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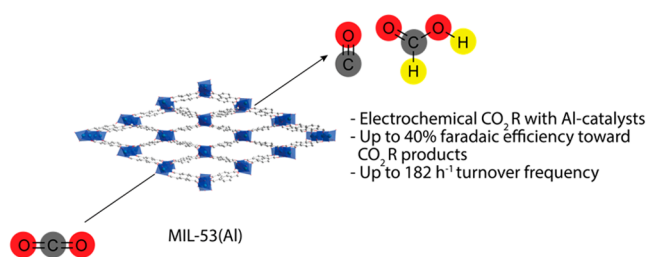
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Aluminum Metal–Organic Framework Triggers Carbon Dioxide Reduction Activity

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ABSTRACT: Confinement of metal centers is a powerful tool to manipulate reactivity and tune selectivity in chemical transformations. While aluminum as a foil is inactive for carbon dioxide reduction and shows high selectivity for the hydrogen evolution reaction, here we show that aluminum confined in a metal–organic framework (MOF), MIL-53(Al), suppresses hydrogen evolution reaction activity and enhances carbon dioxide reduction. This aluminum MOF can produce up to 40% faradaic efficiency for carbon monoxide and formic acid. This study demonstrates that the unique reaction environment created by the MOF enables changes in reaction selectivity and can impart atypical catalytic capabilities to metals.



Nature has been successful in providing highly efficient enzymatic systems in which earth abundant elements catalyze chemical transformations with high selectivity. This selectivity is achieved within a uniquely tailored, confined reaction space called an enzymatic pocket. Drawing inspiration from biological systems, challenging catalytic transformations would benefit from similar design principles, in which catalytic metal centers are placed in confined cavities that promote specific reaction pathways to enhance selectivity.^{1,2}

The electrochemical reduction of CO₂ (CO₂R) is a process in which multiple proton–electron transfers are necessary to yield valuable carbon-based products. CO₂R is one example of a process in which a uniquely tailored, confined reaction environment may be necessary to improve product selectivity. Considerable effort has been devoted to developing both heterogeneous and homogeneous catalysts for selective and efficient electrochemical CO₂ reduction.^{3–5} However, an examination of single-metal foils, for example, demonstrates that the majority of these elements show high activity for the competing hydrogen evolution reaction (HER), in addition to low selectivities between numerous CO₂R products.⁶ Thus, a confined reaction environment offers the opportunity to target the suppression of hydrogen evolution reaction (HER) as well as the promotion of selectivity within CO₂R products.

In this context, MOFs have been reported to provide interesting confinement effects.^{7,8} They allow for efficient heterogeneous catalysis while providing the structural modularity typical of homogeneous catalysts.^{9–11} MOFs as catalysts have demonstrated superior catalytic selectivity, lifetime, and turnover numbers by offering a confined reaction environment

and stabilization of the active catalyst.^{7,8} For example, in Friedel–Crafts alkylations and hydrogenation reactions, MOFs have been shown to provide a confined reaction environment that increases the lifetime of the active catalysts.^{12–14} In addition, in amination of C(sp₃)–H bond reactions, MOFs have been proven to stabilize the active form of the catalyst, thus enabling a unique catalytic performance.¹⁵

Herein, we report the facile synthesis and characterization of an aluminum MOF derivative that is active under electrochemical CO₂R conditions and able to produce important carbon-based products, carbon monoxide (CO), and formic acid. CO is a valuable intermediate in chemical synthesis and toward all other observed products in electrochemical CO₂R. Formic acid is also an attractive product because it can be used as a fuel with practical applications in hydrogen storage and direct formic acid fuel cells.¹⁶ By changing the environment around the Al centers, this metal, which is otherwise only active for HER, is now active in the electrochemical reduction of CO₂ to carbon-based products. To the best of our knowledge, MIL-53(Al) is the first reported MOF that electrocatalytically reduces CO₂ to both CO and formic acid. Most reported MOFs and covalent organic frameworks (COFs) used as CO₂R electrocatalysts in aqueous conditions make use of different metals and can only reduce CO₂ to either

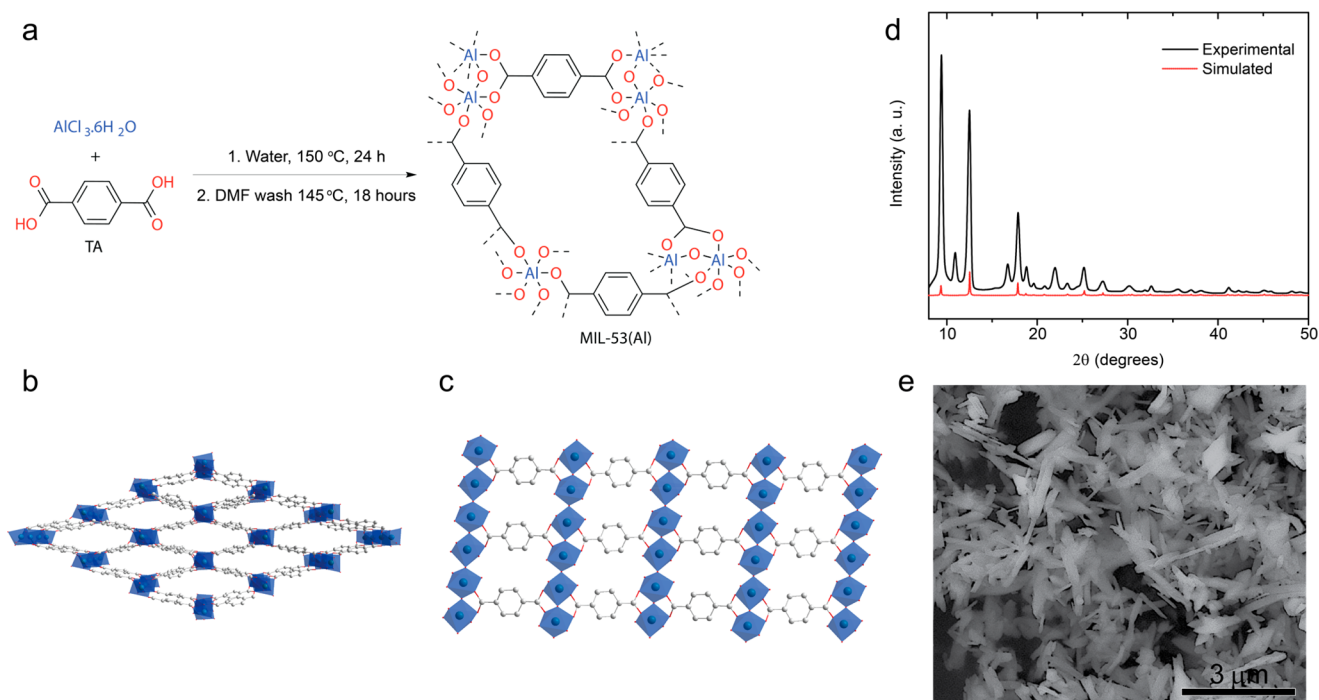


Figure 1. Synthesis and characterization of Al-confined metal–organic framework, MIL-53(Al). (a) Synthesis of MIL-53(Al) from 1:1 $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and terephthalic acid (TA). (b) View of 3D structure of MIL-53(Al) *lt* (monohydrate form). (c) View of MIL-53(Al) *lt* from the side showing Al metal centers are connected through the organic linker, terephthalates. (d) Powder XRD of synthesized MIL-53(Al) showing experimental (solid black) and simulated (dash red) patterns. (e) SEM image of the needle-like crystal structured synthesized MIL-53(Al). Brightness and contrast were adjusted in panel e to improve image quality, and the originally acquired image is shown in Figure S1c.

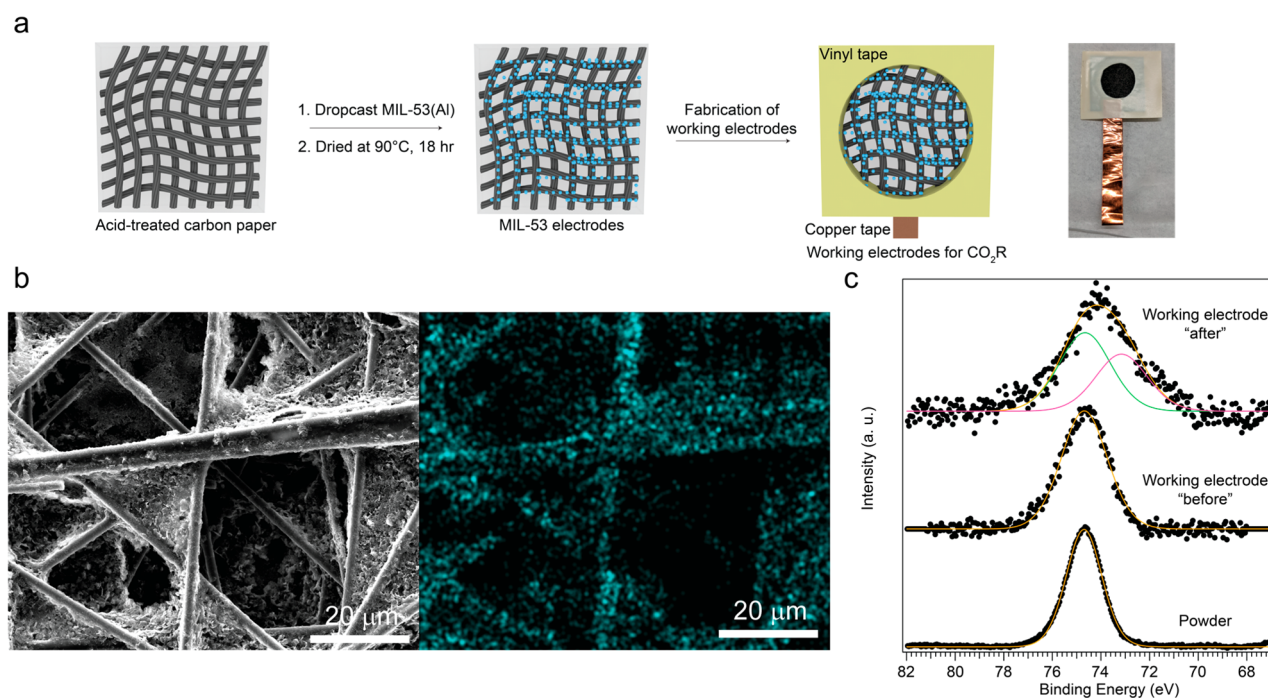


Figure 2. Fabrication and characterization of working electrodes. (a) Scheme to fabricate working electrodes. (b) SEM image (left) showing the topography and corresponding EDX map (right) showing the Al (light blue) distribution ($\text{Al K}\alpha$) on the fabricated working electrode. Al is evenly distributed on the electrode. (c) XPS of Al 2p comparing the powder (bottom) of MIL-53 with the working electrode before (middle) and after (top) electrochemical testing with spectral fitting analysis.

CO or formic acid.^{9,10} At the potential of -1.1 V vs RHE, the turnover frequency (TOF) for carbon-based products reaches 182 h^{-1} per unit cell, with 93 h^{-1} toward CO and 89 h^{-1} toward formic acid, comparable to the TOF for the best

performing COFs.¹⁷ Notably, we also generate Al^0 in addition to Al^{3+} while exposing MIL-53(Al) to electrochemical CO_2R . The presence of Al^0 supports the transformation of Al metal centers in MIL-53 under the catalytic conditions, and we

hypothesize that this species is responsible for the observed catalytic activity toward CO₂R. In addition, the presence of Al⁰, which usually readily oxidizes to Al³⁺ in air, indicates that the organic framework can stabilize the metal center in the confined environment. Thus, MIL-53(Al) demonstrates that the search for improved CO₂R catalysts should not be limited to metals that are traditionally used in this process but, rather, that the changes to the catalytic center or to its surrounding environment can be used to drastically tune the catalytic behavior.

Briefly, MIL-53(Al) was synthesized in a hydrothermal reactor from AlCl₃·6H₂O and terephthalic acid (TA) with a slightly modified procedure from the literature (Figure 1a).^{18,19} A 1:1 ratio of AlCl₃·6H₂O and TA was dissolved in ultrapure water in a Teflon-lined steel autoclave, and it was heated at 150 °C for 24 h (see the Supporting Information for full details). The resulting white powder was washed with ultrapure water and dimethylformamide (DMF) to remove the unreacted starting materials. The final product was dried under vacuum. MIL-53(Al) forms one-dimensional pores made of TA linkers, which coordinate AlO₆ octahedra (Figure 1b,c).

X-ray diffraction (XRD) shows the high crystallinity of the final synthesized material, with peaks at 9.4°, 12.5°, and 17.9°, which are in agreement with simulated powder XRD of monohydrate MIL-53(Al) or MIL-53(Al) *lt*, where the channel contracts due to hydrogen bonding between the oxygen atoms of the MOF and exogenous water molecules¹⁸ (Figure 1d). Scanning electron microscopy (SEM) images further support the high crystallinity of MIL-53(Al) (Figure 1e, Figure S1). The synthesized MIL-53(Al) has a needle-like morphology of approximately 1 μm in length.

Working electrodes were prepared by drop casting a MIL-53 suspension onto acid-treated carbon paper (Figure 2a; see the Supporting Information for full details). First, the carbon paper was treated with 70% nitric acid for 15 min to remove metallic impurities that may affect CO₂R catalysis.²⁰ Depositing MOFs onto carbon paper, a highly conductive, porous material, provides highly conductive pathways and improved mass transport, for an increased number of active sites for catalysis.¹⁰ The resulting electrode has an exposed active area of ~1.25 cm².

SEM-energy dispersive X-ray (EDX) maps and X-ray photoelectron spectroscopy (XPS) measurements were taken to ensure the presence of MIL-53(Al) on the surface of the carbon paper electrodes. SEM-EDX maps showed that aluminum (Al, blue) was present and evenly distributed on the surface of the working electrode (Figure 2b). The presence of oxygen and carbon was also detected (not shown) due to the support, carbon paper, in addition to the MOFs' organic linker. XPS analysis of MIL-53(Al) powder shows that the Al 2p peak has a binding energy of 74.69 eV, which is supportive of the presence of Al³⁺ (Figure 2c).²¹ XPS also confirms the presence of Al³⁺ on the surface of the fabricated working electrode, with an Al 2p peak at a binding energy of 74.69 eV, in agreement with the binding energy of the Al 2p peak for the synthesized MIL-53(Al) powder. These data confirm that MIL-53(Al) was successfully deposited on the surface of the working electrode.

To assess the catalytic performance of MIL-53(Al), cyclic voltammetry (CV) of the working electrode was performed under CO₂ atmosphere (Figure 3a and Figure S2) in a two-compartment flow cell (Figure S3). While the carbon paper has no catalytic current in the potential window under study,

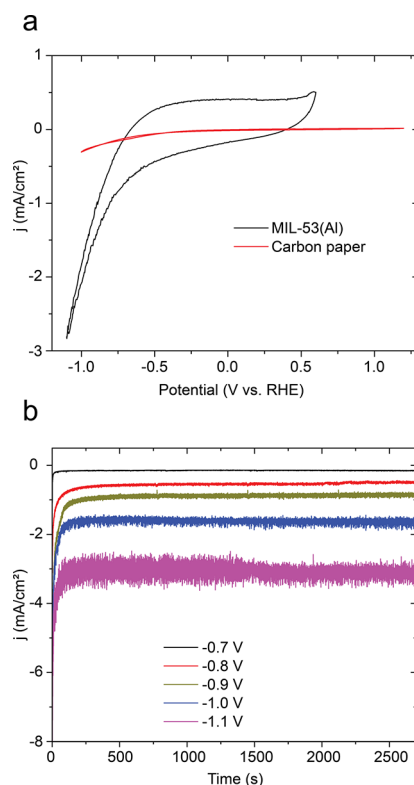


Figure 3. Characterization of MIL-53(Al) electrocatalysts for CO₂R. (a) Cyclic voltammograms of MIL-53(Al) working electrode (blue) and bare carbon paper electrode (red) in CO₂ atmosphere. (b) Chronoamperometry was conducted at five different potentials (−0.7, −0.8, −0.9, −1.0, and −1.1 V vs RHE, black, red, ochre, blue, and magenta, respectively) in CO₂-saturated 0.05 M potassium carbonate electrolyte (pH = 6.8) to investigate the electrocatalyst stability under the reaction conditions.

the MIL-53(Al) working electrode shows an electrocatalytic current with an onset at about −0.4 V vs RHE. To ensure that the production of CO and formic acid are derived from reduction of CO₂ molecules rather than from catalyst decomposition, experiments under nitrogen atmosphere confirmed the absence of carbon products (Table S1). In addition, blank experiments in CO₂ atmosphere using a working electrode of acid-treated carbon paper or carbon paper coated with Nafion, which is used here as the MIL-53(Al) binder, also resulted in no detection of CO₂R products (Table S2 and Table S3). Thus, we can conclude that MIL-53(Al) is the active electrode component in CO₂R to CO and formic acid in MIL-53(Al).

To further test this hypothesis and in order to provide insights into the catalytically active form of the catalyst under operating conditions, we performed XPS analysis after electrochemical testing. Notably, in addition to the Al³⁺ present in the starting material, XPS analysis shows the rise of a second Al 2p component at 73.38 eV, compatible with the presence of Al⁰ present in the material after electrochemical testing (Figure 2c).²¹ Further spectral fitting analysis showed that the ratio of Al⁰ and Al³⁺ is approximately 1:1. This result indicates that Al³⁺ in MIL-53(Al) may undergo transformation during the electrochemical reaction to form an active catalyst that could involve Al⁰. According to the Pourbaix diagram,^{22,23} Al⁰ is reported to be unstable at the potentials and at the pH under study. Therefore, the presence of Al⁰, which usually

rapidly oxidizes to the more stable Al^{3+} species in air,²³ indicates that the confined reaction environment provided by MIL-53 organic framework can stabilize this active form of the catalyst. Chronoamperometry (CA) tests show that the current is stable over time, and SEM-EDX performed after electrochemical testing confirms that Al is still evenly distributed on the surface after electrochemical testing (Figure S4), which further supports the stability of MIL-53(Al) electrodes under operating conditions.

The working electrode was tested at five different potentials from -1.1 V vs RHE to -0.7 V vs RHE with 0.1 V increments by conducting CA for approximately 45 min at each potential (Figure 3b) to further assess the activity of MIL-53(Al) under CO₂R conditions. MIL-53(Al) shows an onset potential for CO and formic acid production as low as -0.7 V vs RHE, with about 10% faradaic efficiency (FE) toward these products (Figure 4, Table S4). At more negative potentials ranging from

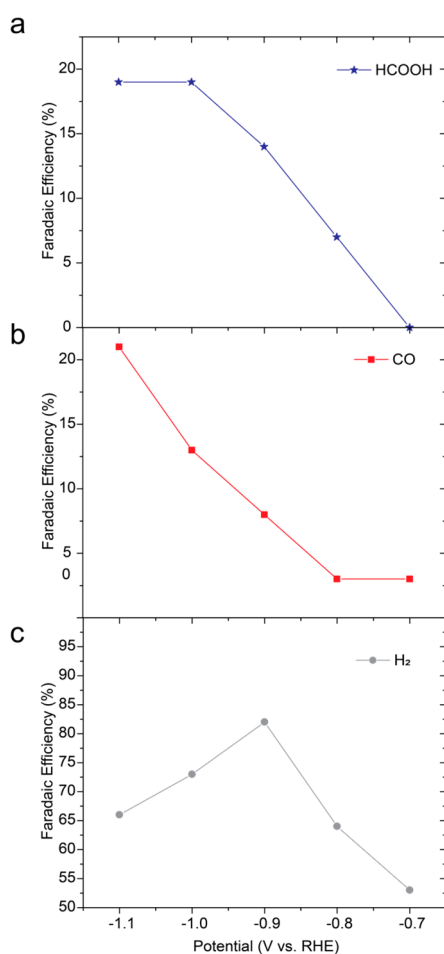


Figure 4. Faradaic efficiency for different CO₂R products. Product detection of CO₂R using MIL-53(Al) as electrocatalyst at various potentials that resulted in formic acid (a), CO (b), and H₂ (c) formation.

-0.9 V vs RHE to -1.1 V vs RHE, substantial CO and formic acid production was detected with 40% FE (Figure 4, Table S5, and Table S6). The formation of CO increased at more negative potentials starting from 8% FE and reaching up to 21% FE, at -0.9 and -1.1 V vs RHE, respectively. Similarly, the FE of formic acid increased from 14% to 19%, at -0.9 and at -1.1 V vs RHE. The increased CO₂R activity at more

negative potential is in agreement with previous reports.^{17,24} Higher potentials (e.g., -1.2 V vs RHE) were also tested. However, the FE for CO, formic acid, and hydrogen as well as the high instability of the current as a function of time point to instability of MIL-53(Al) at high reducing potential (data not shown). Notably, while Al metal foil is known to only be active for HER,^{6,25} we find that confining Al in MOFs, such as MIL-53(Al), provides an active construct for CO₂R at potentials ranging from -1.1 to -0.9 V vs RHE with faradaic efficiencies reaching up to 21% for CO production and 19% for formic acid production. In comparison to the best existing MOFs for CO₂R, which exclusively produce CO (Table S7),^{17,24} MIL-53(Al) can produce both CO and formic acid. These two products are easy to separate since CO is gaseous and formic acid is present in the liquid phase.

We also characterized the catalytic performance by evaluating the partial current density as a measure of the activity of the electrocatalyst. Comparing MIL-53(Al) to Al foil at -1.0 V vs RHE, MIL-53(Al) has more than 60 times partial current density toward CO₂R and HER products (Table S8).⁶ This observation further supports that the confined reaction environment on Al provided by MIL-53 improves Al's electrocatalytic activity.

Production of CO involves a carbon-bound mechanism, which leads to a $^*\text{COOH}$ intermediate that results in CO formation. On the other hand, production of formic acid can occur via two different mechanisms,²⁶ which involve either an oxygen-bound intermediate or the direct addition of CO₂ to a surface of metal hydride (Figure S5). In the latter metal-hydride mechanism, the interaction between the confined Al centers and CO₂ molecules weakens the metal-hydride bonds, thus favoring formic acid formation. However, as stated, formic acid formation may also occur via an oxygen-bound mechanism, which leads to a $^*\text{OCHO}$ intermediate²⁷ (Figure S5). The oxophilic character of Al may corroborate this latter hypothesis. In this scenario, the confinement of Al centers in the environment provided by MIL-53 may enhance the interaction between the confined Al centers with CO₂ molecules through metal-oxygen binding, thus enabling the reaction pathway via an oxygen-bound intermediate. While diverse, the two reaction mechanisms are both supportive of an enhanced interaction between Al metal centers and CO₂ molecules that is aided by the confined environment provided by the metal-organic framework.

To provide further insights on the mechanism and on the active site of MIL-53(Al) electrocatalyst, we performed experiments on Al(OH)₃ drop cast onto acid-treated carbon paper (see Supporting Information for full details) as a working electrode to electrochemically reduce CO₂. Al(OH)₃ may resemble the active site of the catalyst in the absence of the confined reaction environment provided by the metal-organic framework. Using the fabricated working electrode with Al(OH)₃, we conducted electrochemical testing at three different potentials ranging from -1.1 to -0.9 V vs RHE at which MIL-53(Al) is active for CO₂R. Interestingly, at these potentials, we found that the Al(OH)₃ basic sites yield the production of hydrogen and formic acid (Table S9, Table S10, and Figure S6). Additionally, without the uniquely tailored, confined reaction environment provided by MIL-53, the Al³⁺ metal center is not capable of reducing CO₂ to CO, which, together with formic acid, is one of the main carbon-based products from electroreduction of CO₂ catalyzed by MIL-53(Al). This finding suggests that Al centers may have intrinsic

catalytic activity for formic acid formation, yet the presence of the MOF adds changes to the catalytic environment that enable additional reaction pathways toward different products. Therefore, we can conclude that a unique reaction environment is needed to enhance CO₂ reduction capabilities to yield both CO and formic acid formation at higher total faradaic efficiency. This observation also points out the possibility to further tune the local environment around the catalytic center to impart unique catalytic activity.

Finally, to provide further insights into the catalytic performance, we evaluated the activity of the electrocatalysts by calculating the turnover frequency (TOF) for carbon-based products, CO and formic acid (Table S11). At -0.9 V vs RHE, we observed a combined TOF of 34 h⁻¹. At a potential of -1.0 V vs RHE, the combined TOF showed a 2.5-fold increase to 84 h⁻¹. Additionally, at -1.1 V, the combined TOF increased to 182 h⁻¹, which is supportive of the expected exponential correlation between applied potential and TOF (Figure S7).²⁸ The TOF for CO ranges from 12 h⁻¹ at -0.9 V vs RHE to 93 h⁻¹ at -1.1 V vs RHE. The TOF for formic acid ranges from 22 h⁻¹ at -0.9 V vs RHE to 89 h⁻¹ at -1.1 V vs RHE. Interestingly, at -1.1 V vs RHE, MIL-53(Al) shows higher CO₂R activity compared to that of COF-367-Co (165 h⁻¹), one of the best performing molecular organic frameworks for electrochemical CO₂R, at an applied potential of -0.67 V vs RHE (Table S7).¹⁷ A comparison at the same overpotential cannot be conducted because COF-367-Co started to degrade after an hour of CA at an applied potential more negative than -0.7 V vs RHE.¹³ On the other hand, MIL-53(Al) requires an activation potential more negative than -0.7 V vs RHE (Table S4). At an applied potential of -1.1 V vs RHE, MIL-53(Al) also has activity comparable to that of [Al₂(OH)₂TCPP-Co] MOF, which is one of the best performing MOFs used for aqueous CO₂R and has a maximum TOF of ~200 h⁻¹ at -0.67 V vs RHE, where it is most stable.²⁴ In addition to the reported MOFs' stability at low overpotentials, these electrocatalysts exclusively produced CO, whereas, as mentioned above, MIL-53(Al) produces both CO and formic acid.

In conclusion, we demonstrate that MIL-53(Al) can electrochemically reduce CO₂ and produce carbon-based products, reaching up to a total 40% FE of CO and formic acid at an applied potential of -1.1 V vs RHE. This study demonstrates that confining Al centers in MIL-53 frameworks can suppress HER activity and significantly enhance Al centers' ability to electrochemically reducing aqueous CO₂. By modifying the environment surrounding the metal center and providing a restricted reaction space that mimics an enzymatic cavity, this heterogeneous electrocatalyst allows MIL-53 to impart atypical capability to Al centers to reduce CO₂ to valuable carbon-based products. This electrocatalyst is active for CO₂R in aqueous solution and can be systematically tuned like homogeneous electrocatalysts, thus providing a novel route to the design of low-cost, active, and selective CO₂R electrocatalysts with enhanced CO₂ capture capability. Future directions will include studying the effect of substituents in organic linkers to develop more efficient MOFs for CO₂ capture and electroreduction, as well as in situ studies to further understand the mechanism by which the metal center in MOFs catalyzes the electrochemical reduction of CO₂ molecules to valuable carbon-based products. Future studies will be also directed to the use of MIL-53(Al) membranes as gas diffusion electrodes for efficient electrochemical CO₂R systems to convert atmospheric CO₂ to valuable carbon-based

products in gas phase, thus overcoming possible CO₂ solubility limitations in aqueous environment. Our findings open new opportunities to further explore confinement effects of metal centers for metals that traditionally favor the reduction of protons.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.9b02210>.

Synthetic procedures and characterizations of MIL-53(Al) and fabricated working electrodes, electrochemistry procedures and results, turnover frequency calculations, and control experiments (PDF)

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Author Contributions

#M.L. and A.D.R. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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