The sample was first activated under N₂ at 150 °C for 20 min, exposed to the humid CO₂ stream for 20 min at 30 °C, then heated to 150 °C for 20 min during desorption. Throughout 3000 min of cycling for a total of 32 cycles, 88% of the overall capacity was maintained upon repeated exposure to a humid 100% CO₂ stream, suggesting adequate stability for NU-2100 under these conditions (Figure S9).

CO₂ Hydrogenation Reaction. After confirming the selectivity of NU-2100 for CO₂ and H₂ and its excellent stability, we explored its catalytic activity in the hydrogenation of CO₂. We conducted solid-state batch experiments by adding NU-2100 to a Parr reactor and screened various ratios of H₂/CO₂ and temperatures (Table S1). After 24 h, the product was extracted from NU-2100 using deuterated chloroform (CDCl₃) and quantified by ¹H NMR spectroscopic analysis using hexamethylbenzene as an internal standard. The optimal condition for catalysis was determined to be a 3:1 (v/v) H₂/CO₂ gas mixture at 50 °C. Under these conditions, NU-2100 produced formic acid with 100% selectivity and a turnover number (TON) of 8 (Table S1). Aside from CO₂ and H₂, no other gas products were detected in the headspace (Figure S24). Control experiments performed under analogous conditions with NU-2100 replaced by H₂BBTA (Figure S11), CuCl₂ (Figure S12), CuCl (Figure S13), Cu(OAc)₂ (Figure S14), Cu(II)-MFU-4l (Figure S21), or Cu₂Cl₂(BBTA) (Figure S22) did not produce any detectable quantity of formic acid (Table 2). To the best of our knowledge, this is the first

Table 2. Screening of Different Cu-Salts and Ligand for the CO₂ Hydrogenation^a

H ₂ (bar)	CO ₂ (bar)	Catalyst (mmol)	Product (mmol)	TON
3	1	NU-2100 (0.035)	0.3	8.3
3	1	H ₂ BBTA (0.035)	Nil	Nil
3	1	CuCl ₂ (0.035)	Nil	Nil
3	1	CuCl (0.035)	Nil	Nil
3	1	Cu (0.5)	Nil	Nil
3	1	Cu(OAc) ₂ (0.035)	Nil	Nil
3	1	No catalyst	Nil	Nil
3	1	CuCl ₂ /H ₂ BBTA (0.035 each)	Nil	Nil
3	1	CuCl/H ₂ BBTA (0.035 each)	Nil	Nil

^aReaction Catalytic condition: Catalyst (0.035 mmol), Temperature: 50 °C, Time = 24 h.

example of a MOF that can perform integrated CO₂ capture and utilization (iCCU) by selectively adsorbing and converting CO₂ into a value-added product like formic acid (Table S2). Previously, Cu(I) complexes have been shown to perform the hydrogenation of CO₂ in the presence of a strong base.²⁷ In these systems, the catalytic activity is believed to originate from the coordination of low-coordinate Cu(I) species with the base, which generates a reactive hydride species. Based on the strong binding affinity of NU-2100 to H₂,¹⁴ the first step could potentially involve the formation of a Cu(I)-coordinated

polarized H₂ molecule, which then readily reacts with CO₂ and generates the formic acid. However, we found that a reaction performed under 3:1 H₂/CO₂ but with a 2:1 mixture of CuCl₂/CuCl and H₂BBTA did not produce any formic acid (Figure S16 - S17), which indicates that the active site in which Cu(I) coordinates to the BBTA²⁻ linker is crucial for this reactivity. This observation corroborates previous work that illustrated the coordination of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to a Cu(I) center is crucial for reactivity.²⁷

To corroborate that the iCCU reaction takes place within the pores of NU-2100, we first poisoned the surface copper sites²⁸ by exposing NU-2100 to CO at 1 bar for 24 h, then subjected this material to the same catalysis conditions.²² Since NU-2100 shows negligible CO uptake at room temperature (Figure 2a), this eliminates the possibility of CO quenching the inner Cu(I) active sites in the pores. The CO-exposed NU-2100 performed similarly (TON = 8.1) compared to pristine NU-2100 (TON = 8.3), confirming that CO₂ hydrogenation occurs within the pores of NU-2100 rather than on the surface (Table 3, Figure S18). We also confirmed the stability of the

Table 3. Screening of Different Cu-MOFs for the CO₂ Hydrogenation Reaction^a

H ₂ (bar)	CO ₂ (bar)	Catalyst (mmol)	Product (mmol)	TON
3	1	NU-2100 (0.035)*	0.28	8.1
3	1	NU-2100 (0.035) [#]	0.28	8.1
3	1	NU-2100 (0.035) [†]	0.31	8.2
3	1	Cu(II)-MFU-4l (0.035)	Nil	Nil
3	1	Cu ₂ Cl ₂ (BBTA) (0.035)	Nil	Nil

^aNU-2100 was exposed to CO at *(25 °C, 1 bar for 24 h), [#](50 °C, 1 bar for 24 h) and Exposed to SO₂ at [†](25 °C, 1000 ppm for 36 h). Catalytic condition: Catalyst (0.035 mmol), Temperature: 50 °C, Time = 24 h.

catalyst during the reaction. We heated the sample to 50 °C with 1 bar of CO and assessed its performance. The sample also retained its crystallinity, porosity, and reactivity, making it a suitable catalyst under a CO environment (Table 3, Figure S19). A typical flue gas stream is mixed with SO_x components.²⁶ To screen the stability of NU-2100 in SO_x, we have also exposed NU-2100 to 1000 ppm of SO₂ for 36 h at 25 °C. The SO₂-exposed NU-2100 was reactivated and subjected to catalysis. Notably, the SO₂-exposed NU-2100 performed similarly (TON = 8.2) compared to pristine MOF (Table 3, Figure S20). To verify that catalysis occurs because of the presence of Cu(I) active sites rather than the confined pore structure, we conducted analogous experiments using the Cu(II)-based MOFs Cu(II)-MFU-4l and Cu₂Cl₂(BBTA) in place of NU-2100 (Table 3). Despite comparable Cu-amine linkages for Cu(II)-MFU-4l, CuCl₂(BBTA), and NU-2100, the former Cu(II)-based MOFs do not afford any observable amount of formic acid under these conditions, suggesting that the Cu(I) sites in NU-2100 are necessary for catalysis. It is also worth noting that Cu(II) does not interact well with hydrogen, leaving the possibility of polarized hydrogen for the catalytic reaction.^{29,30}

After confirming that NU-2100 is active for the selective capture and hydrogenation of CO₂ under 1 bar CO₂, we then explored the catalytic activity of NU-2100 at lower CO₂ concentrations that are more comparable to those found in flue gas mixtures. Based on TGA experiments (*vide supra*), NU-2100 adsorbs approximately 3 wt % CO₂ from a 15% CO₂

and 85% N₂ gas stream (Figure S4), suggesting NU-2100 should be a competent iCCU catalyst under similar conditions described previously. Indeed, the solid-state batch reaction in which NU-2100 is added to a Parr vessel and pressurized with a mixture of 0.15 bar CO₂/0.85 bar Ar with 3 bar H₂ afforded formic acid with 100% selectivity and a TON of 3.5 (Table 4,

Table 4. Screening of Catalytic Conversion of CO₂ and H₂ to Formic Acid by NU-2100^a

H ₂ (bar)	CO ₂ (bar)	Addition (bar)	Catalyst (mmol)	Product (mmol)	TON
3	0.15	Ar (0.85)	NU-2100 (0.035)	0.12	3.5
0.45	0.15	Ar (0.85)	NU-2100 (0.035)	0.11	3.2
3	0.15	Air (0.85)	NU-2100 (0.035)	0.12	3.5
3	1	D ₂ O (0.5 mL)	NU-2100 (0.035)	0.29	8.1

^aCatalytic condition: Catalyst (0.035 mmol), Temperature: 50 °C, Time = 24 h.

Figure S23). This relatively lower TON is consistent with the lower concentration of CO₂ used in this reaction (compared to a TON of 8.3 when 1 bar CO₂ is used, Table 1). Decreasing the H₂ pressure to maintain the 3:1 H₂/CO₂ ratio (i.e., 0.15 bar CO₂/0.85 bar Ar/0.45 bar H₂) affords similar results with a TON of 3.2 (Table 4, Figure S25). To explore further, we utilized a mixture comprising 15% CO₂ diluted with air (specifically, 0.15 bar CO₂/0.85 bar Air (3:1 N₂/O₂)/3 bar H₂). This mixture effectively produces the desired formic acid with a TON of 3.5, demonstrating that the reaction is unaffected by the presence of oxygen (Table 4, Figure S26). Overall, this result confirms that NU-2100 can perform iCCU at lower CO₂ concentrations that are comparable to those found in typical flue gas streams, indicating that flue gas streams would not need to be pressurized for this catalyst to operate. Notably, given its performance, NU-2100 appears to be well-suited for handling also cement kiln gas, which contains a higher CO₂ concentration (19%) compared to postcombustion flue gas (15%).

To check the effectivity of catalyst in water, we conducted the catalysis in the presence of 0.5 mL D₂O (chosen for improved NMR quantification) within the reaction vessel. The vessel was pressurized with a 3:1 (v/v) H₂/CO₂ gas mixture at 50 °C. After 24 h, the product was extracted using CDCl₃ and analyzed by ¹H NMR. The NMR results indicated that NU-2100 is capable of generating formic acid (TON: 8.1) in the presence of water (Figure S27).

Having established that NU-2100 is a MOF capable of iCCU, we then explored whether NU-2100 could maintain this performance over multiple cycles. These experiments were conducted in Parr vessels with an H₂/CO₂ ratio of 3:1. After each catalytic cycle, the product was extracted using CDCl₃, and the remaining material was dried and resubmitted to the reaction. ¹H NMR spectroscopic analysis of the reaction products revealed that NU-2100 selectively produces formic acid during the first and second cycles but only contains peaks corresponding to linker degradation products during the third cycle (Figure S28), suggesting that NU-2100 loses structural integrity during the third cycle through the concomitant oxidation of Cu(I) sites to Cu(II) and linker degradation. Indeed, X-ray photoelectron spectroscopic (XPS) analysis

performed on the NU-2100 sample isolated during these cycles confirms the presence of Cu(II) species, which presumably terminate the catalytic reaction (Figure S29). To explore the origin of this degradation, we monitored the stability of NU-2100 in formic acid by adding 10 v/v% formic acid to the MOF. PXRD and XPS analysis conducted on NU-2100 following exposure to formic acid indicates oxidation and degradation of the MOF, suggesting that a similar oxidation process may occur under the catalytic reaction conditions after multiple cycles. Our current efforts are targeted toward better understanding this degradation pathway so that we can improve the structural integrity and catalytic activity of NU-2100.

CONCLUSIONS

In conclusion, we have demonstrated the first example of a MOF capable of integrated CO₂ capture and utilization (iCCU) with hydrogen as a coreactant to produce formic acid. In the presence of a 3:1 mixture of H₂/CO₂ at 50 °C and 1 bar CO₂, the robust Cu(I)-MOF NU-2100 can capture CO₂ and convert it to formic acid with 100% selectivity and a turnover number (TON) of about 8. Moreover, NU-2100 exhibits the same selectivity for formic acid when exposed to 0.15 bar CO₂ under comparable conditions, which aligns with CO₂ concentrations typically found in postcombustion flue gas streams. Isotherm experiments demonstrate the high selectivity of NU-2100 for CO₂ over many other gases typically present in flue gas mixtures, including N₂, O₂, and H₂O, as well as other gases like CO and ethylene. This likely originates from the ultramicroporous structure of NU-2100 that kinetically excludes these molecules. Isobar cycling experiments performed using TGA-GCMS analysis with humid CO₂ confirm the selectivity of NU-2100 for CO₂ over water and its ability to retain a significant portion of its CO₂ uptake capacity after repeated adsorption–desorption cycles under these conditions. Although the moderate instability of NU-2100 to formic acid results in limited recyclability for this catalyst, our work represents a significant advance as NU-2100 can perform a single-step iCCU reaction, potentially offering a more economical path for CO₂ capture and utilization compared to processes where capture and utilization are separate steps. Moving forward, we will explore other catalytic pathways to demonstrate the generality of this catalyst design approach.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c08757>.

Experimental procedures, characterization, NMR spectra and isotherms, and data (PDF)

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Notes

The authors declare the following competing financial interest(s): O.K.F. has a financial interest in NuMat Technologies, a startup company that is seeking to commercialize MOFs.

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