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Chapter 14

Metal-organic framework composites as electrocatalyst for carbon dioxide conversion

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Introduction

The escalating concentration of CO_2 in the atmosphere, rising from 280 ppm in the early 1800s to 405 ppm in recent years, poses a severe threat to global climate stability (Li, Wang, et al., 2020). This issue is mostly due to combustion of fossil fuels, causing global warming, ocean acidification, and the risk of catastrophic climate events. To mitigate the CO_2 impacts and prevent further global warming, it is crucial to reduce net anthropogenic CO_2 emissions to zero (Wang et al., 2021; Zhang et al., 2021). While fossil fuels are expected to remain one of the major energy sources in the foreseeable future, the development of technologies for carbon capture, utilization, conversion, and storage is essential. Among promising approaches, electrochemical CO_2 reduction reaction (CO_2RR) offers a pathway to convert CO_2 into fuels and value-added chemicals. Employing renewable energy resources, like wind and solar power, CO_2RR provides a simple way to close the carbon-neutral cycle, as shown in Fig. 14.1 (Kibria et al., 2019; Zhou et al., 2024).

Importance of the electrochemical carbon dioxide reduction reaction

Carbon dioxide or CO_2 can be converted into valuable products through various methods including chemical conversion, biological transformation, and photocatalytic and electrocatalytic reduction (Garg et al., 2020). Among these, the electrochemical CO_2RR stands out due to its:

- Compatibility with renewable energy sources like solar and wind power (Zheng et al., 2018),

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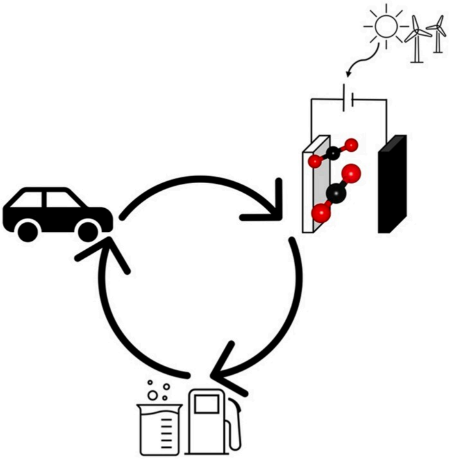

FIGURE 14.1 Schematic of carbon-neutral cycle.

- Ability to produce valuable fuels and chemicals, such as carbon monoxide, formic acid, alcohols, and hydrocarbons (Zou & Wang, 2021),
- Simple, scalable process that can operate under mild conditions (Kumar et al., 2016),
- Highly manageable reaction steps, enabling the adjustment of electrochemical parameters with a relatively high level of efficiency in conversion (Long et al., 2019),
- Products are heavily utilized in petrochemical-based processes—for example, syngas as a building block—or as fuels, thus no new infrastructure is needed (Hernández et al., 2017).

The direct electroreduction of CO_2 is particularly promising as it allows for selective conversion into products like formate, ethanol, ethylene, and syngas, which can be integrated into existing carbon recycling systems and offer opportunities for renewable energy storage (Zhang et al., 2020). Despite the stability of the CO_2 molecule due to its linear and centrosymmetric structure, which typically requires harsh conditions for conversion (Zhang et al., 2017), advances in electrocatalysis have demonstrated the potential of CO_2RR as an environmentally compatible and economically feasible solution for reducing CO_2 emissions and utilizing CO_2 as a resource.

The development of CO_2RR is although, hindered due to a number of reasons, one, as mentioned, being the thermodynamic stability of the CO_2 molecule. The stable linear structure of CO_2, with its strong C=O bonds and zero dipole moment, requires significant overpotentials to break, making the reaction kinetically sluggish (Fan et al., 2018; Gong et al., 2023). Moreover, the competitive hydrogen evolution reaction (HER) leads to challenges in achieving high CO_2RR activity and selectivity (Goyal et al., 2020). Catalysts are crucial in activating CO_2 and determining the reaction pathways. Metal-based electrocatalysts have been extensively studied and classified based on the products they could produce, such as formate, CO, hydrocarbons, or HER. However, the interaction between CO_2 and catalyst surfaces influences the efficiency of the reaction, overcoming these kinetic barriers while achieving high selectivity at low overpotentials is essential (Choi et al., 2020). Despite advances, further research is needed to design catalysts with improved structure–property relationships, especially those that can operate efficiently through multiple conversion cycles.

Metal-organic framework composites for carbon dioxide reduction reaction

Metal-organic frameworks (MOFs) are crystalline, porous structures composed of inorganic metal nodes and organic linkers (Zhan et al., 2022). MOFs, owing to their high tunability, have attracted great attention in research in recent years, including heterogeneous catalysis (see Fig. 14.2) (Liang et al., 2018). Moreover, their distinct and beneficial characteristics—such as a high surface area, customizable pore structures, and controllable, facile synthesis—make them excellent candidates for catalysts in various fields, including CO_2RR (Furukawa et al., 2013; Rowsell & Yaghi, 2005).

However, the catalytic centers in pristine MOFs are typically confined to coordinatively unsaturated metal sites, which function as Lewis acid centers, and the active groups on the organic linkers, usually consisting of acid or base sites. This limitation restricts the range of catalytic reactions that MOFs can effectively perform (Jiao et al., 2018). The structure of MOFs can be modified in several ways to improve their performances as electrocatalysts. For instance, the inherent surface of MOFs can serve as an active support for loading functional guest components, such as metal/metal oxide nanoparticles

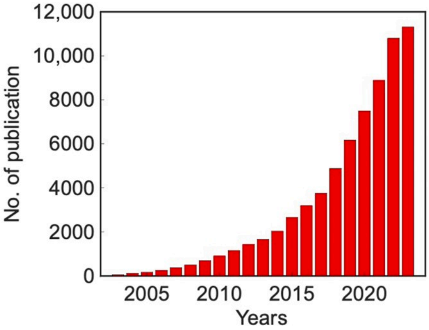

FIGURE 14.2 Number metal-organic framework-related research articles in the last 25 years using Scopus database (Adegoke et al., 2024).

(Singh et al., 2020). Additionally, given the presence of organic molecules in their structures, postsynthesis calcination of MOFs could generate high surface area functional materials, including doped and pure carbon-based nanostructures and metal/carbon (M/C) hybrids. Beyond creating functional materials directly from MOFs, various synthesis approaches enable the customization of MOFs on highly conductive substrates, such as carbon nanotubes (CNTs), hexagonally-ordered mesoporous carbon, and graphene (Vinoth et al., 2020). By effectively combining the benefits of both MOFs and functional materials, MOF composites exhibit abundant functions and significantly enhanced performance compared with the pristine MOFs, in many catalytic processes (Chen et al., 2024).

Scopes and objectives

This chapter aims to review the fundamentals of CO_2RR and explore the catalytic mechanism behind the reduction of CO_2. With a focus on MOF composites as electrocatalysts, recent advances on catalytic design and performance improvement will be discussed. The current state-of-the-art MOF composites including metal and metal oxide nanoparticle@MOFs, metal/metal oxide@pyrolyzed MOF, MOF@conductive substrates, MOF@carbon substrates, MOF@MOF, MOF@polymers, and polyoxometalates and MOF–MXene composites are discussed and their potential performance in CO_2RR are summarized. This chapter aims to highlight the benefits of MOF composites, such as flexible composition and structure, porosity, surface area, active single-site structure, and synthesis through design.

Electrocatalytic mechanism of carbon dioxide reduction reaction

Electrochemical CO_2RR is one of the most promising carbon capture and utilization strategies (Kou et al., 2022). This technology enables the production of various chemical feedstocks or materials for recycling within industrial plants, including carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4), methanol (CH_3OH), ethanol (CH_3CH_2OH), and formic acid (HCOOH) (Sajna et al., 2023). Products, such as alcohols and formic acid can be sold on commodity markets, while CO or syngas can be recycled as carbon feedstock to lower production costs and CO_2 emissions (Xu & Carter, 2019). A notable application is in iron–steel mills, where CO_2 produced from blast furnaces could be electrochemically converted to CO using low-carbon energy sources (e.g., solar or wind) to further reduce iron ores in the blast furnace, helping achieve carbon neutrality (Li, Garg, et al., 2020). CO_2RR is a multielectron process that results in variety of products depending on the numbers of electrons and protons present in the reaction which are listed in Table 14.1 (Kortlever et al., 2015). The particular product or range of products varies based on the nature of the catalytic

TABLE 14.1 Standard redox potentials for carbon dioxide reduction related half reactions (Kortlever et al., 2015; Zhang, Hu, et al., 2018).

Half reactions	E^o (V vs RHE)
$CO_2+2H^++2e^-\rightarrow HCOOH$	–0.2 (for pH < 4)
$CO_2+2H^++2e^-\rightarrow CO+H_2O$	–0.1
$CO_2+4H^++4e^-\rightarrow HCHO+H_2O$	–0.07
$CO_2+6H^++6e^-\rightarrow CH_3OH+H_2O$	0.02
$CO_2+8H^++8e^-\rightarrow CH_4+2H_2O$	0.17
$CO_2+12H^++12e^-\rightarrow CH_2CH_2+4H_2O$	0.08
$CO_2+12H^++12e^-\rightarrow CH_3CH_2OH+3H_2O$	0.09

material. For instance, 16 different products have been identified in the case of metallic copper as electrocatalyst (Gu et al., 2018).

Additionally, CO_2RR involves a complex mechanism with sluggish reaction kinetics. Given that CO_2 molecule has an extraordinarily stable linear structure, substantial negative potential is needed to turn adsorbed CO_2 molecules into $*CO_2^-$, which may further be transformed into a variety of chemicals or intermediates (Jin et al., 2021). This step is usually considered to be the rate determining step (RDS) in CO_2 conversion reaction. Another key challenge of CO_2RR is the competitive HER, which as schematically shown in Fig. 14.3, occurs at the interface of the cathode/electrolyte in aqueous media together with CO_2RR. HER occupies catalytic active sites that could otherwise interact with CO_2, significantly reducing the efficiency of CO_2 reduction (Kou et al., 2022). Moreover, as a multielectron (2–12 electrons) transfer process, with multi intermediates, CO_2 thermodynamically could be reduced to a mixture of C_1, C_2, and C_3 products, being selective toward one specific product is challenging (Jin et al., 2021). To decrease the postreaction separation costs, selectivity is the key parameter.

Given these challenges, the main focus of CO_2RR research has shifted toward finding suitable electrocatalyst materials that can efficiently and selectively convert CO_2 into valuable chemicals. The ideal catalyst would be highly active and selective, optimizing the conversion rate and favoring a specific reaction pathway. Although noble metals like Au, Ag, and Pd exhibit strong selectivity for CO_2RR over HER, their limited availability and high cost make them impractical for industrial use (Lu et al., 2018). Therefore the consensus is that effective CO_2RR electrocatalysts should be affordable, offer abundant active sites, possess high electrical conductivity, preferentially drive CO_2RR over HER, and have a large surface area, while ideally producing a single CO_2RR product.

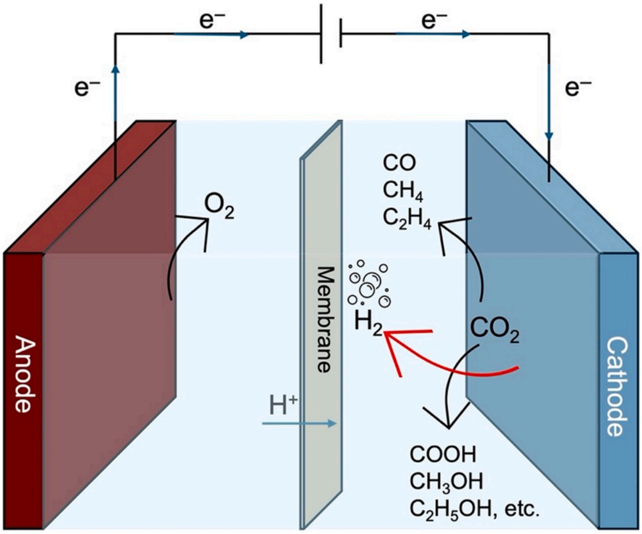

FIGURE 14.3 Schematic of a carbon dioxide reduction reaction electrolyzer (Kou et al., 2022).

Electrochatalyst materials for carbon dioxide reduction reaction

In analyzing the performance of electrocatalysts for electrochemical CO_2 reduction, key parameters include Faraday efficiency (FE), overpotential, and current density. FE quantifies the selectivity of the catalyst for producing specific products using the following equation:

$$\mathrm{FE} = n_i\, NF/jt$$

where n_i represents the number of moles of the detected product, N is the number of the transferred electrons in a reaction, F is the Faraday constant, j is the current density, and t is the time of the measurement. Overpotential reflects the difference between the applied and required thermodynamic potential to initiate the reaction. Additionally, current density, representing the production rate normalized by the electrochemical active surface area. An ideal catalyst should exhibit high current density and low overpotential to reduce the cost of scaling up the process.

Based on Hori's research (Hori et al., 1994), in which the catalytic CO_2RR for the first time was investigated, transition metal (TM) catalysts are classified into four groups:

- TMs producing CO,
- Metals producing formate,
- Metals with minimal activity, and
- Copper, which generates a range of products.

The performance of these catalysts is influenced by their electronic structural properties and surface-active sites. Further, progress in electrochemical CO_2 reduction (ECR) research has shifted from material properties to structural effects on catalyst performance. The geometry of the metal catalyst in terms of the size and the number of active centers, seems to be crucial to improving the efficiency of the process and blocking HER to promote CO_2RR (Cai et al., 2018). Nanostructured electrocatalysts demonstrate enhanced activity, stability, and selectivity compared to bulk materials due to their increased surface-active sites. Reducing the particle size, particularly for metals like copper, gold, and silver, improves current density and selectivity (Tekalgne et al., 2020; Xie et al., 2018). Moreover, while TMs have shown high FE for CO_2RR, their high electron mobility under reaction conditions along with low long-term stability and high price, hamper their industrial utilization. Thus TM oxide-derived catalysts are explored by increasing surface roughness and/or providing subsurface oxygen species to improve long-term stability and increase charge transfer capabilities, respectively (Tayyebi et al., 2018). For instance, it has been shown that the oxygen vacancy in Cu_2O crystals, is the active site for C_2H_4 formation, indicating that oxide catalysts could be useful for selective production of C_2-plus (C_{2+}) products (Handoko et al., 2016). Furthermore, nonmetallic catalysts have also been reported in literature, such as MoS_2 showing comparable efficiency in both HER and CO_2RR. The molybdenum-terminated edge of MoS_2 exhibits high activity in reducing CO_2 to CO, especially in an ionic liquid-modified electrolyte (Lu & Jiao, 2016). As an example, Asadi et al. (2014) demonstrated that bulk Mo_2S can achieve equal or superior CO_2 reduction performance compared to state-of-the-art metallic catalysts. Density functional theory (DFT) calculations revealed that Mo edge atoms, with their d-orbital electron states near the Fermi level, are responsible for the high catalytic activity, though further experimental studies are needed to validate these findings. Recent advancements in nanostructure synthesis and the manipulation of compositional and structural properties have expanded the capabilities of metallic and metal oxide nanomaterials, paving the way for more efficient and selective CO_2RR catalysts.

Mechanistic study of carbon dioxide reduction reaction

Over the years, both experimental and theoretical methods have been employed to propose mechanisms for the reduction of CO_2 in various products. These methods include theoretical DFT as well as several in situ techniques, such as Raman spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS), all of which help identify the intermediate species formed during the reduction process (Lu & Jiao, 2016). CO_2 is an amphoteric molecule with a Lewis acidic carbon center and basic oxygen atoms, making it more effective as an electron acceptor than a donor.

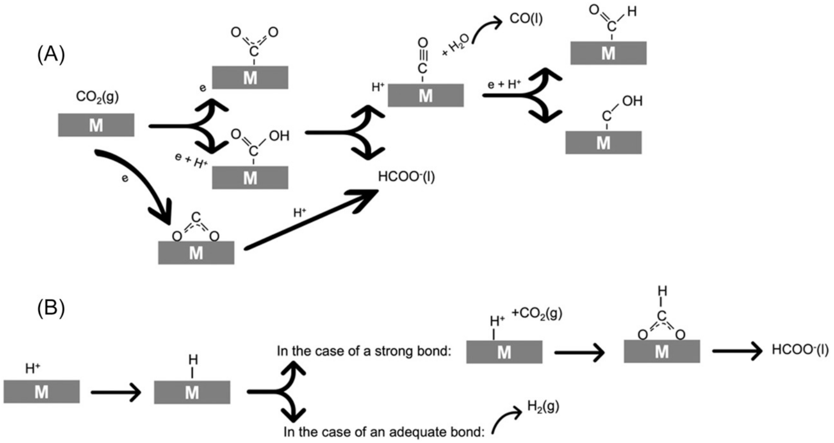

FIGURE 14.4 Plausible pathways of carbon dioxide reduction reaction (M = metal). (A) Pathways to carbon monoxide and formic acid. (B) Pathway of carbon dioxide reduction to formate and hydrogen evolution reaction in the case of H^+ adsorption on the metal surface (Saha et al., 2022). *http://doi.org/10.1021/acs.accounts.1c00678*, *http://pubs.acs.org/journal/achre4*

This electrophilic nature of carbon dominates in CO_2RR, where most reduction pathways involve either the binding of CO_2 to the metal center (see Fig. 14.4A) of the catalyst or insertion into a metal–hydride bond (see Fig. 14.4B) (Saha et al., 2022). C_2 production pathway, the critical step for forming the C–C bond involves CO dimerization, resulting in the formation of a *OCCO– intermediate. Proton transfer occurs after the negatively charged CO dimer has been adsorbed, which dimerization considered to be the RDS in the C_2 production process (Kortlever et al., 2015).

Metal-organic framework composites as electrocatalysts

A composite is a solid material made up of two or more distinct substances, each maintaining its own characteristics while enhancing the overall properties of the combined material. MOFs are a class of highly porous materials consisting of inorganic ions or clusters linked to organic ligands. These structures form a framework with an extraordinarily large surface area, reaching thousands of square meters per gram of material (Furukawa et al., 2013). Although an important research stream on MOFs focuses on synthesizing novel two/three dimensional structure using innovative approaches, a new research trend investigates the combination of MOFs with a variety of nano- and microparticles known as MOF composites (Yu et al., 2017). MOF composites are combination of functional materials, such as carbon substrates, nanoparticles, polymers, and enzymes with MOF which have further improved physico-chemical properties like mechanical stability, conductivity, and catalytic performance. The reported MOF composites through the years are:

- Metal and metal oxide nanoparticles (Falcaro et al., 2016),
- Polyoxometalates (POMs) and polymers (Kalaj et al., 2020),
- Graphene and CNTs (Yan et al., 2020),
- Enzymes and bio molecules (Lian et al., 2017),
- Quantum dots (Wu, Liu, et al., 2020).

In the context of CO_2RR electrocatalysis, to compensate for the limited electrical conductivity of pure MOFs, MOF composites are utilized. In most cases, pristine MOFs are employed as supporting materials for a variety of species, including metal/metal oxide/metal complexes nano/microparticles. This is mostly due to high porosity of MOFs which leads to maintaining higher active surface area for the reaction. Although many MOFs have been directly used as a precursor to derive catalysts for CO_2RR (Deng et al., 2010; Liu et al., 2023).

Recent advances on metal-organic framework composites for electrocatalytic carbon dioxide reduction reaction

In this section, different classes of MOF composites will be discussed, with a focus on their applications in CO_2RR and their performance as electrocatalysts.

Pristine metal-organic frameworks

It is well known that downsizing metal nanostructures into atomically distributed centers, known as single atom catalysis, is an effective approach for metal catalysts (Li, Wang, et al., 2020). MOFs, due to their metal atomic centers, are categorized as single-atom catalysts for CO_2RR. MOFs tend to produce lighter products like CO and formic acid because their complex structure and single-atom dispersion hinder C–C coupling in most cases, limiting the formation of heavier C_{2+} products. Moreover, the coordination environment of the metal active sites, influenced by MOF linkers, plays a critical role in catalytic selectivity (Kornienko et al., 2015). By altering the coordination environment using different linkers, MOFs can break the linear scaling relationship existing between key intermediates, making it possible to tune selectivity toward specific products. Thus tunable coordination environment of MOFs offers a unique advantage for controlling product formation in CO_2RR (Ko et al., 2018). However, despite their advantages in improving the selectivity, the use of MOFs in electrocatalyst applications has been hindered by poor conductivity, therefore low activity (Downes & Marinescu, 2017). This issue arises mainly from the presence of carboxylate linkers in the multidimensional frameworks. The high electronegativity of the oxygen atoms in these carboxylates increases the potential barrier for electron transfer through the organic linkers (Sun et al., 2016). As a result, the overlap between oxygen atoms and metal d-orbitals is reduced, causing the low conductivity typically seen in most MOFs (Xie et al., 2020). This limitation leads to the production of different MOF composites to tune the conductivity and electrochemical activity.

Metal-organic frameworks as supports

This group of MOF composites has been extensively researched for CO_2RR, utilizing materials in which the MOF acts as a porous support with active catalytic sites, such as metal and metal oxide nanoparticles (MNPs) deposited on its surface (Zhao et al., 2018). The incorporation of MOFs, improves the electrocatalytic performance of MNPS due to their porous structures and large specific surface area. Cu_2O particles, known for their tunable crystal facets and relatively stable bulk-phase structure, are considered promising candidates for studying the mechanism of CO_2 reduction. However, significant hydrogen production during the electrocatalytic process often results in a reduced FE for hydrocarbons. To improve the overall hydrocarbon FE, it is crucial to enhance the CO_2 adsorption capacity of Cu_2O. The Cu_2O@Cu-MOF catalyst, when used as an electrocatalyst for the electrochemical reduction of CO_2, demonstrates exceptional performance, achieving a total FE for hydrocarbons (CH_4 and C_2H_4) of 79.4%, with a notable FE of 63.2% for CH_4 (Tan et al., 2019). The multifunctionality of the synthesized Cu_2O@Cu-MOF, encompassing adsorption, activation, and catalysis, stems from the synergistic interaction between Cu-MOF and Cu_2O.

In addition, metallic nanoparticles are recognized as suitable catalysts for CO_2RRs; however, their tendency to agglomerate diminishes their catalytic efficiency (Liu et al., 2023). MOFs, with their high surface area and notable porosity, can prevent this agglomeration and enhance the catalytic performance of NPs encapsulated within them. Silver is one of the most extensively studied metals for ECR, producing CO as the main product due to weak CO adsorption on its surface (Zhang, Jin, et al., 2018). Both CO_2 electroreduction to CO and the competing HER take place concurrently on Ag NPs. In this regard, Jiang et al. (2017) investigated the Ag/ZIF-7 MOF composite as a CO_2 electroreduction catalyst and higher CO FE and current density was observed (80.5% and 26.2 mA/cm^2 at −1.2 V) compared to its pristine components. This improved performance is attributed to the large accessible surface area and the synergistic interaction between Ag nanoparticles and ZIF-7 MOF.

As another example of MOF supports, in a study by Yi et al. (2020) uniform Cu_2O(111) NPs were fabricated on a conductive CuHHTP (HHTP= 2,3,6,7,10,11-hexahydroxytriphenylene) framework via electrochemical treatment, resulting in conversion of some Cu^{2+} centers within MOF into 3.5 nm Cu_2O NPs with exposed (111) crystal planes. The Cu_2O@CuHHTP composite demonstrated high conductivity and excellent performance in CO_2 electroreduction to CH_4, achieving 73% FE and 10.8 mA/cm^2 partial current density. The small size of the MNPs, exposed crystal planes, and released hydroxyl groups (OH^-) from the HHTP ligand contributed to the high CH_4 selectivity, while the CuHHTP support enhanced electron transfer for better current density. Furthermore, in a more recent study zirconium-based PCN-222 MOFs with metalloporphyrin Cu centers and incorporated gold nanoneedles were successfully synthesized using ligand carboxylates as reducing agents. Compared to similar MOF components, AuNN@PCN-222(Cu) exhibited a significantly enhanced ethylene production with a FE of 52.5% (Xie et al., 2022) (Fig. 14.5A–D). Some of the other metal/metal oxide–MOF composites and their CO_2RR performance are listed in Table 14.2.

Metal/metal oxide MOF composites could be synthesized with various methods, such as liquid impregnation. In this method, desolvated MOFs are soaked in metal precursor solutions and then reduced to form MNPs within the pores. Incipient wetness impregnation involves using a solution with a volume equal to the MOF's pore volume for precise control over metal loading. Gas-phase infiltration (MOCVD) is another method which exposes desolvated MOFs to volatile metal precursors under vacuum, followed by reduction or decomposition to produce MNPs. The double solvent method employs both hydrophilic and hydrophobic solvents to minimize MNP aggregation on the MOF surface. Redox-active MOFs use the inherent redox properties of MOF to reduce metal ions into nanoparticles without additional reducing agents. Photochemical reduction leverages light to facilitate MNP formation within MOFs, while colloidal deposition and urea precipitation methods, though effective, often result in surface aggregation of MNPs (Zhu & Xu, 2014). One method of preparing metal-based MOF-derived composites is pyrolysis or carbonization of the pristine MOF.

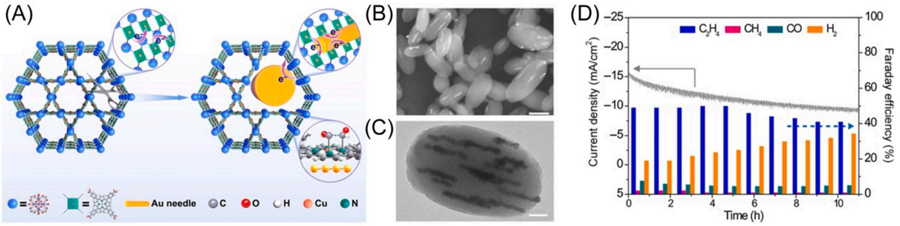

FIGURE 14.5 (A) Incorporation of Au nanoneedles into PCN-222(Cu) to alter the charge transfer and pathway of the carbon dioxide reduction reaction; (B) Scanning electron microscope (SEM) image of the composite (scale bar: 250 nm); (C) Transmission electron microscopy (TEM) image of the composite (scale bar: 50 nm); (D) Chronoamperometry stability tests for AuNN@PCN-222(Cu) at −1.2 V vs. RHE.

TABLE 14.2 List of studied metal/metal oxide–metal-organic framework composites and their performance for carbon dioxide reduction reaction (Adegoke et al. (2024), Liu et al. (2023), Huang et al. (2023).

MOF composite	Electrolyte	Potential	Product(s)	FE (%)	Reference
Ag/Co-MOF	0.1M $KHCO_3$	–1.8 V versus SCE	CO	55.6	Zhang, Jin, et al. (2018)
CuO/Cu-MOF	0.1M $KHCO_3$	–1.1 V	C_2H_4	50	Skoulidas (2004)
Ag@Al-PMOF	0.1M $KHCO_3$	–1.1 V	CO	55.8 ± 2.8	Guntern et al. (2019)
Cu_2O/Cu-MOF	0.1M $KHCO_3$	–1.71 V versus RHE	CH_4	63.2	Tan et al. (2019)
Cu_2O/Cu-MOF	0.1M $KHCO_3$	–1.71 V versus RHE	CH_4	63.2	Tan et al. (2019)
Bi_2O_3/2D-Zr-TATB (triaminotrinitrobenzene)-MOF	0.5M $KHCO_3$	–0.97 V versus RHE	HCOOH	≈85	Liu et al. (2022)
SnO_2/2D-Zr-TATB-MOF	0.5M $KHCO_3$	–0.97 V versus RHE	HCOOH	≈35	Liu et al. (2022)
In_2O_3/2D-Zr-TATB-MOF	0.5M $KHCO_3$	–0.97 V versus RHE	HCOOH	≈45	Liu et al. (2022)

FE, Faraday efficiency; *MOF*, metal-organic framework; *2D*, two-dimensional.

Carbonization is a process frequently used to produce carbon rods and other carbon nano-sized materials. In this process, by increasing the temperature, bonds between carbon and other elements (i.e., O, N, S, and TMs) in the organic building unit within MOF structure, break. These elements leave the material, allowing carbon atoms to bond with each other, resulting in a framework composed of pure carbon (Wang et al., 2011). Metallic centers, on the other hand, do not evaporate, resulting in a TM-decorated porous carbon framework. Since pure carbon structures have much higher electrical conductivity than organic linkers, the metal-doped nanoporous carbon exhibits higher conductivity than pristine MOF. Additionally, nanoporous carbons are known for their chemical stability (Bhadra et al., 2019). To ensure a desired structure, proper carbonization settings are crucial. Factors, such as ramp-up temperature speed, carbonization temperature, process duration, and inert gas flow influence the final product, among which, the holding temperature is the most significant (Abdelkader-Fernández et al., 2020).

Fig. 14.6 represents the scanning electron microscopic images of carbonized HKUST-1 MOF known as Cu-BTC, at the holding temperature of 650°C. As can be seen, the copper clusters form on the surface of the carbon framework with similar morphology as the pristine MOF crystals. These clusters act now as catalytic sites whereas the carbon framework in the substrate helps with better charge transfer resulting in higher current density than the pristine MOF. In this regard, Zhao et al. (2017) carbonized Cu-BTC at 900°C, 1000°C, and 1100°C. The results showed that the 1000°C sample has an FE of about 45% for CH_3OH and 27 % for C_2H_5OH at a potential of –0.3 V versus standard hydrogen electrode. The electrode was made of an ink containing active material, high purity water, and Nafion deposited on commercial carbon paper using a spin coating technique. A two-compartment electrolysis cell was filled with 0.1 M $KHCO_3$ electrolyte and equipped with a Nafion membrane for ion transport. They also found that with increasing

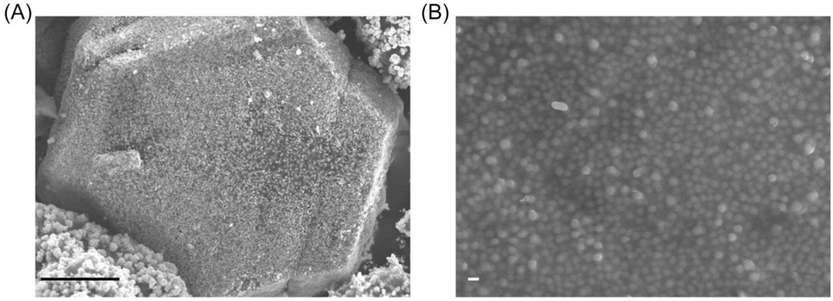

FIGURE 14.6 SEM figures of carbonized Cu-BTC at 650°C in different magnifications. (A) 10 μm and (B) 100 nm. Formation of copper clusters smaller than 100 nm on the surface of metal-organic framework is visible (results from our group) (Zhao et al., 2017).

temperature, the pore size and thus the specific surface area decreases. Nevertheless, the 1000°C sample showed better performance for CO_2RR than the 900°C one. This was attributed to the lower charge transfer resistance of the 1000°C sample, showing that the specific surface area is not the only important factor to consider for a CO_2RR catalyst when considering the charge transfer parameter.

Among the electrocatalytic materials produced by MOF template carbonization for CO_2RR, ZIF-derived carbons are predominant, with those derived from ZIF-8 being particularly noteworthy. In studies on carbonized MOFs, since zinc is not an electrocatalytically active metal for CO_2RR, it is removed during high-temperature carbonization. As a result, various strategies have been developed to incorporate active TM into the structure. Consequently, several studies have combined Fe with ZIF-8 to produce Fe-containing N-doped carbon electrocatalysts for CO_2-to-CO conversion (Abdelkader-Fernández et al., 2020). This material achieved 97% FE for CO at –0.56 V versus RHE, whereas its Fe-free counterpart reached 100% FE(C)O but required a higher potential of versus 0.86 V versus RHE.

Metal-organic frameworks on conductive substrates

One of the limitations of MOFs is their low electrical conductivity, which restricts their electrochemical applications. Graphene which is a one atom thick carbon lattice with a cellular structure, offers exceptional electronic conductivity and a large surface area (Peng et al., 2022). These properties enhance interactions with MOFs, making them an ideal anchor material with significant potential for improving the performance of MOF-based electrocatalysts (Li & Huo, 2015). Moreover, the two-dimensional (2D) nonmetallic semiconductor g-C_3N_4 has garnered significant attention in recent scientific research. g-C_3N_4 possesses remarkable characteristics, such as excellent physicochemical properties, an ideal band gap, a distinctive optoelectronic structure, high stability in air (up to 600°C), low cost, and abundant availability in nature. Although this specific composite has mostly been utilized as a photo(electro)catalyst in CO_2RR due to its small bandgap (Usman et al., 2022). In addition to these materials, CNTs are emerging as another highly promising candidate for functional applications. CNTs are highly structured carbon allotropes with a large aspect ratio. They exist in two primary forms: single-walled CNTs, with diameters ranging from 0.4 to 2 nm, and multiwalled CNTs, with diameters spanning 2–100 nm (Kempahanumakkagari et al., 2018). Both types are characterized by exceptional tensile strength, ultra-lightweight nature, and remarkable chemical and thermal stability. One example of this composite is [PCN-222(Fe)/CNTs], synthesized via a solvothermal method by incorporating iron porphyrin-centered PCN-222(Fe) onto CNTs. This composite exhibited excellent performance in CO_2 electroreduction, achieving a FE of 90% for CO production at an overpotential of –0.6 V, at the optimal ratio of m(Fe-TCPP):m(CNTs)=1:30. The enhanced performance was attributed to the conductive support provided by CNTs, which increased electrical conductivity and improved the overall structure of the MOF composite (Xu et al., 2022).

In another example, a $ReL(CO)_3Cl$ (L=2,2-bipyridine-5,5-dicarboxylic acid) thin film was grown on the surface of a fluorine-doped tin oxide (FTO) conductive glass electrode, exhibiting 93% ± 5% Faradaic efficiency for CO production, which is the highest reported so far and exceeds those reported for covalent organic frameworks thin films (Ye et al., 2016). In the context of MOF–FTO composites, in a study by Kornienko et al. (2015), examination of a cobalt–porphyrin MOF, $Al_2(OH)_2$TCPP-Co (TCPP-H_2—4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) revealed a selectivity for CO production in excess of 76% and stability over 7 hours (Fig. 14.7A and B).

Metal-organic frameworks on porous materials

MOFs could be also incorporated inside other porous structures, such as porous carbon, Ni foam, and in the form of core shell with other MOFs (Liu et al., 2021). Considering the inherent diversity of MOFs, combining different MOFs offers significant potential for advancements in synthesis, structural design, and performance applications (Xue et al., 2019). Building MOFs@MOFs is not only of interest for structural research but also an efficient approach to boost application performance by harnessing the synergistic properties of two distinct MOFs. In a 2020 review study by Wu, Liu et al., it is well discussed that for selective catalysis, many MOFs@MOFs catalysts are typically designed with active metal nanoparticle-loaded MOFs as core materials and MOFs with tailored pore sizes serving as the filtering shell (Wu, Liu, et al., 2020). While limited research has focused on creating selective MOFs@MOFs catalysts electrochemical CO_2RR, this approach holds significant potential for further development. An example of MOF@MOF composites is CuBi-based MOFs (HKUST-1 and CAU-17) supported in gas diffusion electrodes showed the FE of 28.3% for production of ethanol. The findings initially revealed that incorporating bismuth as a cocatalyst reduced the required overpotential, indicating a synergistic interaction between copper and bismuth in the CO_2 reduction pathway (Albo et al., 2019). A similar case applies to the incorporation of MOFs into porous carbon materials, such as carbon black. In a study by Raut et al., it was demonstrated that MOF-5 on carbon black supports exhibits significantly higher conductivity compared to either pristine MOF-5 or carbon black alone in alkaline solutions, which could be advantageous for CO_2RR (Raut et al., 2021). Another example of a MOF–porous carbon composite is a recent study by Sathiyan et al. (2023), which demonstrates the high efficiency of a composite of HKUST-1 and activated carbon as an electrocatalyst for CO_2 reduction. In this study, HKUST-1 NPs were embedded into a conductive porous carbon, creating strong π–π interactions between the aromatic linkers of

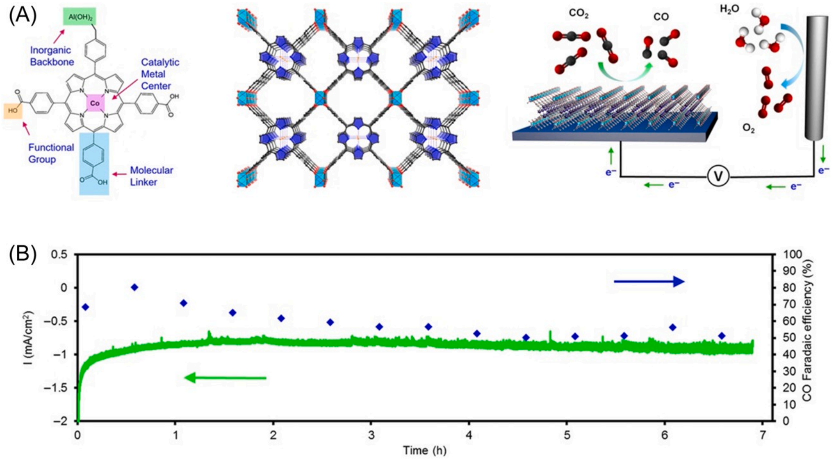

FIGURE 14.7 (A) The organic building units, in the form of cobalt-metalated TCPP, are assembled into a 3D metal-organic framework, $Al_2(OH)_2$TCPP-Co, with variable inorganic building blocks. In the structure (middle), each carboxylate is bound to the aluminum inorganic backbone. The metal-organic framework is integrated with a conductive substrate to form a functional carbon dioxide electrochemical reduction system (right). (B) Stability of the metal-organic framework catalyst evaluated by chronoamperometric measurements and faradaic efficiency (Kornienko et al., 2015).

MOF and the graphitic carbon, leading to a lateral conductivity of 17.2 S/m. The composite demonstrated a high electroactive surface coverage of 155 nmol/cm² and exhibited excellent catalytic performance under CO_2-saturated conditions. The onset potential for CO_2 reduction was –0.31 V versus RHE, with a high reduction current density of –18 mA/cm² at –1.0 V. Additionally, the composite remained stable over 12 hours of operation, with formic acid identified as the main product.

Metal-organic framework-polymer/polyoxometalate composites

The commercialization of MOFs has been hindered by their crystalline or microcrystalline forms (e.g., powders), which limit their integration into various technologies (Chen et al., 2021). To address this, efforts have been made to develop processable materials that combine MOFs with polymers, enhancing their practical utility. These materials are being developed using two approaches: a top-down method where MOFs are synthesized first and then integrated into polymers, and a bottom-up method where hybrid materials are formed concurrently with MOF synthesis. Common polymers used in the synthesis of MOF/polymer composites are shown in Fig. 14.8. The use of MOF/polymer composites in CO_2RR requires more scientific attention. In a

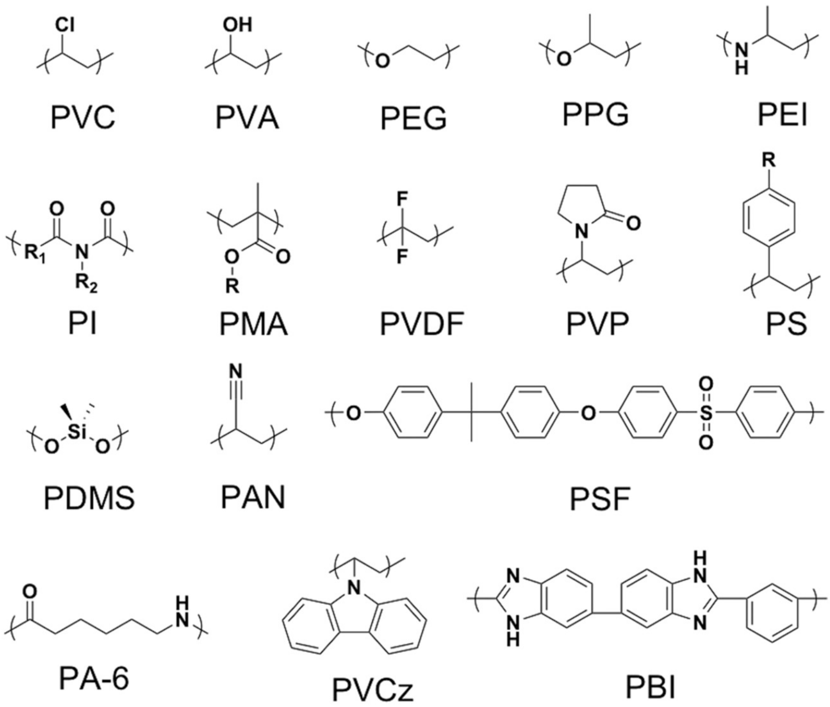

FIGURE 14.8 Common polymers used in the synthesis of metal-organic framework-polymer hybrid materials (Kalaj et al., 2020).

2020 study, Yang et al. used a Ni–MOF–polymer composite as a precursor for pyrolysis to prepare a catalyst consisting of highly dispersed Ni–N_x species. The study demonstrated that incorporating a polymer within the MOF pores helps stabilize the collapsible MOF structure and prevents nickel aggregation during pyrolysis. This process results in the formation of single-atom nickel species within nitrogen-doped carbon, significantly enhancing activity, CO selectivity, and stability (Deeraj et al., 2023; Yang et al., 2020).

POMs are nanoscale, discrete metal-oxygen clusters composed of earth-abundant metals and exhibit unique structures. Often referred to as electronic sponges (Liu et al., 2021). POMs can hold a large number of electrons and engage in reversible, stepwise multielectron transfer processes while maintaining their structural integrity. Incorporating POMs into MOF channels can shorten the electron transport distance and improve the efficiency of electron transfer from the electrode to the active sites of the electrocatalyst, thereby enhancing the effectiveness of CO_2RR (Du et al., 2022; Li et al., 2019). Research into POMs and MOFs is currently gaining momentum due to their unique structural features, catalytic potential, and other inherent properties. For instance, due to their high electron mobility, PCN-222(Co) has increasingly been selected as a supportive framework for Co-metalloporphyrins, which consist of active single cobalt metal sites and conjugated π-electron porphyrin planes (Liu et al., 2023).

As an example, a directional electron-transfer channel was successfully constructed at a molecular level by synthesizing mixed-valence POM@MOFs composites through postmodification. The combination of POMs and catalytic single-metal site Co in the porphyrin-based MOF resulted in a composite with enhanced electron-transfer efficiency. Catalytic CO_2RR using H-POM@PCN-222(Co) exhibited a high FE for CO (96.2%) and satisfying stability for over 10 hours. DFT calculations confirmed that POM introduction accelerated multielectron transfer, enriching the electron density at the Co center and reducing RDS energy in the CO_2RR process (Sun et al., 2021).

Furthermore, assembling reductive POMs and metaloporphyrins to construct MOFs is shown to be promising candidates to enhance the efficiency and selectivity of CO_2RR. POM-metalloporphyrin organic frameworks (PMOFs) facilitate efficient electron transfer in electrocatalytic CO_2 reduction due to the direct communication between the POM unit and metalloporphyrin. As reported in a novel study by Wang et al. (2018), Co-PMOF stands out, selectively converting CO_2 to CO with a remarkable 99% FE, at –0.8 V (Fig. 14.9), and excellent stability for over 36 hours. Moreover, DFT calculations highlight the superior performance of Co-PMOF and the synergistic effect between reductive POM and Co-porphyrin.

Metal-organic framework/MXene composites

MOFs offer the combined benefits of both heterogeneous and homogeneous catalysts. Integrating MOFs with conductive 2D MXene nanosheets can further enhance their electrocatalytic efficiency. The MOF/MXene composites exhibit superior performance due to their increased surface area, greater number of accessible active sites, enhanced catalytic activity, and improved stability (Xu et al., 2023). An example of this is Fe–Nx/N/Ti_3C_2, which was synthesized by pyrolyzing MOFs supported on Ti_3C_2 MXene. The negative charge of Ti_3C_2 MXene allows MOFs to anchor firmly on its surface, preventing aggregation, while its metallic conductivity enhances electron transfer. The strong interaction between Fe–N_x–C and Ti_3C_2 MXene also helps regulate the catalytic activity (Gu et al., 2022). However, there are limited studies on the use of MOF/MXene composites for CO_2RR; nevertheless, this example highlights the high potential of these materials.

Conclusion and outlook

MOF composites, due to their unique structural features, are increasingly being developed to replace conventional electrocatalysts for converting CO_2 into

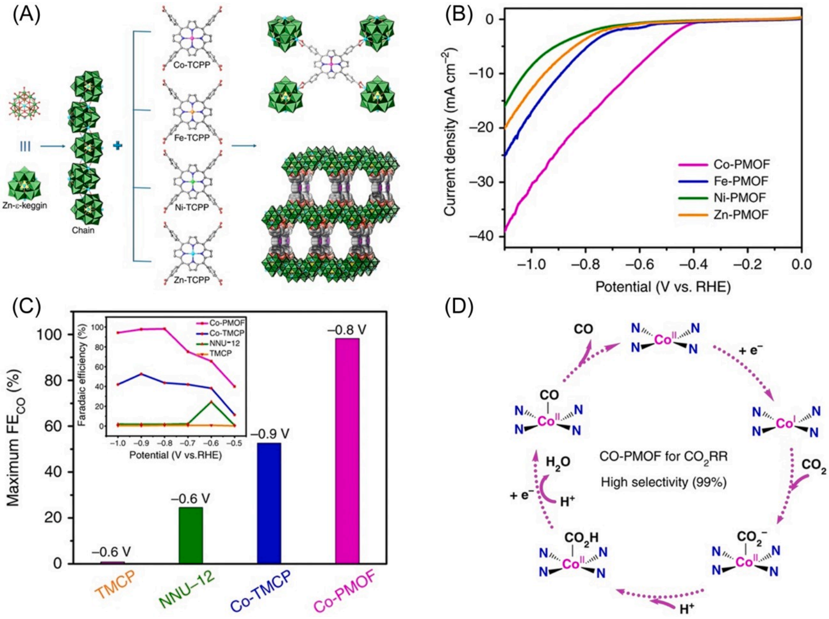

FIGURE 14.9 (A) Schematic illustration of the structures of M-polyoxometalate-metalloporphyrin organic frameworks (PMOFs) (M=Co, Fe, Ni, Zn). Linker=TCPP and zigzag polyoxometalate chains, (B) Linear sweep voltammetric curves showing electrocatalytic performances of different composites, (C) Maximum FECO of different composites, and (D) Proposed mechanistic scheme for the carbon dioxide reduction reaction on Co-PMOF (Wang et al., 2018).

valuable products. While the application of MOF composites for CO_2RR has shown promise, there are not many studies on this topic. In this regard, a better understanding of the performance of MOF composites as electrocatalysts will help in designing more efficient compounds. Moreover, most CO_2RR studies using MOF composites have only been conducted in laboratories, and scaling this process to an industrial level is crucial for addressing atmospheric CO_2. Notably, MOF composite electrocatalysts are considered cost-effective catalyst materials. Thus further studies are essential to refine these materials for ECR. Current research indicates that MOF composites have significantly improved electrocatalytic performance for CO_2RR compared to conventional catalyst materials. Despite advancements, their use in this area is still in the early stages. Practical applications are hindered by challenges, such as limited recycling and stability under certain reaction conditions. Therefore, the development of MOF composites with more stable structures is necessary for broader applications.

Additionally, while many methods for synthesizing MOF composites have been reported, each comes with limitations. It is essential to explore new, versatile approaches to constructing functional MOF materials, particularly for controlling guest species within MOF matrices. Significant attention has also been given to MOFs that are responsive to environmental stimuli, opening up the possibility of creating smart, responsive electrocatalysts. Further research will clarify the relationship between the structure and function of MOF composites and aid in the design of innovative materials for CO_2RR and other energy conversion applications.

In summary, addressing the current challenges through more in-depth research will pave the way for the development of low-cost, high-performance MOF composites. This progress will ultimately enable benchmark performance for ECR in practical renewable energy applications.

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