
Ana Sofia Varela,* Wen Ju, and Peter Strasser*

The CO₂ electrochemical reduction reaction (CO₂RR) is a promising technology for converting CO₂ into chemicals and fuels, using surplus electricity from renewable sources. The technological viability of this process, however, is contingent on finding affordable and efficient catalysts. A range of materials containing abundant elements, such as N, C, and non-noble metals, ranging from well-defined immobilized complexes to doped carbon materials have emerged as a promising alternative. One of the main products of the CO₂RR is CO, which is produced on these catalysts with selectivities comparable to those of noble metal catalysts. Furthermore, other valuable products, such as formic acid, hydrocarbons, and alcohols, have also been reported. The factors that control the catalytic performance of these materials, however, are not yet fully understood. A review of recent work is presented on heterogeneous nitrogen-containing carbon catalysts for the CO₂RR. The synthesis and characterization of these materials as well as their electrocatalytic performance are discussed. Combined experimental and theoretical studies are included to bring insight on the active sites and the reaction mechanism. This knowledge is key for developing optimal catalyst materials that meet the requirement in terms of activity, selectivity, and stability needed for commercial applications.

1. The CO₂ Electrochemical Reduction

Direct CO₂ electrochemical reduction reaction (CO₂RR) is a promising alternative enabling converting CO₂ into carbon based chemicals and fuels, using surplus electricity from renewable sources.

1.1. The Importance of the CO₂ Electrochemical Reduction

As the levels of carbon emissions continue to rise, it has become evident that a combination of efforts including the use of renewable energies (such as wind and solar) and the development of carbon, capture, utilization, and storage (CCUS) technologies is needed to reduce the levels of atmospheric CO₂.[1] Carbon utilization implies that CO₂ is not only stored but it also serves a function. This function can be directly utilizing it, for example as a solvent, or converting it to other products such as fuels and chemical precursors.[2]

The cathodic process of the CO₂RR is normally coupled to the oxygen evolution reaction at the anode side (Figure 1a), and hence is often referred to as water–CO₂ co-electrolysis.

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]  
\[ (1) \]

Alternatively, CO₂RR could be coupled to the anodic chlorine production, which is technologically used for Cl₂ production from NaCl via aqueous electrolysis.

\[ 2Cl^- \rightarrow 2Cl_2 + 2e^- \]  
\[ (2) \]

Today, this process is the largest scale electrosynthesis, and as such it is a huge consumer of electricity.[6] During the chloralkaline process Cl₂ is produced in the anode according to reaction 2, while H₂ and caustic soda are generated as co-products at the cathode. Instead, coupling CO₂RR to the Cl₂ production...
would allowed to reduce CO$_2$ to valuable carbon-based products, while producing Cl$_2$ at the anode. As a result, this would result in a highly efficient process in which valuable products are formed in both compartment (Faradaic efficiency up to 200%) (Figure 1b). Furthermore, if high purity CO streams are produced on the cathode side, it could be combined with the Cl$_2$ generated in the anodic chamber to produce phosgene, which is a highly valuable chemical used as building block for synthesis of various types of chemicals, including polymers. This direct CO/Cl$_2$ coproduction would replace the very CO$_2$ emission-intensive CO production from methane, which is currently operated in chloralkaline plants where phosgene is a critical intermediate for the production of polyurethanes and polycarbonates.

At the current stage, the technological viability of CO$_2$RR is still facing several crucial limitations such as the low selectivity of the process. As the CO$_2$RR is usually carried out in aqueous electrolytes, it is accompanied by the competitive process of the hydrogen evolution reaction (HER)

$$\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E_0 = 0 \text{ V vs RHE} \quad (3)$$

This process is kinetically favored over the production of C-based products from CO$_2$ reduction. Moreover, unlike the HER or oxygen evolution reaction (OER) that are single product reactions, the CO$_2$ can be reduced to different carbon base products such as formate, CO, hydrocarbons, and alcohols

$$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O} \quad E_0 = +0.08 \text{ V vs RHE} \quad (4)$$

$$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E_0 = +0.17 \text{ V vs RHE} \quad (5)$$

$$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{C}_2\text{H}_4\text{OH} + 3\text{H}_2\text{O} \quad E_0 = +0.08 \text{ V vs RHE} \quad (6)$$

$$3\text{CO}_2 + 18\text{H}^+ + 18e^- \rightarrow \text{C}_2\text{H}_4\text{OH} + 5\text{H}_2\text{O} \quad E_0 = +0.09 \text{ V vs RHE} \quad (7)$$

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E_0 = -0.11 \text{ V vs RHE} \quad (8)$$

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH} \quad E_0 = -0.22 \text{ V vs RHE} \quad (9)$$

In addition, the high kinetic barrier associated with the reduction of CO$_2$, combined with the multiple proton/electron transfers needed for hydrocarbons formation, results in high overpotentials for the CO$_2$RR, which translate to significant energy loses.$^{[7,8]}$

Cathodic reactions versus reversible hydrogen electrode (RHE).

1.2. Catalyst for the Electrochemical CO$_2$ Reduction

The product distribution of the CO$_2$RR is greatly affected by the cathode materials,$^{[9]}$ and therefore, several studies have been carried out in order to find the optimal catalyst for the process.$^{[10]}$ For instance, when working with materials known to be good HER catalyst, such as Pt, the main product is H$_2$.

Copper has been found to be a particular interesting material on which CO$_2$ is directly reduced to alcohols and hydrocarbons.$^{[11]}$ According to the reactions thermodynamics, those products should be formed at similar potential as dihydrogen. In practice, however, hydrocarbon production on Cu takes
place at high overpotentials, producing a mixture of products. Therefore, despite copper’s unique catalytic performance, it is not an optimal catalyst for CO2RR. An ideal candidate for this process should exhibit high catalytic activity (i.e., high current density) to selectively reduce CO2 into one particular product at low overpotential. In addition, it should have a low activity toward competing processes like the HER and be chemically and mechanically stable under reaction conditions.[12]

The high overpotentials (energy loss) required for hydrocarbons production can be partly attributed to the multiple proton/electron transfers involved in the process. In particular, for methane formation, the proton coupled electron transfer (reduction) of CO has been proposed as the rate limiting step, while for C2 products, a decoupled proton–electron transfer coupled to a CO dimerization was suggested as the limiting step.[13,14] In contrast to hydrocarbon formation, the CO2 reduction to CO requires only the transfer of two electrons and two protons, making it a significantly less hindered process. The formation of CO is usually accompanied by HER resulting in syngas production, which can be used as feedstock in synthetic fuels production via the catalytic Fischer–Tropsch process.[15] Other industries as the previously mentioned chloralkaline electrolysis-based polyurethane and polycarbonate production, however, would need the production of CO pure streams as a chemical precursor (Figure 1b).

Catalysts based on noble metals such as gold and silver are known to selectively reduce CO2 to CO at low overpotentials. Already in the 1980s, Hori et al. showed that gold reduces CO2 to CO at −1.10 V versus normal hydrogen electrode (NHE) with a faradaic selectivity of 91% and a partial current density of 3.7 mA cm−2 making it the most efficient CO2 to CO electrocatalyst in its polycrystalline form.[16] More recently, studies on nanostructured gold catalyst have also shown promising results achieving higher current densities.[17–19] Nevertheless, given the low abundance and high price of gold, it is not an appropriate candidate to be produced for large scale investment. For this reason, it is necessary to find materials with a comparable catalytic performance to that of gold, but substantially less expensive and more abundant. With this purpose Lu et al. recently studied a nanoporous silver catalyst. They reported that this material is highly active and selective for CO2 reduction with a 92% faradaic efficiency toward CO.[20]

Ultimately, however, earth-abundant catalyst materials will be needed to develop affordable electrolyzers for the reduction CO2 to CO. In this regard, alternatives to metallic catalyst have been explored in recent years. One option is the use of metal dichalcogenides, Asadi et al. first reported that MoS2 shows superior catalytic performance for CO2RR in ionic liquids in comparison with noble metals.[21] A more detailed study of different transition metal dichalcogenides for CO2RR in ionic liquids indicates that WSe2 is a more promising alternative than MoS2, reaching CO faradaic efficiencies of 90% and current densities over 300 mA cm−2.[22]

In recent year, heteroatom-doped carbon materials (N, P, S and B) have emerged as a promising alternative to metallic catalysts, since they can selectively reduce CO2 to CO at low overpotentials and with reported current densities up to 28.6 mA cm−2. These materials made of earth abundant elements also offer the advantage of having high surface area and the possibility of introducing different concentrations of a variety of elements allows to have a compositional tuning to optimize the catalytic performance. Therefore, new studies, both computational and experimental, have emerged dealing with understanding and optimizing of heterotopic carbon materials as catalyst.

Most of the studied on doped carbon materials have focus on nitrogen-doped carbon (N–C materials) and on metal nitrogen-doped carbon (M–N–C). Many of these MNC materials contain catalytically active “MNx” sites, similar the MN4 sites in molecular macrocyclic N–C complexes, such as metal porphyrins, which have been known to be efficient homogeneous catalyst for the CO2RR. Therefore, such “MNx” sites in solid carbon materials are believed to be active for the CO2RR as well. Nevertheless, metal free nitrogen-doped carbon materials have also been shown to reduce CO2 to CO and hydrocarbons, indicating that other N–C functionalities may play a role in the catalytic process.

Herein, we present a review on recent achievements on nitrogen-containing solid carbons which have been shown to be active and selective catalysts for the CO2RR. Furthermore, we also discuss combined experimental and theoretical studies to bring insight into the active catalytic sites and the detailed reaction mechanism of such materials. This will provide useful information for identifying new materials and optimizing
the catalytic performance of known members of this class of materials.

### 2. Immobilized N–C Complexes

Since the 1970s, transition metal complexes such as porphyrins and phthalocyanines containing earth-abundant elements N, C, or non-noble transition metals have been widely studied as catalysts for the electrochemical reduction of CO$_2$ to CO (Figure 2). The first report on the catalytic activity of this complexes was published by Meshtitsuka et al. who explored the use of immobilized cobalt- and nickel phthalocyanines for the CO2RR. In their pioneer work, however, it is not clear which products were formed. Later, Fisher and Eisenberg showed that tetraazomacrocyclic complexes of cobalt and nickel can act as homogeneous catalysts for the reduction of CO$_2$ to CO at potentials between –1.3 and –1.6 V versus saturated calomel electrode (SCE).\[^{24}\] Promising results were also reported by Sauvage, who worked with Ni (cyclam) complexes, which exhibit CO faradaic efficiencies up to 96%.\[^{25}\] Since then, different metal complexes centers have also been reported as active sites for the CO2RR, such as Re in bipyridine complexes,\[^{26}\] Co porphyrins,\[^{27}\] and Fe porphyrins.\[^{28}\] In particular, Hammouche and Savéant showed that iron (0) porphyrins are capable of reducing CO$_2$ to CO at –1.8 V versus SCE in dimethyl formamide (DMF).\[^{29}\] Furthermore, the catalytic performance and stability of these catalysts were improved by the addition of an electrophile, such as Mg$^{2+}$, or a weak Bronsted acid. This suggests that the iron centers initiate the CO$_2$ reduction while an acid is needed for breaking the C–O bond and form CO.\[^{30}\]

Despite the promising performance of these homogeneous catalysts, there is much interest in identifying solid materials that can act as efficient heterogeneous catalyst. The heterogeneous approach in catalysis has important advantages, such as easier recovery of the catalyst and a more facile purification or concentration of liquid products. Furthermore, the interfacial electron transfer between a supporting electrode and the catalytic site tends to be more efficient when working with heterogeneous solid electrode catalysts, in comparison to having the catalyst untethered or nonimmobilized in solution (Figure 3). Therefore, transition metal N–C complexes immobilized on electrode surface are an attractive alternative as CO2RR, as they can combine the good catalytic performance of homogeneous catalyst with the recovery and electron transfer advantages of heterogeneous catalysts. Moreover, the use of these molecular catalysts in their heterogeneous form can help to mitigate deactivation processes such as dimerization or aggregation and allows the use of variety of electrolytes, such as aqueous solutions, that otherwise could not be utilized because of solubility and stability limitations.

The interest on immobilized transition metal N–C complexes began decades ago and different techniques have been studied to achieve this goal. One of the most common approaches is adsorption, which is usually achieved via the interaction of aromatic structure with the electrode surface. This was the technique used in the early work by Meshitsuka et al. in 1974 to immobilize cobalt and nickel phthalocyanines on graphite electrodes\[^{23}\] and by Lieber and Lewis a decade later\[^{30}\] who immobilized Co phthalocyanine onto carbon clothes.

The attachment of the homogeneous catalyst can also be achieved by chemisorption, which involves a chemical reaction between the electrode surface and the catalyst, forming new chemical bonds. In 1991, Atoguchi et al. reported a cobalt(II) tetraphenylporphyrin (Co(II)TPP)–pyridine complex modified glassy carbon electrode.\[^{31}\] To ensure the catalyst chemisorption onto the electrode surface, they first modified the electrode by anodic oxidation followed by reflux in SOCl$_2$ for chlorination. The electrode was exposed to 4 aminopyridine to form an amide bond between the electrode surface and the pyridine. Then the anchored pyridine was coordinated to the Co(II)TPP. Atoguchi et al. corroborated the fixation of the catalysts by Fourier transform infrared spectrometer (FTIR); furthermore, they were able to verify that CO was formed as a major product of the CO2RR.

Another approach for immobilizing molecular catalyst is polymerization. An early report from Guadalupe et al. explored this method using electropolymerized films of cobalt terypyridine on Pt electrodes. Cyclic voltammetry analysis showed that this system is active for the CO2RR in DMF, while mass spectrometry analysis indicated the presence of CO as one of the reaction products.\[^{32}\] Contrary to other methods, polymerization usually allows to attach several catalyst layers, which results in a higher density of active sites. Nevertheless, if the

![Figure 2](image-url) Examples of metal N macrocyclic complexes used as efficient CO2RR catalysts. a) and b) reported by Fisher et al.,\[^{24}\] c) reported by Behar et al.,\[^{27}\] and d) reported by Savéant et al.\[^{29}\]
film is densely packed, not all the active sites are accessible resulting in overall low activities.

2.1. Recent Studies on N–C Immobilized Catalysts

Following these early studies, several immobilized molecular catalysts have been reported as efficient catalysts for CO2RR. These studies have included various metal centers as well as different supports. For an extensive account of these studies there are already excellent reviews and book chapters. Nevertheless, in recent years the increasing interest on the CO2RR as an alternative for converting CO2 waste streams into carbon based chemicals has resulted in a renewed interest on the study of immobilized N–C macrocyclic complexes as electrocatalysts for this process. Many of these new studies include careful product quantification, showing that such complexes can selectively reduce CO2 to CO with faradaic efficiencies higher than 90%. Furthermore, many of the recent studies have focus on aqueous electrolytes, which is desirable as to have a sustainable catalytic process. This work on immobilized complexes also serves as a precedent to understand the nature of the active sites of the other solid catalysts such as Metal Organic Frameworks (MOFs) and MNC materials.

That is the case of the work by Tornow et al. who in 2012 reported the use of organometallic silver catalysts attached to carbon Vulcan as electrocatalyst for the reduction of CO2 in an aqueous electrolyte (1 M KOH). They observed that these immobilized complexes were able to reduce CO2 to CO with faradaic efficiencies higher than 90%. Such complexes outperform the catalytic performance of pure Ag on C, suggesting that not only the metal center but also the ligands play a role on the catalysts performance. This opens an interesting opportunity to control the catalytic activity of MN macrocyclic complexes by finding an appropriate ligand. In particular, the cyano groups can act as electron-withdrawing groups facilitating the Co(I) regeneration resulting in a high catalytic activity of CoPC–CN/CNT.

Interestingly other studies on CoPC do not report the same high selectivity toward CO as that observed by Zhang et al. For instance Kramer and McCrory reported a CO faradaic efficiency of 36% on CoPC deposited onto a graphite disc electrode. A possible explanation for this discrepancy could be the use of different supports, as we will discuss later. Furthermore, Kramer and McCrory also observed that immobilization of CoPC in polymer membrane (poly-4-vinylpyridine, P4VP) dramatically increases the selectivity toward CO, reaching a faradaic efficiency of 89%. On one hand, the P4VP inhibits the competing process of the HER and, on the other hand, it also facilitates the CO2 reduction. The enhancement toward CO2RR

2.1.1. Cobalt Catalysts

To achieve high CO selectivity, however, it is not necessary to work with noble metal centers. In particular, several examples of immobilized cobalt complexes have been shown to be highly selective toward the reduction of CO2 to CO (see Table 1). As an example, Aoi et al. investigated a Co N-macro cyclic complex (CoII(Ch)) adsorbed on multiwalled carbon nanotubes showing that CO2 is produced as a major product with a faradaic efficiency up to 92% which was maintained for at least 10 h of reaction. The authors attribute the excellent catalytic performance of their catalysts to a rapid electron transfer from the electrode to the reaction site of the other solid catalysts such as Metal Organic Frameworks (MOFs) and MNC materials.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Working potential [V]</th>
<th>Product efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(II) Polypyridyl Carbene Complex</td>
<td>1.13 ± 0.1 nmol cm⁻² on fluorine-doped tin oxide (FTO)</td>
<td>0.5 M NaHCO₃ pH = 7.3</td>
<td>−0.96 to −1.06 V vs NHE</td>
<td>CO₂ to C₂H₄ TOF: 308 in 900 s</td>
<td>Wang et al.⁴⁷</td>
</tr>
<tr>
<td>(Co⁶⁺(CH₃)) adsorbed on multi-walled carbon nanotubes</td>
<td>10 nmol on Glassy Carbon (GC)</td>
<td>5.0 × 10⁻³ M Na₂SO₄ pH = 4.6</td>
<td>−1.1 V vs NHE</td>
<td>CO: 89% TOF: 140 h⁻¹</td>
<td>Aoi et al.⁴⁶</td>
</tr>
<tr>
<td>Co-phthalocyanine</td>
<td>0.4 mg cm⁻² on Carbon Fiber Paper</td>
<td>0.1 M KHCO₃ pH = 6.8</td>
<td>−0.59 V vs RHE</td>
<td>CO: 70%</td>
<td>Zhang et al.⁴⁵</td>
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<tr>
<td>Co-phthalocyanine on CNT</td>
<td>CoPC/CNT</td>
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<td>Co-phthalocyanine on CB</td>
<td>CoPC/CB</td>
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<tr>
<td>Co-phthalocyanine on RGO</td>
<td>CoPC/RGO</td>
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<tr>
<td>Phthalocyanine on CNT</td>
<td>Pc/CNT</td>
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<tr>
<td>Cyano Substituted</td>
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<tr>
<td>Co-Phthalocyanine on CNT</td>
<td>CoPC/CN/CNT</td>
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<tr>
<td>Perfluorinated cobalt phthalocyanine (CoPC)</td>
<td>13 nmol cm⁻² on Carbon Cloth</td>
<td>0.5 M NaHCO₃ pH = 7.3</td>
<td>−0.8 V vs RHE</td>
<td>CO: 93% TOF: 1.61 s⁻¹</td>
<td>Morlanes et al.⁴⁹</td>
</tr>
<tr>
<td>Co protoporphyrin-coated PG (CoPP-PG)</td>
<td>0.4 nmol cm⁻² on Pyrolytic Graphite</td>
<td>NaClO₄/HClO₄ pH = 3</td>
<td>−0.6 V vs RHE</td>
<td>CO: 60%</td>
<td>Shen et al.⁵¹</td>
</tr>
<tr>
<td>Iron-Porphyrin Catalyst</td>
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<tr>
<td>(Fe-PP)</td>
<td>24 nmol cm⁻² on GC</td>
<td>0.5 M NaHCO₃ pH = 7.3</td>
<td>−1.03 V vs NHE</td>
<td>CO: 91% TOF: 144 h⁻¹</td>
<td>Maurin &amp; Robert ⁵²</td>
</tr>
<tr>
<td>Fer porphyrin on carbon nanotubes (Fe-PP/CNT)</td>
<td>6.4 nmol cm⁻² on GC</td>
<td>0.5 M NaHCO₃ pH = 7.3</td>
<td>−1.06 V vs SHE</td>
<td>CO: 85.3% TOF: 178 h⁻¹</td>
<td>Maurin &amp; Robert ⁵²</td>
</tr>
<tr>
<td>water-soluble iron porphyrin (WSCAT)</td>
<td>370 – 740 × 10⁻⁶ m² cm⁻² on porous carbon paper</td>
<td>0.1 M KCl + 0.5 M KHCO₃ pH = 7.3</td>
<td>−0.96 V vs SHE</td>
<td>CO: 90%</td>
<td>Tatin et al.⁵³</td>
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<tr>
<td>Rh-PP</td>
<td>Pyrolytic Graphite</td>
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<td>In-PP</td>
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<tr>
<td>Sn-PP</td>
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<tr>
<td>[MnBr(2,2-bipyridine) (CO₂)]⁺</td>
<td>NMCNT/GC</td>
<td>0.5 M KHCO₃ pH = 7.4</td>
<td>−1.1 V vs SHE</td>
<td>CO: 10%</td>
<td>Reuillard et al.⁵⁶</td>
</tr>
<tr>
<td>copper-porphyrin complex</td>
<td>0.25 mg cm⁻² on polytetrafluoroethylene-treated carbon fiber paper</td>
<td>0.5 M KHCO₃ pH = 7.3</td>
<td>−0.976 V vs RHE</td>
<td>CO: 12% CH₄: 27% TOF_C₂H₄ 4.3 s⁻¹ C₂H₆: 4.5% TOF_C₂H₆ 1.8 s⁻¹</td>
<td>Weng et al.⁵⁷</td>
</tr>
<tr>
<td>silver pyrazole supported on carbon (AgPz/C)</td>
<td>1 mg cm⁻² on Graphite Gas Diffusion layer (GDL)</td>
<td>CO₂ sat. 1 M KOH pH = 7.8</td>
<td>−1.8 V vs Ag/AgCl</td>
<td>CO: 90% jco &gt; 80 mA cm⁻² (1700 mA mg⁻¹ Ag)</td>
<td>Tornow et al.⁵⁸</td>
</tr>
</tbody>
</table>
is an indication that the presence of this N group on P4VP facilitates this process acting as a cocatalyst.

The effect of the support was also observed by Hu et al., who investigated the catalytic activity of cobalt meso-tetraphenylporphyrin (CoTPP) immobilized onto carbon nanotubes, which turns out to be a selective catalyst for the CO2RR in aqueous electrolytes. Based on this result, it is important to keep in mind that catalytic activity of metal complex as a homogeneous catalyst does not translate directly to its activity as heterogeneous catalyst when immobilized on a support, as this could also influence the catalytic activity of the metal macrocycle.

These Co complexes have also been shown to be active catalysts for oxygen evolution reaction,[47,48] which is usually the anodic process during the CO2RR in aqueous electrolytes.

Table 1. Continued.

<table>
<thead>
<tr>
<th>Catalysts</th>
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<th>Electrolyte</th>
<th>Working potential [V]</th>
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<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>silver phthalocyanine supported on carbon (AgPc/C)</td>
<td>on graphite disc electrode</td>
<td>0.1 M NaH2PO4 pH = 4.7</td>
<td>-1.25 V vs SCE</td>
<td>-0.98</td>
<td>CO: 80%</td>
</tr>
<tr>
<td>TRP: u-(meso-5,10,15,20-tetraphenylporphyrin)</td>
<td>Co-Pc-P4VP</td>
<td>0.5 M HCOOH pH = 7.3</td>
<td>-1.35 V vs SCE</td>
<td>-1.08</td>
<td>CO: 28%</td>
</tr>
<tr>
<td>silver 3,5-diamino-1,2,4-triazole supported on carbon (AgDAT/C)</td>
<td>Co-Pc-P2VP</td>
<td>DMF/H2O solution</td>
<td>-1.7 V vs SHE</td>
<td>-1.7</td>
<td>CO: 95%</td>
</tr>
</tbody>
</table>

When CoTPP was tested as a homogenous catalyst in N,N-dimethylformamide as solvent, both the reaction rate and CO selectivity were lower even at higher overpotentials. This effect could be attributed to the different environment of the heterogeneous catalyst which seems to play an important role in the CO2 adsorption and further reduction. Based on this result, it is important to keep in mind that catalytic activity of metal complex as a homogeneous catalyst does not translate directly to its activity as heterogeneous catalyst when immobilized on a support, as this could also influence the catalytic activity of the metal macrocycle.

These Co complexes have also been shown to be active catalysts for oxygen evolution reaction,[47,48] which is usually the anodic process during the CO2RR in aqueous electrolytes.
Therefore, Morlanés et al. performed electrolysis of CO$_2$/H$_2$O into CO/O$_2$ using perfluorinated cobalt phthalocyanine (CoFPc) immobilized onto a carbon cloth as the cathode for CO$_2$ reduction and the anode oxygen evolution.[49] When testing CoFPc as electrocatalyst for CO$_2$RR in a three electrode cell, the reduction of CO$_2$ became apparent at $-0.5$ V versus RHE, and the maximum CO faradaic efficiency reached 93% at $-0.8$ V versus RHE. Whereas for the two compartments electrolysis experiments, a cell voltage between 2.5 and 3 V was applied maintaining a faradaic efficiency toward carbon monoxide of about 90%. This interesting study showed that the same Co based complex can be used in a CO$_2$ reduction electrolyzer. The overall currents, however, remained between 1 and 6 mA cm$^{-2}$, which are still lower than the desired one for a commercial electrolyzer.

Most of the tested electrodes containing immobilized Co complexes have been prepared by adsorption. Nevertheless other techniques for immobilizing complexes such as electropolymerization have also been used as was the case in the study of Pander et al. on immobilized Co protoporphyrin. This material was shown to be selective for the CO production; however, the obtained current densities were below 0.5 mA cm$^{-2}$. This could be attributed to formation of a dense film, as it usually occurs during electropolymerization in which not all the Co sites are accessible. In addition, Pander et al. observed that the selectivity of the process is affected by the electrolyte’s pH and the working potential.[50] In particular, the faradaic efficiency toward the formation of hydrogen (the competing process) increased at lower pH values (high proton concentration) as this rate limiting step of the HER involves a proton transfer. By contrast, as we discuss in a later section, the rate-limiting step for CO$_2$ reduction to CO on Co complexes does not involve a proton transfer and, as a consequence, electrolytes with neutral pH were found to be optimal for the CO$_2$RR. In particular, a faradaic efficiency toward CO of 84 $\pm$ 2% was observed near neutral pH (K$_2$SO$_4$ pH = 6.5) with 450 mV of overpotential. At higher overpotentials, however, the HER was enhanced reducing the faradaic efficiency (FE) toward CO formation.

In addition to the production of CO, other products of the CO$_2$RR can be obtained on this class of catalysts. Shen et al. worked on immobilized cobalt protoporphyrins on a pyrolytic graphite electrode as a CO$_2$RR catalysts in aqueous acidic solution.[51] They observed that, despite having lower faradaic efficiencies toward CO (between 50 and 60%) with respect to other reports, traces of methane were also formed indicating that these CoN$_4$ centers can also catalyze the complex 8 electron reduction of CO$_2$ to CH$_4$. In addition, Shen et al. observed that selectivity of the process is affected by the reaction conditions (Figure 5). Consistent with previous studies by Sonoyama,

Figure 5. Faradaic efficiencies toward a) CO and b) CH$_4$ for the CO$_2$RR on cobalt protoporphyrins on a pyrolytic graphite in CO$_2$ saturated 0.1 M perchlorate solution. Yellow bars: pH = 1, PCO$_2$ = 1 atm; blue bars: pH = 1, PCO$_2$ = 10 atm; magenta bars: pH = 3, PCO$_2$ = 1 atm and black bars pH = 3, PCO$_2$ = 10 atm. Adapted with permission.[51] Copyright 2016, Springer Nature.
et al.\cite{33} they observed that when working at pH = 3 and lower overpotentials (~0.6 to ~0.8 V vs RHE), the CO₂ selectivity was enhanced with a higher CO₂ pressure. This could suggest that the CO₂ reduction is limited by mass transport limitations of CO₂ to the active sites of the catalysts. They also observed that the pH plays an important role on the reaction selectivity. At pH = 1, the faradaic efficiency toward CO and CH₄ is low, since a high concentration of protons facilitates the competing process of the hydrogen evolution reaction, and as a result H₂ is the major reaction product. Interestingly, the faradaic efficiency toward CH₄ is clearly higher at pH = 1. In fact, under these conditions more methane is produced than CO, suggesting that a high concentration of protons is facilitating the reduction of CO to CH₄.

2.1.2. Iron Catalysts

Besides Co, other abundant transition metal complexes have been tested. In particular, there are several examples of immobilized Fe N-macrocyclic complexes that have also been reported to be selective catalyst for the CO₂RR to CO. As an example, Maurin and Robert investigated an iron triphenyl porphyrin immobilized on carbon nanotubes via noncovalent interactions. These nanotubes were then deposited on glassy carbon and tested as CO₂RR catalysts in CO₂-saturated aqueous electrolyte (pH 7.3, NaHCO₃ 0.5 M)\cite{32}. The potential electrolysis experiments showed that this catalyst is as selective as the best Co based catalyst with a 96:4 CO:CH₄ ratio at an overpotential of 480 mV. Furthermore, a remarkably high turn-over number (TON) of 432 for CO formation was obtained, relative to the total quantity of catalyst immobilized onto the cathode, while a turn over frequency of 144 h⁻¹ was obtained. Despite these promising results, the obtained current density of 0.4 mA cm⁻², however, is too low for real applications. Furthermore, the activity deceased during the first two hours of reaction. This exemplifies the two main challenges of working with immobilized metal N–C macrocyclic complexes: having enough active surface sites to achieve high current densities for technological applications (≥50 mA cm⁻²) and maintaining the catalytic activity for long periods of time.

One of the key questions regarding these metal based complexes is to determine the oxidation state of the metal center during the catalytic process. This issue was addressed by Maurin and Robert who studied the catalytic performance of iron tetraphenylporphyrin covalently attached via an amide linkage to carbon nanotubes.\cite{53} Similar to their previous study, they observed a high CO selectivity (90%) indicating that the good catalytic selectivity of the tetraphenylporphyrin is maintained when it is covalently attached to carbon nanotubes and that the amide linkage has no impact on its catalytic performance. In addition, the authors used cyclic voltammetry to investigate the Fe oxidation state as a function of potential. They identified the Fe(III)/Fe(II) and Fe(II)/Fe(I) redox waves at ~0.1 V versus standard hydrogen electrode (SHE) and ~0.95 V versus SHE respectively. The Fe(I)/Fe(0), however, could not be distinguished. The authors state that this transition occurs close to the water reduction signal, making it difficult to distinguish.

This would suggest that the Fe oxidation state during the CO₂RR is 0. Nevertheless, other operando techniques such as X-ray absorption spectroscopy would be more useful for confirming the oxidation state of the metal center under reaction conditions, which could lead to a better understanding of the reaction mechanism.

As it has been observed on Co catalysts, the support is also crucial on determining the catalytic performance of immobilized complexes. Consistently, Mohamed et al. observed that the activity of an Fe porphyrin was dependent on the SnO₂ support.\cite{54} While the activity of the immobilized iron porphyrin attached via a phosphonic acid linkage on a fluorine-doped tin oxide electrode was only 0.25 mA cm⁻², it was increased to 3 mA cm⁻² when they used a sintered mesoporous thin film of SnO₂ particles on the fluorine doped tin oxide (FTO) electrode to immobilize the Fe porphyrin. This test, however, was performed in an organic solvent (DMF/5% H₂O/0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) solution saturated with CO₂). By contrast, the CO₂ electrolysis in a neutral aqueous 0.1 M borate solution (pH 7.0) resulted in a dramatic drop of current density reaching 0.04 mA cm⁻², which shows the important role of the electrolyte during the CO₂RR. The authors hypothesized that the activity is hampered by the FTO surface with a hydrophobic alkyl group through phosphonic acid anchors (n-butyl phosphoric acid, n-BuPO₃H₂) to protect the electrode against its own reduction. With this strategy, the authors were successful in enhancing the catalytic performance of the immobilized porphyrin dimer. The FTO/SnO₂/Fe₂DT-PFPP-PO₃H₂/n-BuPO₃H₂ showed a stable current of 1.47 mA cm⁻² during electrolysis in CO₂-saturated 0.1 M borate buffered solution (pH 7.0) reaching a CO FE of 70% at overpotential of 0.42 V.

Immobilized iron porphyrin complexes have not only been investigated in a 3-electrode setup but also in an actual two electrode electrolyzer. Tatin et al. used an iron porphyrin immobilized onto a conductive Nafion/carbon powder layer as a cathode, coupled to a water oxidation phosphate cobalt oxide anode.\cite{55} This inexpensive setup proved to be selective toward CO₂ reduction to CO, with a faradaic efficiency of 90%, by applying 2.5 V of cell voltage. Under these conditions, the high CO selectivity was maintained for at least 30 h. The obtained overall current of 1 mA cm⁻², however, is low for commercial application. Furthermore, the cell energy efficiency (EE), obtained from the product of the faradaic efficiency for CO production and the ratio of the thermodynamics of the reaction versus the cell voltage (Reaction (10)), was calculated to be 50% at 1 mA. Therefore, despite the promising results using immobilized complexes of earth abundant catalysts, further improvements are needed. One of the key challenges is precisely increasing the density of active sites to run the electrolysis at relevant current densities.

\[
EE = \frac{F_{Co}^{0} \cdot (E_{O_{2}/H_{2}O}^{0} - E_{Co/CO}^{0})}{U_{cell}}
\]  

(10)
2.1.3. Catalysts Containing Other Metal Centers

Nitrogen containing complexes of other metal centers have also been shown to be active catalysts for the reduction of CO₂ to CO. For example, immobilized [Mn(bpy(tBu)₂)(CO)Br] (in which (bpy(tBu)₂) = 4,4′-di-tert-butyl-bipyridine) complexes were proven to be active in the reduction of CO₂ to CO in aqueous solvents at neutral pH values, showing that other non-noble metal centers are active for the CO₂RR and opening the door to explore other complexes. [46] The CO/H₂ ratio of 0.33 observed by Walsh et al., however, is lower than that observed on Fe and Co complexes. Despite its low CO selectivity, this Mn complex could be useful for syngas production which could later be converted into hydrocarbons via the Fischer–Tropsch. Interestingly, this study also showed that the activity of a given metal center is influenced by the type of ligands. In this case, other Mn complexes, namely Mn(bpy(COOH)₂)(CO)₃Br and [Mn(bpy(OH)₂)(CO)₂Br], exhibit no significant activity when immobilized on multiwall carbon nanotubes, showing that the metal center is not the only parameter that plays a role on the catalytic activity of metal/nitrogen-doped carbon (MNC) macrocyclic complexes. To understand the role of the ligand, however, more systematic studies on how the electronic properties of the ligand affect the catalytic performance of a metal center are still needed. More interestingly, Mn(bpy(COOH)₂)(CO)₃Br and [Mn(bpy(OH)₂)(CO)₂Br], which were not active as immobilized catalysts, were able to reduce CO₂ to CO as homogenous catalysts in acetonitrile. As observed for Co based catalysts, the good activity of a complex in its homogenous form does not necessary translate to an efficient immobilized catalyst, as the support and the chemical environment of the active sites also play a role in determining its catalytic activity.

It is well known that, in addition to the formation of CO, CO₂ can be reduced to other carbon-based products. In particular, an alternative reaction pathway via two electron/two proton transfer leads to the formation of HCOO⁻. The selectivity between these two possible pathways is highly dependent on the catalyst material. In the case of immobilized N–C complexes, the metal center seems to play an important role in determining which product is formed. Birdja et al. tested the activity toward the CO₂RR on several metalloprotoporphyrins immobilized on a pyrolytic graphite electrode and observed that some of them produced important amounts of HCOO⁻, while on other metal centers no HCOO⁻ was formed. [56] In particular, the CO₂RR at pH = 3 using Rh, In, and Sn produced significant amounts of formic acid, whereas on Ni-, Pd-, Cu-, and Ga-protoporphyrins only small amounts of formic acid were detected. By contrast, on Mn-, Co-, and Fe-protoporphyrins, no formic acid was detected as a product of the CO₂RR. Among the metalloprotoporphyrins that produce significant amounts of formic acid, it was shown that a higher activity toward the hydrogen evolution reaction leads to a lower selectivity toward formic acid. As a result, InPP, which was the least active porphyrin toward HER, showed the highest faradaic efficiency toward HCOOH. This illustrated another important parameter to choose a catalyst for CO₂RR. An optimal should have a low activity toward the competing process of HER, allowing it to selectively reduce the CO₂.

Birdja et al. also looked into the effect of the pH, showing, once again, that it has a crucial role in determining the product selectivity. As the HER activity was enhanced at lower pH, those are not the best conditions to obtain high selectivity toward the CO₂RR. For the example, in the case of the InPP, the selectivity of the HCOOH faradaic efficiency varies from less than 50% at pH = 4 to 70% at pH = 10.

Another metal center that has been investigated is Zn, in particular Wu et al. investigated zinc(II) 5,10,15,20-tetramethylporphyrin (PorZn) immobilized onto polytetrafluoroethylene-treated carbon fiber paper. [57] These studies show CO as the main product from the CO₂RR in an organic electrolyte of PorZn in 0.1 m TBAPF₆ in DMF/H₂O (V_H₂O:V_DMF = 1:9). Under these conditions, the CO faradaic efficiency reached a maximum of 95% at −1.7 V versus SHE with a current density of ≈2.1 mA cm⁻². Control experiments using blank carbon fiber paper and metal-free porphyrin as the working electrode showed H₂ as the only product, confirming that PorZn is responsible for the observed CO₂RR activity.

In addition to the catalytic tests, Wu et al. carried out operando X-ray absorption spectroscopic studies to gain further insight on the role of the Zn centers during the catalytic process. Interestingly, no visible changes in the Zn K-edge X-ray absorption near edge structure (XANES) spectra were observed at the working potentials suggesting that the Zn center remains in its 2⁺ oxidation state during the CO₂RR. In addition, the extended X-ray absorption fine structure (EXAFS) indicates only minimal changes in the Zn coordination number and bond distances during electrolysis experiments. These results seemed to suggest that the Zn centers are not involved in the catalytic process. Nevertheless, the experiments on metal-free porphyrin showed that the Zn centers are crucial for the catalytic activity of PorZn toward the CO₂RR. The authors proposed that the Zn remains redox-inactive, while the porphyrin ligand in the presence of Zn is likely to be responsible for the two-electron reduction of CO₂ to CO. This involvement of the ligand in the catalytic process is different from other reported transition-metal-based molecular catalysts, yet it shows that other active sites could be involved in the CO₂RR. This knowledge could be crucial for understanding the catalytic activity of other nitrogen carbon based materials in which N functionalities without metal can also be involved in the reduction of CO₂.

As we have discussed, the metal center is not the only parameter that controls the reaction selectivity. One must take into account also the electrolyte and the chemical environment of the metal complexes, which could also have an important effect on the products selectivity. This was shown in the recent study from Reuillard et al. who investigated the catalytic activity of [MnBr(2,2′-bipyridine)(CO)₃] complex anchored to a carbon nanotube electrode via a pyrene unit in aqueous KHCO₃ (0.5 m, pH 7.4). [58] Despite HER being the predominant process, both CO and HCOO⁻ were also detected as products of the CO₂RR. Interestingly, it was found that the product selectivity toward CO or HCOO⁻ can be tuned by changing the catalyst loading on the nanotube surface. In particular, CO was observed as the main product from the CO₂RR at high catalyst loadings, whereas, at low catalyst loadings, formate was the major carbon containing product (Figure 6). UV–vis and surface-sensitive IR spectro-electrochemical techniques were used to identify the reaction intermediates in order to gain insight in the reaction pathways leading to the formation of these two products. At
high surface loading of [MnBr(2,2'-bipyridine)(CO)₃] complexes on carbon nanotubes are reduced to dimeric Mn⁰ species on which CO₂ is reduced to CO. By contrast, at low loading Mn-hydride species are formed resulting in an increased production of formic acid. Thus, proving that the chemical environment of the metal center is crucial on determining the reaction selectivity. In this case, going from dimeric Mn⁰ sites to Mn-hydrides affects the reaction pathway and the final product.

As reported by Shen et al., it is possible to use immobilized N–C complexes as catalyst for the direct reduction of CO₂ to hydrocarbons, such as methane. In general, hydrocarbons are seen as more valuable products, as they can be directly utilized as fuels within the existing technologies. Furthermore, hydrocarbons such as ethylene are important precursors in the chemical industry. Therefore, there is interest in developing heterogeneous catalysts that can reduce CO₂ to hydrocarbons in considerable amounts. This process, however, is substantially hindered given the multiple electron/proton transfers required. Up to date, the most promising heterogeneous catalysts are those based on Cu which can produce CH₄ and C₂H₄ with high selectivity.[11] Furthermore, it has been shown that pre-oxidized Cu catalysts selectively reduce CO₂ to ethylene at low overpotentials.[17,59,60]

In a recent study by Wang and co-workers, it was shown that a molecular copper–porphyrin complex can also reduce CO₂ to hydrocarbons. In particular, they used copper(II)-5,10,15,20-tetrakis(2,6-dihydroxyphenyl)porphyrin) deposited onto carbon paper and observed that it can catalyze the multistep reduction to form hydrocarbons (Table 1). Hydrocarbons, namely, CH₄ and ethylene, were produced with a faradaic efficiency of 44% and a combined geometric current density of 21 mA cm⁻² resulting in turnover frequencies (TOFs) of 4.3 methane and 1.8 ethylene molecules per site per second.[61] Hydrocarbon production started at around −0.9 V which is a higher overpotential than that on metal Cu and peroxided copper catalysts. Nevertheless the achieved geometric current density is remarkably high, which could partially be attributed to the use of gas diffusion electrodes, but it also shows that this immobilized Cu complex is a promising catalyst for the direct CO2RR to hydrocarbons. Interestingly, the results by Wang and co-workers also indicate that the presence of hydroxyl groups in porphyrin ligands is crucial for hydrocarbon production. In a control experiment, the OH-free PorCH₃Cu was tested under the same conditions, producing CO as a main product of the CO2RR with a faradaic efficiency of <28%. Despite the clear importance of the hydroxyl groups, the reason is still uncertain. Nevertheless, it shows that changing substituent groups present in metal–N complexes presents an interesting opportunity to tune catalytic activity toward the CO2RR. It is hypothesized that substituents could facilitate binding of certain reaction intermediates or provide an intramolecular source of protons, which can facilitate the CO protonation and hydrocarbon formation.

### 2.2. Reaction Mechanism

As described in the previous section, the catalytic activity of some of these immobilized N–C complexes is comparable or even better than that of metallic CO₂ reduction catalysts. In particular, for CO production, Cu and Fe complexes have been promising candidates. For example, the cobalt meso-tetraphenylporphyrin on carbon black (CoTPP/CB) prepared by Hu et al. reaches a CO faradaic efficiency of 97% which is competitive with state of the art Ag catalysts. The activity of these complexes, however, depends on different properties such as the metal center, the ligands, and the reaction conditions. In order to fully understand the role of these parameters, it is necessary to have information about the reaction mechanism. In that regard, some theory studies have been carried out in order to determine the key reaction intermediates.

Leung et al. used density functional theory (DFT) calculations with hybrid functionals in combination with ab initio molecular dynamics simulations to analyze the two-electron, multi-step CO2RR to CO in water using cobalt porphyrin as a catalyst.[64] Their proposed mechanism involves first the reduction to [Co(I)P]⁺, which absorbs CO₂ and forms the [Co(P)–(CO₂)]²⁻ intermediate after a second electron transfer. This intermediate is then protonated to give [Co(P)–(COOH)]⁺, which later readily decomposes to form CO (Figure 7a).

More recently, Shen et al. also used DFT to study the CO2RR mechanism on Co porphyrin.[65] Consistently with Leung et al., they found that the reduction of CO₂ occurs via a decoupled proton electron transfer (PET) forming CO₂⁻. This key intermediate is only formed after the cobalt center of the complex is
reduced to Co(I). According to their study, the $[\text{Co(P)}-(\text{CO}_2)]^-$ does not undergo a second electron transfer, but instead it acts as Brønsted base abstracting a proton from a nearby water molecule to form the $[\text{Co(P)}-(\text{COOH})]^-$. This intermediate then is reduced via coupled PET forming water and $[\text{Co(P)}-(\text{CO})]$ from which the weakly bonded CO can be desorbed (Figure 7b).

Alternatively to this mechanism, Shen et al. also discussed the formation of a “formate-type” intermediate, $[\text{Co(P)}-(\text{OCHO})]^0$ or $[\text{Co(P)}-(\text{OCHO})]^-$, which is formed via Reactions (10) and (11) leading to a competing pathway for formic acid production

$$[\text{Co(P)}]+\text{CO}_2+\text{H}^++e^- \rightarrow [\text{Co(P)}-(\text{OCHO})]^0 \quad (11)$$

$$[\text{Co(P)}-(\text{CO}_2)]^0+\text{H}^++e^- \rightarrow [\text{Co(P)}-(\text{OCHO})]^-(12)$$

The formation of $[\text{Co(P)}-(\text{OCHO})]^0$ is not thermodynamically favored, as the equilibrium potential of the reaction is significantly negative ($-0.92 \text{ V}$). By contrast, the equilibrium potential for the formation of the $[\text{Co(P)}-(\text{OCHO})]^-$ intermediate is considerably less negative ($-0.21 \text{ V}$), which would indicate that formate can be formed at the working potentials. Nevertheless, formate is not observed as a major product of the CO$_2$RR on Co NC complexes, suggesting that Reaction (11) is probably kinetically hindered by a large thermal activation barrier.

The likelihood of a concerted or decoupled PET, however, is not only determined by the catalyst. The working pH also plays an important role. In a recent study by Gottle and Koper, DFT simulations were used to investigate the competition between the concerted and decoupled pathways for PETs on cobalt porphyrin catalyst.$^{[66]}$ They predict that the pathway for the formation of $[\text{Co(P)}-(\text{COOH})]$ via the previously mentioned decoupled PET (Figure 7b) becomes competitive at pH 3.5, which corresponds to the intermediate’s pKa. The formation of the $^{*}\text{COOH}$ adduct is unlikely to take place at higher pH values and, consequently, the reaction is more likely to occur via coupled PET to form $^{*}\text{COOH}^-$. These results show that the pH does not only play a crucial role on inhibiting the competing processes of the HER, but it also affects the reaction mechanism, which can also have an important effect on the selectivity of the process.

As was previously shown by Shen et al., the direct reduction of CO$_2$ to hydrocarbons is also possible on Co porphyrin catalysts.$^{[64]}$ Therefore, in their recent DFT study, they also investigated the possible reaction mechanism for CH$_4$ formation, which could be the result of the reduction of a carboxyl intermediate $[\text{Co(P)}-(\text{COOH})]$ or “formate-type” intermediate $[\text{Co(P)}-(\text{OCHO})]$. They found that the reduction of the most stable formate intermediate $[\text{Co(P)}-(\text{OCHO})]^-$ is difficult due to the negative equilibrium potential for the formation of $[\text{Co(P)}-(\text{OCH}_2\text{O})]^-$ of $-1.79 \text{ V}$ indicating that the formate intermediate is not reduced any further. The $[\text{Co(P)}-(\text{CO})]$, by contrast, could be further reduced to produce CH$_4$ which has been observed experimentally as a minor product. Since experimental work showed that the electrochemical reductions of formaldehyde under the same conditions also produce methane, it is plausible to consider that CH$_4$ formation goes through one of the following intermediates: $[\text{Co(P)}-(\text{OCH}_2\text{J})]$ or $[\text{Co(P)}-(\text{CH}_2\text{O})]$. The further reduction of $[\text{Co(P)}-(\text{CH}_2\text{O})]$, however, is not thermodynamically favorable and therefore it is considered an unlikely intermediate for methane formation. Nevertheless, to determine the actual pathway to CH$_4$, it will be necessary to carry out calculations of the free energy barrier between possible intermediates.

Yao et al. also studied the mechanism of the further reduction of CO Co-porphyrin by first principles methods. Instead of a concerted PET, they proposed the reduction of $^{*}\text{CO}$ to $^{*}\text{COH}^-$. This intermediate can then be protonated on the oxygen or carbon atom. According to Yao et al., the latter option is more favorable by 1.43 eV compared to $^{*}\text{COH}$ formation. A second decoupled PET is proposed for the reduction $^{*}\text{CHO}$ to $^{*}\text{CHOH}$ which then is protonated. Interestingly, $^{*}\text{OCH}_2$ is proposed as the most thermodynamically favored intermediate. The bond breaking process to form this intermediate, however, is accompanied by a large energy barrier, which was estimated to be as high as 1.99 eV. The formation of $^{*}\text{COH}$, by contrast, is a barrier-free step (except for the proton transferring barrier <0.3 eV), and thus it is suggested as a reaction intermediate. The $^{*}\text{COH}$ will then be reduced to form $^{*}\text{CH}_2\text{OH}$ which later be reduced to MeOH. Nevertheless, methanol has not been detected as a product, the authors speculate that MeOH can be further reduced to methane and therefore this is the product observed experimentally, but this has yet to

Figure 7. Mechanism for the CO$_2$ reduction to CO on cobalt N–C macrocycle a) as proposed by Leung et al.$^{[64]}$ b) as proposed by Shen et al.$^{[65]}$
be proven. These studies show that the reaction mechanism for the reduction of Co-porphyrin is still not fully understood. Therefore, further theoretical and experimental studies are needed to reach a consensus about the reaction mechanism and to identify the key intermediate. This knowledge would allow a better understanding of how different parameters help to stabilize the key intermediate leading to a rational catalysts design.

3. Metal Organic Frameworks (MOFs)

Despite the promising catalytic CO$_2$ reduction activity observed on immobilized metal N–C macrocyclic complexes, a key challenge for potential application arises from the low density of active sites on most of these catalysts and the consequential rather low current densities. In many cases, the molecular surface coverage, achieved by adsorption or chemisorption, resulted in less than a monolayer. Polymerization can be used to prepare multilayer films, but unfortunately the resulting films are usually densely packed and hence the CO$_2$ diffusion toward the active sites is limited. Furthermore, the cost of the electrode preparation is also an important factor to consider, and therefore the development of inexpensive catalyst synthesis methods is also desirable. Therefore, other methods for preparing heterogeneous catalyst containing M–N$_x$ centers have been explored in recent years.

In contrast to a densely packed polymerized film, MOFs create an ordered, porous heterogeneous network, which allows free permeation of electrolyte, counter ions, and dissolved CO$_2$ into the interior of the film. As their name suggests, MOFs consist of metal-containing inorganic building blocks coordinated to multidentate organic ligands to form 3D interconnected networks (Figure 8).[68] They are a subclass of coordination polymers characterized by an open framework which results in a characteristic high porosity (fraction of void volume to total volume) and high specific surface, making them ideal candidates for multiple applications such as gas storage, gas purification, and catalysis. In particular, for catalysis applications, the high porosity and large surface area provided by MOFs result in a variety of advantages, i.e., mainly a high density of active sites and a facile diffusion of reactants.

In recent years, MOFs have emerged as attractive catalyst materials and they have been widely studied for this purpose.[69] One of the reasons for the interest in these materials is the use of abundant elements, such as first row transition metals, like Fe, Co, Cu, Ni, and Mn and organic ligands consisting of C, H, O, and N. Furthermore, the diversity of organic ligands and inorganic building blocks allows to tailor the MOF’s properties to optimize their affinity toward key intermediates and the pore size to have an optimal diffusion of reactants. This tailorable nature is ideal for catalyst design, and thus they have been investigated as electrocatalysts for a variety of processes including oxygen reduction reaction (ORR), OER, and HER.[70] More recently, MOFs containing different metal centers, such as Fe, Co, and Cu, have also been investigated as electrocatalyst for the CO2RR.

3.1. Metal Organic Frameworks as Catalyst for the CO$_2$ Reduction Reaction

3.1.1. Cu Containing MOFs

One of the early examples of MOFs as catalyst for the CO2RR was reported by 2012 Kumar et al. who studied the catalytic performance of a Cu based MOF with an oxygen ligand (Cu$_3$(BTC)$_2$-MOF) in a non-aqueous medium, namely, CO$_2$-saturated N,N-dimethylformamide containing tetrabutylammonium tetrafluoroborate (TBATFB).[71] Cu$_3$(BTC)$_2$-MOF was synthesized by electrolysis using two copper plates as electrodes in a solution of the organic linker (0.1 M BTC) and supporting electrolyte (TBATFB) in 50 mL of methanol solution. The Cu$_3$(BTC)$_2$ was then deposited on glassy carbon electrode surface by drop dry method. This electrode was shown to be an active catalyst for the reduction of CO$_2$ to oxalate via a 2-electron reduction and dimerization mechanism. The formation of oxalate was first observed by FTIR recorded during the course of reaction and then confirmed after bulk electrolysis experiments by gas chromatograph coupled mass spectrometer (GCMS). According to this analysis, oxalic acid was produced with a faradic efficiency of 51%. The incomplete reduction into H$_2$C$_2$O$_4$ may be due to the poor conductivity of Cu$_3$(BTC)$_2$, which is one of the main challenges when working with MOF electrocatalysts.

In the same year, Hinogami et al. reported the use of copper rubeanate metal organic framework (CR-MOF) in an aqueous electrolyte.[72] The synthesized CR-MOF particles were dropped on carbon paper (CP) to form a working electrode and tested as electrocatalyst in 0.5 M KHCO$_3$ solution. Cyclic voltammetry in CO$_2$ saturate electrolyte indicated that the CR-MOF is more active than a Cu electrode, furthermore the CR-MOF catalysts showed a more positive onset potential by about 0.2 V. Product analysis after bulk electrolysis experiments showed that the CR-MOF electrodes produced HCOOH with a current efficiency of 30% while the rest of the charge is attributed to H$_2$ formation. Traces of CO were also detected at high overpotentials as the only other product from the CO2RR. Despite the low selectivity toward CO2RR in comparison to HER, this work...
shows the ability of MOF structures to reduce CO\textsubscript{2} in aqueous electrolytes. The varying selectivity observed on this Cu based MOF with respect to that of metallic Cu catalysts is attributed to distinct electronic structures from which catalytic properties ensue that are different from those of bulk Cu. One must not forget that the electronic environment of a metal can change dramatically when coordinated to organic ligands in comparison with their structure as a bulk metal. As a result, it is not surprising that the activity of a metal center in a MOF structure is clearly different from that of the bulk metal catalysts. Understanding how these electronic properties affect the catalytic performance of MOF structures will be crucial for the design of future catalysts.

While it is clear that Cu based MOFs are active toward the CO\textsubscript{2}RR, these two Cu based MOFs catalysts reduce CO\textsubscript{2} to different products. This could be attributed to the different organic ligands. While Kumar et al. ligand with O donor atoms, the work of Hinogami et al. was carried out with a ligand with N and S donor atoms. This difference could affect the electronic structure of the metal center resulting in a different catalytic activity. Nevertheless, as we have already mentioned, the reaction media is another important parameter to consider. The work from Kumar et al. was carried out in an organic solvent, in which the availability of protons is low. Consequently, the reduction product does not involve a proton transfer. The formation of oxalate requires only an electron transfer and the C–C coupling. Interestingly, this coupling occurred even without having neighboring Cu centers, which shows that multicarbon products can be formed in this family of catalysts, the mechanism, however, has yet to be understood. By contrast, Hinogami et al. worked in aqueous electrolyte with more available protons, facilitating the reduction of CO\textsubscript{2} to CO and HCOOH rather than the C–C coupling. This would suggest that the electrolyte is crucial on determining the main product; however, as we will see in the later section, other catalysts also reduced CO\textsubscript{2} to CO in organic solvents, indicating that more systematic studies are needed to fully understand the different parameters that control the selectivity during the CO\textsubscript{2}RR.

### 3.1.2. Fe and Co Containing MOFs

MOFs containing other metal centers than copper have also been tested as CO\textsubscript{2}RR catalyst. For example, Hod et al. prepared a Zn-based MOF-525 with Fe-porphyrin units and compared its catalytic activity to that of the corresponding homogeneous Fe-porphyrin catalysts.\textsuperscript{[73]} Bulk electrolysis experiments in acetonitrile yield CO and H\textsubscript{2} as the two major reaction products in a ratio of roughly 1:1 with a total faradaic efficiency close to 100\%. Interestingly, despite working in an aprotic solvent, there was an important amount of H\textsubscript{2} formed. It is believed that the protons needed to form H\textsubscript{2}, and to reduce CO\textsubscript{2} to CO\textsubscript{2}, are provided via residual water in the electrolyte. It is worth noticing that the current density measured on the heterogeneous MOFs catalyst of 2.3 m\textsuperscript{A} cm\textsuperscript{−2} was 2 to 3 times higher than the one observed on the homogeneous Fe-porphyrin catalyst. This difference was attributed to a higher concentration of active centers near the electrode surface on the immobilized MOF backbone. These results are an indication that MOFs represent a promising alternative to prepare heterogeneous catalysts due to a comparable number of active sites as those present in homogeneous catalysts but with a higher density of active sites near the electrode. Nevertheless, the overall activity was still lower than desired, which needs to be improved for industrial applications. The authors hypothesized that, in this case, the catalytic currents are limited by the rate of charge diffusion through the MOF, rather than by the molecular-scale kinetics. Therefore, this is another important parameter to consider when optimizing MOFs as electrocatalyst for CO\textsubscript{2}RR. Furthermore, the activity of this Fe-MOF decreased during the 4 h of reaction, pointing that stability is still a key challenge for this type of catalysts.

One approach to overcome the challenges related with the low conductivity of MOFs is to work with covalent organic frameworks (COFs), which can have a better conductivity due to the conjugated double bonds. That is the case of the work of Lin et al. using a COF made of cobalt porphyrin units linked by organic struts through imine bonds. They observed this material is a selective catalysts for the aqueous electrochemical reduction of CO\textsubscript{2} to CO.\textsuperscript{[74]} The catalytic performance of this Co-COF was optimal at ~0.67 V, reaching a current of 5 mA mg\textsuperscript{−1} of catalyst (~80 mA mg\textsuperscript{−1} of cobalt), with a CO faradaic efficiency of 90\%. In this case, the heterogeneous catalyst also performed better in comparison with the molecular cobalt, showing more than 10\% increase in CO FE in comparison with the molecular catalysts. More interestingly, Lin et al. optimized the catalytic performance of the Co-COF by changing the organic linker to generate a larger pore size that would allow higher capacity of CO\textsubscript{2} adsorption and an increased accessibility to the catalytic cobalt porphyrin active sites (Figure 9). Cyclic voltammetry was used to estimate the concentration of electrochemically active cobalt porphyrin sites of the two materials by integrating the reduction wave assigned to the Co(II)/Co(I) redox couple. According to this test, the integrated area of the initial Co-COF was estimated to be 10\textsuperscript{−8} mol cm\textsuperscript{−2}, whereas the area for the modified COF was 2 \times 10\textsuperscript{−8} mol cm\textsuperscript{−2}, indicating twice the number of accessible Co sites. As a result, a 2.2-fold current enhancement was observed at ~0.67 V maintaining a high CO faradaic efficiency of 91\%. This result nicely exemplifies the possibility of this class of materials for tuning their catalytic performances by changing the building blocks, which opens new opportunities for catalyst design. Furthermore, this optimized COF was more stable than most of the heterogeneous nitrogen containing carbon-based catalysts, maintaining its catalytic activity for up to 24 h. After this time, however, the activity started to decrease.

In order to gain insight on the catalytic process, Kornienko et al. investigated thin films of nanosized Co-MOFs using in situ spectro-electrochemical measurements to study the cobalt oxidation state during the course of reaction.\textsuperscript{[75]} The catalytic activity of their cobalt-porphyrin MOF was first investigated via cyclic voltammetry in CO\textsubscript{2} and Ar-saturated 0.5 M K\textsubscript{2}CO\textsubscript{3}. The resulting voltammogram showed an enhanced current density under a CO\textsubscript{2}-saturated electrolyte in comparison to the Ar-saturated electrolyte which is a first indication of that the catalyst is not only active for the competing process of the HER but also to the CO\textsubscript{2}RR. The potential control electrolysis experiments showed CO and H\textsubscript{2} as the major reaction products, with CO faradaic efficiency of 76\%, while traces of formate and methane...
were also observed. In addition, the catalytic activity was maintained for up to 7 h. In situ spectro-electrochemical measurements were then used to assess the oxidation state of the Co centers under reaction conditions. This study revealed that the majority of the Co centers are redox accessible and that they are reduced during the course of the reaction from Co(II) to Co(I), which is consistent with what has been proposed on immobilized Co porphyrins on which the reduction of Co is the first step of the reaction mechanism. Once Co is reduced to Co(I), CO₂ is adsorbed on the metal center and then reduced further to form CO.

3.1.3. Other Metal Centers

MOFs containing other metal centers have also been reported to be efficient CO₂RR catalyst. For example, Ye et al. investigated the catalytic activity of a highly oriented Re-based MOFs prepared via layer-by-layer deposition of ReL(CO)₃Cl (L = 2,2’-bipyridine-5,5’-dicarboxylic acid)).[76] According to X-ray diffraction (XRD) analysis, this preparation method resulted in an oriented film grown exclusively along the (001) direction. Electrocatalytic measurements were carried out in a nonaqueous electrolyte (0.1 M tetrabutylammonium hydroxide (TBAH) acetonitrile solution with 5% trifluoroethanol). Controlled potential electrolysis experiments at −1.6 V versus NHE showed a current density reaching values of up to 2.5 mA cm⁻² in CO₂-saturated electrolyte. By contrast, the current density in N₂-saturated electrolyte was only 0.4 mA cm⁻². This difference in current density is a first indication that the reduction current in the presence of CO₂ is mainly attributed to CO₂RR. In order to gain insight on the reaction selectivity, the reaction products after 2 h of electrolysis were analyzed by gas chromatography and ¹H-nuclear magnetic resonance (NMR). These analyses indicate that the main product is CO with a remarkably high FE of 93 ± 5%, accompanied by a small amount of H₂. According to these results, the studied Re-based MOF is a highly selective catalyst for the CO₂RR to CO outperforming previously reported MOFs (see Table 2). Nevertheless, these results were obtained in a nonaqueous electrolyte which might help to inhibit the competing process of the HER and to stabilize reaction intermediates of the CO₂RR.

Despite not being one of the most common metal centers in N–C macrocyclic complexes as CO₂RR catalyst, zinc imidazolate MOF (ZIF-8) has also shown promising activity as heterogeneous catalyst for this process.[77] In recent years, ZIFs have emerged as versatile materials for catalysis, in particular, they are known to have high CO₂ adsorption properties, which is an attractive property for CO₂RR catalysts as it would suggest that CO₂ can diffuse through the pores and interact with the active sites. Cyclic voltammetry of these materials showed a cathodic peak, which corresponded to the Zn(II)/Zn(I) transition at less negative potential than the CO₂ reduction current. The authors suggested that Zn(I) is the active species during the catalytic process. To confirm this, however, other operando studies are needed. Controlled-potential electrolysis showed that the selectivity of the CO₂RR is affected by the Zn sources and the working electrolyte. Among the studied Zn sources (ZnSO₄, Zn(NO₃)₂, and Zn(AC)₂), ZnSO₄ showed the best catalytic performance, reaching a CO faradaic efficiency of 68.9% and the broadest potential range suitable for CO₂ reduction to CO (−1.5 to −1.9 V vs SCE). Furthermore, its activity and selectivity were stable during 4 h of reaction. Therefore, the effect of the electrolyte was tested using ZIFN-8SO₄ as catalyst in 0.5 M NaHCO₃, NaCl, and NaClO₄. Once again they observed that the CO selectivity was affected by the electrolyte in the order NaHCO₃ ≤ NaClO₄ ≤ NaCl. The authors hypothesized that the Cl⁻ anion, with smaller hydrated radius compared to ClO₄⁻ and HCO₃⁻, can easily absorb and desorb from the MOF pores, giving it a better mobility to balance the charge more...
efficiently during reduction processes leading to a better catalytic performance. Nevertheless, other effects such as the local pH need to be taken into consideration, and in the nonbuffer electrolytes NaClO₄ and NaCl, it can be expected that the pH in the interphase increases, lowering the concentration of protons and consequently the competing process of the HER. As a result, the CO faradaic efficiency is expected to increase, which is what has been observed in these catalysts.

It has also been demonstrated that Zn-MOF based catalyst can directly reduce CO₂ to hydrocarbons. In a recent study Zn–1,3,5-benzenetricarboxylic acid metal organic frameworks (Zn–BTCMOFs) deposited on carbon paper were used as electrocatalyst for the CO₂RR in ionic liquids. After 2 h of electrolysis, there was no product detected in the liquid phase, while CH₄ was the predominant product in the gas phase, with a faradaic efficiency higher than 80%. The remaining current was attributed to the formation of small amounts of CO and H₂. The high selectivity toward CH₄ production is attributed to an effect of both the catalyst material and the working electrolyte. In particular, imidazolium based ionic liquids can interact with CO₂ allowing a high concentration of CO₂ near the electrode and facilitating its reduction. To look into the effect of the electrolyte, the CO₂RR was carried out in different imidazolium based ionic liquids, 1-butyl-3-methylimidazolium trihexylmethylphosphonium (BmimOTf), 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆), and 1-butyl-3-methylimidazolium perchlorate (BmimClO₄). The current density was higher in the ionic liquids containing fluorine, which was attributed to a higher CO₂ affinity. A higher current, however, also correlates with a higher selectivity toward H₂ indicating that this enhanced activity does not correlate directly with a higher selectivity toward the CO₂RR (Table 3). The important role of the ionic liquid in the production of CH₄ was confirmed by working with other electrolytes. Namely 0.01 M TBABF₄ in DMF, 0.1 M TBAPF₆ in MeCN, and 0.1 M BmimBF₄ in MeCN. In these electrolytes, the CH₄ faradaic efficiencies were considerably lower than those in ionic liquids confirming the important role of the electrolyte in the production of CH₄. In particular, these results show that carrying out the CO₂RR in ionic liquids facilitates the further reduction of CO, which suggests an involvement

Table 2. Summary of the catalytic performance toward CO₂RR on MOF catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Working potential [V]</th>
<th>Product efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reported</td>
<td>Cal. NHE</td>
<td>Cal. RHE</td>
</tr>
<tr>
<td>Cobalt Porphyrin based Co-va lent organic frameworks (COF-367-Co(1%))</td>
<td>20 nmol cm⁻² on GC</td>
<td>0.5 M KHCO₃ pH = 7.3</td>
<td>-0.67 V vs RHE</td>
<td>-1.1</td>
<td>-0.67</td>
</tr>
<tr>
<td>cobalt-porphyrin MOF, Al₂(OH)₃TCP-Po-Co (TCP-Po = 4,4,4,4-porphyrin-5,10,15,20-tetrayl) tetrabenzoate)</td>
<td>110 nmol cm⁻² cobalt on FTO</td>
<td>0.5 M K₂CO₃ pH = 7.8</td>
<td>-0.7 V vs RHE</td>
<td>-1.16</td>
<td>-0.7</td>
</tr>
<tr>
<td>ZnSO₄ derived ZIF-8⁺⁺⁺⁺</td>
<td>0.7 mg cm⁻² on GC</td>
<td>0.5 M NaCl pH = 5</td>
<td>-1.8 V vs SHE</td>
<td>-1.8</td>
<td>-1.5</td>
</tr>
<tr>
<td>Zn(NO₃)₂ derived ZIF-8⁺⁺⁺⁺</td>
<td></td>
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</tr>
<tr>
<td>Zn(AC)₂ derived ZIF-8⁺⁺⁺⁺</td>
<td></td>
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</tr>
<tr>
<td>Copper rubeinate metal organic framework (CR-MOF)</td>
<td>18.33 mg cm⁻² on carbon paper</td>
<td>CO₂ sat. 0.5 M KHCO₃ pH = 7.3</td>
<td>-1.6 V vs SHE</td>
<td>-1.6</td>
<td>-1.17</td>
</tr>
<tr>
<td>Re-Sure-grafted metal organic framework (Re-SURMOF)</td>
<td>70 nmol cm⁻² on FTO</td>
<td>0.1 M tetraethylammonium hydroxide acetoniitrile solution with 5%vol ethanol</td>
<td>-1.6 V vs NHE</td>
<td>-1.6</td>
<td></td>
</tr>
<tr>
<td>Fe-Porphyrin-Based MOF-525 film</td>
<td>62 nmol cm⁻² on FTO</td>
<td>1 M TBAPF₆ in DMF</td>
<td>-1.3 V vs NHE</td>
<td>-1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M TBAPF₆ in DMF with 2,2,2-trifluoroethanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₃(BTC)₂-MOF</td>
<td>GC</td>
<td>CO₂/1TBA/DMF solution</td>
<td>-2.5 V vs Ag/Ag⁺</td>
<td>-1.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. CO₂ reduction performance of Zn-MOF/CP cathodes in imidazolium based IL electrolytes after 2 h at an applied potential of −2.2 V versus Ag/Ag⁺.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>jmax [mA cm⁻²]</th>
<th>FE CH₄ [%]</th>
<th>FE CO [%]</th>
<th>FE H₂ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BmimBF₄</td>
<td>3.1 ± 0.5</td>
<td>80.1 ± 2.6</td>
<td>7.9 ± 2.6</td>
<td>12.0 ± 3.3</td>
</tr>
<tr>
<td>BmimOTf</td>
<td>2.1 ± 0.3</td>
<td>85.4 ± 3.2</td>
<td>4.6 ± 1.2</td>
<td>10.0 ± 2.5</td>
</tr>
<tr>
<td>BmimPF₆</td>
<td>1.6 ± 0.3</td>
<td>87.7 ± 5.1</td>
<td>5.4 ± 2.0</td>
<td>6.9 ± 3.0</td>
</tr>
<tr>
<td>BmimClO₄</td>
<td>0.5 ± 0.2</td>
<td>88.3 ± 3.8</td>
<td>6.8 ± 2.1</td>
<td>4.9 ± 1.0</td>
</tr>
</tbody>
</table>
of the ionic liquid acting as a cocatalyst stabilizing reaction intermediates.

3.2. Reaction Mechanisms

Apart from the experimental studies, computational approaches have also been used to bring insight on the catalytic performance of metal organic frameworks toward the CO2RR. Wannakao et al. have used DFT calculations to investigate the thermodynamic stabilization of relevant intermediates on the M-Porphyrin-R (M-Por) surface.\[81\] For this work, the following metal centers were considered: Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Ir, Pt, and Au. In order to simulate porphyrin framework structures with a reasonable computational cost, metalloporphyrin frameworks were modeled as 2D structures linked with phenyl rings. The authors evaluated the competition between CO2RR and HER on pristine M-Por by plotting $\Delta G^\circ$H versus $\Delta G^\circ$COOH and $\Delta G^\circ$H versus $\Delta G^\circ$OCHO, as seen in Figure 10. The black dotted line corresponds to the $\Delta G^\circ$H = $\Delta G^\circ$COOH, OCHO and it is used to determine the selectivity of the reaction. Above it, the HER is expected to be the predominant process, while porphyrins below the black lines are predicted to be selective toward the CO2RR. According to these calculations, using Cr and Mn as the metal center allows the formation of formic acid at low overpotentials via $\Diamond OCHO$, which is yet to be confirmed experimentally. In addition, consistent with previous experiments, cobalt- and iron-based metalloporphyrins are predicted to be active for the reduction of CO2 to CO, with small potential barriers for the formation of the key intermediate, adsorbed COOH, which leads to CO formation.

As is shown in Figure 10, the HER is clearly a competing process for most of the metalloporphyrins. The authors proposed that this competing process can be limited by using a catalyst design concept to favor the CO2RR and exploiting the versatility of the MOFs as a framework which allows to specifically stabilize the key CO2RR intermediates. In particular, they propose to use H-bonding groups, such as $\Diamond OH$ and $\Diamond CH_2OH$, to functionalize the metalloporphyrin frameworks creating H-bonding pockets. According to the calculations, these groups reduce the required overpotential of the CO2RR. In particular, it was found that Co-Por-CH_2OH is a promising catalyst for the reduction of CO_2 to CO as the process has a limiting free energy of only 0.09 eV. On the other hand, it was found that the reduction of CO_2 to HCOOH at low overpotentials was favored on Cr-Por-R and Mn-Por-R, regardless of the H-bonding groups ($\Diamond OH$ or $\Diamond CH_2OH$). Furthermore, structural factors, such as interlayer distance, affect the computed reaction selectivity. In particular, the $\Diamond COOH$ intermediate was destabilized by a reduced interlayer distance, which would result in a lower selectivity toward CO production.

These calculations can serve as a starting point for future experimental studies on elucidating the relationships between the structure of the catalysts and its activity toward the CO2RR. In particular, looking into the effect of different groups on the ligand presents an interesting opportunity for tuning the catalytic activity of MOF catalysts.

4. MNC Materials

Another approach to incorporate catalytically active MN_x sites into heterogeneous solid catalysts is a heat treatment of individually mixed metal salt precursors, one or several nitrogen containing compounds, and a carbon precursor. In these MNC materials, the nitrogen is incorporated to the carbon structure creating different functionalities, such as pyridinic, pyrrolic, and graphitic nitrogen (Figure 11). The metal atoms are coordinated to these N functionalities creating similar active sites as those on the Metal-N-macrocycles on a conductive solid catalysts. These materials were initially developed as low cost alternative for Pt in fuel cell cathodes, as they are good catalysts for the oxygen reduction reaction.\[82–86\] Recently they have also been studied as CO2RR, as this synthesis method represents a less expensive alternative to prepare heterogeneous catalyst containing MN_x functionalities.

Initially, this class of materials were prepared via pyrolysis of carbon-supported metal N_4 macrocycles and tested as electrocatalyst for the ORR.\[87–90\] During this process, depending on the heat-treatment temperatures, the M–N_4 moiety was partially or completely decomposed, forming new functionalities and catalytic sites. These materials can also be prepared by heat treatment of MOFs, as was done by Zhao et al. who prepared Ni–N-doped carbon starting from a metal organic framework (ZIF-8).\[81\] For the syntheses, first an ionic exchange between Zn nodes and Ni ions within the cavities of the MOF was performed. Then, the mixture was pyrolyzed at 1000 °C under Ar flow. During this heat treatment, the organic linkers were transformed into an N-doped carbon skeleton, in which single Ni sites were coordinated to the N atoms, with an actual
Ni loading of 1.53% according to inductively coupled plasma-optical emission spectrometry (ICP-OES). Furthermore, both X-ray absorption spectroscopy (XPS) and XANES suggest an electronic structure of Ni$^{\delta+}$. The resulting material was tested as a CO$_2$RR catalysts in 0.5 M KHCO$_3$, showing good selectivity for CO production. At an overpotential of 0.89 V, CO was produced at high partial current density of 10.48 mA cm$^{-2}$, which represent a CO faradaic efficiency of 71.9% and a turn over frequency 5273 h$^{-1}$. Furthermore, the catalytic activity and selectivity were maintained for 60 h indicating that this is one of the most stable heterogeneous nitrogen containing carbon-based catalysts for the CO$_2$RR. Importantly, as a control experiment CO$_2$RR was also tested on pyrolyzed metal free ZIF. Both the current density and CO faradaic efficiency were clearly lower in the absence of Ni, indicating that the metal sites play an important role in the catalytic process. More interestingly, the catalytic activity of this material is also better than that of commercial Ni foam, on which a low current and a high H$_2$ faradaic efficiency were observed. These results suggest that the isolated Ni$^{\delta+}$ sites coordinated to nitrogen atoms are responsible for the promising catalytic performance toward the CO$_2$RR on this Ni containing material.

It would be desirable, however, to prepare CO$_2$ reduction catalysts using inexpensive precursors, such as common inorganic salts, carbon, and an affordable N-containing compound. In this regard, Gupta et al. were able to prepare the first ORR catalyst from non-N$_4$-macrocycles as the nitrogen source. They performed heat treatment of polycrylonitrile (PAN), mixed with Co(II) or Fe(II) salts and high-area carbon.$^{[82]}$ Since then, different nitrogen sources such as NH$_3$,$^{[84]}$ ethylenediamine,$^{[92]}$ cynamide,$^{[93]}$ and aniline$^{[83]}$ have been successfully utilized for the preparation of MNC materials.

In 2015, Varela et al. reported the use polyaniline (PANI) derived carbon materials as efficient catalyst for CO$_2$RR in 0.1 M KHCO$_3$ electrolyte.$^{[94]}$ We prepared these materials following the procedure reported by Wu et al., in which aniline is used as a source of nitrogen by mixing it with a high carbon surface area (Ketjenblack EC-300J) and an inorganic metal salt.$^{[83]}$ Later, ammonium persulfate was added to polymerize the aniline. After polymerization, the resulting solid was subjected to a heat treatment to fully incorporate the nitrogen and metal ions to the carbon structure. In the study by Varela et al., three different mono and bimetallic PANI derived solid carbon catalysts Fe–N–C, Mn–N–C, and FeMn–N–C were tested and their catalytic performance was also compared with that of the metal free PANI derived solid carbon material (N–C). Interestingly, all four materials show a high selectivity toward CO production with a faradaic selectivity close to 80% at around −0.55 V versus RHE Table 4. The current density, however, is clearly enhanced by the presence of Fe and Mn, confirming not only the important role of the metal centers, but suggesting additional synergistic effects in the electrocatalytic process of bimetallic-nitrogen doped carbons. Despite the low activity of the metal free catalysts, it is also selective for the reduction of CO$_2$ to CO and therefore, the authors hypothesize that the nitrogen moieties are also involved as an active surface site in the CO$_2$RR. In addition to the production of CO, traces of CH$_4$ were also observed as a reaction product when the materials containing Fe centers were used as catalyst. This result suggested that, depending on the metal center, CO can be further reduced into hydrocarbons. As it was shown by temperature programmed CO desorption studies, the CO desorption energy correlates with CH$_4$ formation. Whereas no methane was observed in Mn–N–C, which had the lower temperature for CO desorption, the FeMn–N–C catalysts, which exhibit the highest CH$_4$ production rate, bind stronger to CO in comparison with the other materials. These results confirmed that the binding energy of the reaction intermediates is crucial on determining a catalysts performance. In this case, a high binding energy between CO and the metal center facilitates the direct reduction of CO$_2$ to hydrocarbons.

When working with this class of materials, it is important to consider that a variety of possible active sites are present. One first question that needs to be addressed is if the activity can indeed be attributed to the coordinated metal centers, to other N functionalities or to some metal based nanoparticles in the carbon support. Therefore, Huan et al. investigated a series of Fe based catalyst controlling the ratio of isolated Fe$_4$ sites versus Fe-based nanoparticles.$^{[95]}$ Using Mössbauer spectroscopy, the...
authors were able to identify the presence of different Fe species, namely crystalline structures and atomically dispersed Fe ions in the N-doped carbon matrix, mainly square-planar FeN4. Linear sweep voltammetry in CO2-saturated NaHCO3 showed a much lower current on the iron free material which indicates a much lower current on the iron free material which indicates a lower catalytic activity. In addition, the catalysts with the lowest amount of FeN4 sites show a higher onset potential and more rapid current increase once the reduction reaction starts. This suggested a different catalytic process than that observed on the materials with a high number of FeN4 sites. Controlled potential electrolysis showed that CO selectivity correlates with the concentration FeN4 sites, reaching a maximum of 80% at −0.5 V versus RHE. By contrast, materials containing metallic Fe particles (or iron carbides) are mainly active for the HER, confirming that the CO2RR activity correlates with Fe incorporated to the carbon structure via N coordination and that other forms of Fe are more likely to be involved in the competing process of the HER.

The importance of having Fe sites coordinated to nitrogen in a CO2RR catalyst was confirmed by the work of Genovese et al. who studied Fe oxyhydroxide nanostructures supported on O- and N-doped carbon (Fe/O–C and Fe/N–C) as catalysts. The selectivity CO2 electrolysis was highly dependent on the graphitic support. While the Fe/O–C produced mainly H2 (FE 94.9%), the CO2RR was the predominant process when the Fe oxyhydroxide was supported on N-doped carbon with a faradaic efficiency of 97.4%. Interestingly, the reduction products on Fe/N–C were HCOOH and CH3COOH with the last one being the preferred product. The authors used a combination of electron microscopy, operando X-ray spectroscopy techniques, and density functional theory simulations to correlate the catalyst structure with its activity. They found that the HER correlated with the formation of metallic Fe, while the formation of acetic acid is related to the formation of nitrogen-coordinated iron species. According to their studies the N atoms have a double effect on the catalytic activity toward the CO2RR: On one hand, N atoms stabilize reaction intermediates. On the other hand, N also stabilizes Fe(II) species hindering the formation of Fe 0, which is more active toward the competing process of the HER. It is important to notice that the catalyst studied by Genovese et al. is clearly different than those previously discussed in this section. An important difference is that this Fe/N–C has Fe sites coordinated to both nitrogen and oxygen which might be one of the reasons behind its distinct selectivity toward the formation of carboxylic acids.

Table 4. Summary table of the catalytic performance toward CO2RR on MNC catalysts materials.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Working potential [V]</th>
<th>Product efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reported</td>
<td>Cal. NHE</td>
<td>Cal. RHE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni single atoms distributed in nitrogen-doped porous carbon (Ni:5A/N-C)</td>
<td>0.2 mg on 2 cm² carbon fiber paper</td>
<td>0.5 µ M KHCO3 pH = 7.3</td>
<td>−1.0 V vs RHE −1.43 −1.0</td>
<td>CO: 71.9% TOF: 5273 h⁻¹ jCO: 10.48 mA cm⁻²</td>
<td>Zhao et al[97]</td>
</tr>
<tr>
<td>PANi-derived-Fe-N-C</td>
<td>0.78 mg cm⁻² on GC</td>
<td>0.1 µ M KHCO3 pH = 6.8</td>
<td>−0.55 V vs RHE −0.95 −0.95</td>
<td>CO: 80% jCO = 6 A g⁻¹</td>
<td>Varela et al[94]</td>
</tr>
<tr>
<td>Mn-N-C</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Mn-Fe-N-C</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ZIF-derived-FeO2-N-C</td>
<td>1.0 mg cm⁻² on GDL</td>
<td>0.5 µ M NaHCO3 pH = 7.3</td>
<td>−0.5 V vs RHE −0.9 −0.5</td>
<td>CO: 75% Rate: 0.017 µmol s⁻¹</td>
<td>Huan et al[98]</td>
</tr>
<tr>
<td>Fe-N-C</td>
<td>0.75 mg cm⁻² on GC</td>
<td>0.1 µ M KHCO3 pH = 6.8</td>
<td>−0.55 V vs RHE −0.95 −0.95</td>
<td>CO: 70% jCO = 4 A g⁻¹</td>
<td>Su et al[100]</td>
</tr>
<tr>
<td>Ni-N-C</td>
<td>0.8 mg cm⁻² on GC</td>
<td>0.1 µ M KHCO3 pH = 6.8</td>
<td>−0.8 V vs RHE −1.2 −0.8</td>
<td>CO: 88% jCO = 12.5 A g⁻¹</td>
<td>Jiang et al[104]</td>
</tr>
<tr>
<td>Ni-N-Graphene</td>
<td>0.3 mg cm⁻² on GC</td>
<td>0.1 µ M KHCO3 pH = 6.8</td>
<td>−0.7 to −0.9 V vs RHE −1.1 to −1.3 −0.7 to −0.9</td>
<td>CO: 90% (max.)</td>
<td>Su et al[100]</td>
</tr>
<tr>
<td>Ni-CS</td>
<td>0.2 mg cm⁻² on GC</td>
<td>0.1 µ M KHCO3 pH = 7.3</td>
<td>−0.82 V vs RHE −1.25 −0.82</td>
<td>CO: 93.2% jCO = 20 A mg⁻¹ TOF: 2700 h⁻¹</td>
<td>Su et al[100]</td>
</tr>
<tr>
<td></td>
<td>0.2 mg cm⁻² on Sig- racet 35 BC GDL</td>
<td>0.5 µ M KHCO3 pH = 7.3</td>
<td>−0.6 V vs RHE −1.03 −0.6</td>
<td>CO: 87% jCO = 31.4 A mg⁻¹</td>
<td>Li et al[105]</td>
</tr>
<tr>
<td>Exclusive Ni-N2-C</td>
<td>0.2 µg cm⁻² on GC</td>
<td>0.5 µ M KHCO3 pH = 7.3</td>
<td>−0.81 V vs RHE −1.24 −0.81</td>
<td>CO: 99%</td>
<td>Li et al[105]</td>
</tr>
<tr>
<td>Fe-NS-C</td>
<td>300 µg cm⁻² on GC</td>
<td>0.1 µ M KHCO3 pH = 6.8</td>
<td>−1.3 V vs SCE −1.03 −0.63</td>
<td>CO: 90% CH4: 0.02%</td>
<td>Dembinska et al[103]</td>
</tr>
</tbody>
</table>
highlighting a structural advantage of catalytic materials containing FeN active sites. This inhibition relies on two effects: First, the single sites in a porphyrin-like structure require an axial vacancy for hydrogen on top binding, compared to the hollow site on a metal catalyst surface. According to their calculations, the top H binding is generally weaker than the hollow binding which leads to a higher barrier for the HER on porphyrin-like structures. Second, for the single sites of the MNC materials, the HER has to follow a Heyrovsky reaction mechanism instead of the energetically favored Tafel mechanism. These two effects inhibit the HER resulting in a minimum of 0.3 eV advantage to the CO2RR versus HER (based on COOH* vs H*) in MNC materials compared to metal surfaces, which makes these materials selective catalysts for the CO2RR (Figure 12).

4.1. The Role of the Metal Center

In addition to the reduction of CO2 to CO, the theoretical study of Tripkovic et al. suggests that, depending on the metal center, CO2 can be further reduced to CH4 or MeOH. For example, Fe centers were predicted to reduce CO to CH4, which was later corroborated by Varela et al. Nevertheless, the selectivity toward CH4 on FeN materials was lower than 1%. More interestingly, Rh-functionalized porphyrin-like graphene was predicted to efficiently reduce CO to methanol at an overpotential of 0.22 V, which is considerably lower than the observed overpotential on the extended metal surfaces. This prediction, however, has not been corroborated experimentally.

The importance of the nature of the metal center on the activity and selectivity toward the CO2RR was latter investigated by Ju et al. In this work, we presented a combined experimental and theory study on the CO2RR using M-N doped nanoporous carbon using five different metal centers, Fe, Mn, Cu, Co, and Ni as catalysts. Consistently with Varela et al., they observed a maximum for CO selectivity on Mn and Fe catalysts at around −0.55 V versus RHE, when the potential was more negative, the HER became the dominant process. The selectivity toward CO, however, was clearly different, on Fe–N–C the CO faradaic efficiency reached 65%, whereas the faradaic efficiency toward CO on Mn–NC was only 40%. In addition, traces of CH4 were also detected on these two metal centers, confirming that CO2 can be directly reduced to hydrocarbons using this class of materials as electrocatalysts. By contrast, the CO selectivity on Cu–N–C and Co–N–C remained low across the potential range tested (−0.4 to 0.85 V vs RHE) and H2 production was clearly the predominant process (Figure 13a,b). The low CO selectivity on the Co containing catalysts is particularly surprising, as Co N–C macrocycles and Co containing MOFs have shown to be selective catalysts for the CO2RR to CO. This result suggests that the trends observed on immobilized complexes are not directly translated to MNC materials. Among the tested metal centers, the highest faradaic efficiency toward CO was observed on Ni–N–C reaching 85% at −0.78 V versus RHE, indicating that Ni containing catalysts are good candidates for the selective reduction of CO2 to CO using MNC materials.

In order to bring insight on the role of the nature of the metal center on the catalytic performance of MNCs, Ju et al. also performed DFT simulations considering a single-site motif MN4 as active site. Despite the presence of other Mn functionalities, previous computational studies showed that the metal center is the dominating factor on the catalytic performance of these materials in comparison with the role of other Mn functionalities. Nevertheless, when dealing with this class of materials it is important to remember that more than one possible active site is present on the catalysts surface. The simulations indicate that the onset potential for CO2RR correlates with the free energy of COOH. Nevertheless, as the overpotential increases, there are other factors that need to be taken into consideration. At an intermediate overpotential, the rate-controlling intermediate shifts from COOH to CO. Increasing CO chemisorption now scales with gaseous CO product yields. At increasing overpotentials, the CO yield of the FeNC catalyst drops, suggesting a rate limitation by the non-faradaic water desorption process. Finally, at high over potentials, the competition process of the HER becomes more relevant. The Co–N–C was found to be the most efficient catalyst for this H2 formation and as a result it displays the highest faradaic efficiency for H2. By contrast, the Ni centers exhibit a very weak biding energy toward H making the HER thermodynamically unfavorable at −0.8 V RHE and resulting in the observed low production of H2 and high CO selectivity (Figure 13c,d). Furthermore, in agreement with the previous results by Varela et al., at high overpotentials, the reduction of CO to CH4 correlates with a
strong *CO binding energy. Among the studied metal centers, the highest CH\textsubscript{4} production rate is observed on the Fe–N–C on which CO is predicted to bind stronger and long enough to undergo further reduction. On the contrary, on Ni and Cu containing catalysts, the *CO detaching is energetically favored preventing its transformation.

Traces of CH\textsubscript{4} were also observed as a reaction product from the CO\textsubscript{2}RR on nitrogen and sulfur codoped iron-containing highly porous carbon gel, indicating that the presence of Fe centers facilitates CH\textsubscript{4} production even in the presence of other heteroatoms.\textsuperscript{[101]} This material was synthesized through pyrolysis of an organic gel which was prepared via sol–gel polycondensation of resorcinol together with the mixture of two heterocyclic aldehydes containing nitrogen and sulfur, namely, 2-pyrrolecarboxaldehyde and 2-thiophenecarboxaldehyde. Gas chromatography was used to corroborate the formation of CO as the major reaction, which was obtained with a maximum FE of 85\% at \(-1.3\) \text{V} versus SHE. In addition, traces of CH\textsubscript{4} were also detected, even lower than that observed on FeNC materials reaching only 0.03\%. Despite the low activity toward CH\textsubscript{4} this study confirms the ability of Fe centers to reduce CO\textsubscript{2} to hydrocarbons and it serves as a first example of a sulfur containing carbon materials as electrocatalyst for CO\textsubscript{2}RR.

4.2. Ni–N–C Highly Selective CO Production Catalysts

In agreement with the high CO faradaic efficiency observed on Ni–N–C by Ju et al., a remarkably high faradaic efficiency toward CO of \(\geq 90\%\) has been observed in Ni–N-modified graphene (Ni–N–Gr).\textsuperscript{[102]} Sun et al. prepared this material via heat treatment of Ni-pentaethylenediamine and graphene oxides under inert atmosphere. The characterization of the resulted material using XPS and EXAFS confirmed the incorporation of the Ni atoms coordinated to N into graphene structure. The electrocatalytic tests carried out in CO\textsubscript{2}-saturated KHCO\textsubscript{3} electrolyte showed that Ni–N–Gr exhibits a high CO faradaic efficiency of around 90\% in a potential range of \(-0.7\) to \(-0.9\) \text{V} versus RHE. Furthermore, five hour electrolysis experiments showed only a small decrease in activity and selectivity. In order to confirm the importance of the Ni center on the catalytic activity of Ni–N–Gr, Sun et al. also investigated Cu–N modified graphene (Cu–N–Gr) and metal free N modified graphene (N–Gr). Both of these materials exhibit poor CO\textsubscript{2} reduction activity. In particular, N–Gr reduced CO\textsubscript{2} to CO with a faradaic efficiency of 20\% showing that despite some catalytic activity of the N functionalities toward CO\textsubscript{2}RR, the Ni centers are crucial for the high CO selectivity observed on Ni–N–Gr.

With the aim of having a better understanding of the catalytic process on the Ni centers, Jiang et al. have recently published a combined experimental and theory study on Ni–N graphene sheets (Ni-GS).\textsuperscript{[104]} In agreement with previous reports, they observe that this material is a highly active electrocatalyst for CO\textsubscript{2} reduction to CO in an aqueous electrolyte (CO\textsubscript{2}-saturated KHCO\textsubscript{3} solution). This catalyst exhibits a low CO\textsubscript{2}RR onset potential, as CO detection starts at \(-0.35\) \text{V} versus RHE, a high selectivity (FE \(93\%\) at \(-0.75\) \text{V} vs RHE) and a high CO current density of 20 mA mg\textsuperscript{-1} (4 mA cm\textsuperscript{-2}). In addition, a 80\% FE toward CO was maintained after 20 h of continued CO\textsubscript{2} electrolysis. Based on different control experiments, the authors attribute this excellent catalytic performance to the presence of insolated Ni sites. On one hand the Ni nanoparticles on Ni-GS present nearly no activity toward the
CO2RR being H2 the major reaction product. In addition, acid leaching of these Ni atoms results in a dramatically decreased CO evolution activity which suggests that the CO2RR activity is dominated by the Ni site and not by the N functionalities. Finally, the Co and Fe catalysts exhibit a lower activity than their Ni analog.

Jiang et al. have also performed density functional theory calculations to understand the origin of the high activity of the Ni–N-GS toward the CO2RR. With this purpose they have calculated the free energy diagram of the reduction of CO2 through *COOH and *CO on different possible Ni centers. In particular, they have considered single or double vacancies coordinated to both nitrogen and carbon atoms and compared it with that of metallic Ni (see Figure 14). According to their calculations, the CO2 activation barrier is dramatically lower on the Ni in graphene than that of metallic Ni, consistent with the experimental observations. Contrary to what is commonly believed for this class of materials, the authors found that the Ni bound to nitrogen is not necessary the only active site for the reaction, as other Ni centers in which Ni is bound to carbon are predicted to be more reactive towards the CO2RR. In a more recent study, Jiang et al. used in situ X-ray absorption spectroscopy to confirm the presence of both Ni bound to C and Ni bound to N on Ni–N-doped graphene suggesting that both sites could be playing a role on the CO2RR. The presence of Ni active sites other than NiN4 could be one of the reasons for which the activity trends observed on MN-C macrocycle catalysts cannot be directly translated to MNC materials.

The nature of the active sites on MNC materials, however, is still under debate. The importance of NiN4 sites involvement in the catalytic process was demonstrated in the work by Li et al. who tested the catalytic activity of a Ni–N–C containing exclusively NiN4 sites.[105] This material was prepared using topochemical transformation strategy, by dispersing Ni doped C3N4 in a glucose containing solution and heated it at a 180 °C in an autoclave before thermal annealing at 1000 °C. Synchrotron-based EXAFS was used to determine the chemical configurations around Ni sites. These results suggested Ni–N4 as the only Ni site present in Ni–N–C. By contrast, the direct pyrolysis of Ni doped C3N4 to prepare Ni@N–C resulted in the formation of different Ni sites. Linear sweep voltammetry of the Ni–N4–C in CO2-saturated KHCO3 solution indicates a remarkably high activity of Ni–N4–C (1.41 wt% Ni loading) reaching a current density of 36.2 mA cm−2 at −0.91 V. This value was considerably higher than that of the metal free catalyst and that of Ni@N–C. More interestingly, product analysis revealed that Ni–N4–C is highly active and selective toward CO production, reaching a maximum FE of 99% at −0.81 V with a current density of 28.6 mA cm−2, making Ni–N4–C one of the most promising catalysts to be used in the selective production of CO. By contrast, the faradaic efficiencies of N–C and Ni@N–C were considerably lower, reaching only 64% and 65%, respectively. These results confirmed the importance of the presence of NiN4 sites on carbon materials in the reduction of CO2 to CO, suggesting that the NiN4 sites are not only active but also selective toward the CO2RR and as such there is little production of H2. Bimetallic nitrogen doped carbons M1/M2-N-C, such as FeMn-N-C or FeNi-N-C have shown new synergistic effects, such as improved selectivity or performance stability, and hold the promise for more unexpected catalytic synergies in the future.
4.3. Other Effects on the Selectivity of M–N–C Catalysts

In addition to a variety of metal active sites that can be incorporated on N doped carbon materials, MNC materials also have a variety of N functionalities which need to be considered in order to understand the nature of the possible active sites. In a recent study by Leonard et al., the role of different nitrogen functionalities was investigated by exploring the addition of secondary nitrogen precursors to polyaniline based FeNC catalysts.[106] They found that the addition of the secondary nitrogen precursor has a clear effect on the catalyst's performance, in particular melamine based Fe-PANI catalysed was the most active and selective in the reduction of CO2 to CO, reaching a CO faradaic efficiency of 85% and a CO partial current density of over 5 mA cm\(^{-2}\). In order to understand better the effect of the secondary nitrogen, the surface area normalized partial current density was correlated to the concentration of the different N functionalities obtained via XPS. We found that the catalytic activity does not correlate directly to the N–Fe and that other N moieties are also involved in the catalytic process. In particular, the results suggest that both N–Fe and pyridinic species are likely to be actives sites and that both of them contribute roughly equally to catalytic activity of the FeNC catalysts. In addition, we performed operando X-ray absorption experiments and found that the Fe centers are reduced at around −0.9 V versus RHE, which correlates with the redox potential of Fe 0/2+. Interestingly, this reduction coincides with an increase in CH\(_4\) production, suggesting this change in the oxidation of the inactive site favors the reduction of CO.

The studies described above have shown that different material properties can affect the catalytic behavior of the MNC materials, such as the nature of the metal center, its coordination to nitrogen and carbon, and the presence of different nitrogen functionalities. In addition, Zhu et al. proposed that also the carbon structure of such catalyst plays a role in determining catalytic performance of these class of materials.[107] In particular, they looked into a curvature-dependent selectivity of CO\(_2\) reduction on cobalt-porphyrin nanotubes (CoPorNTs). Using first-principles calculations, they have studied the trends in binding energies of CO2RR reaction intermediates on different tube sizes CoPorNTs. Their study suggests that these are promising and selective catalysts for the CO2RR and that the reaction selectivity can be tuned by changing the curvature of the carbon nanotubes. In particular, they predict that highly curved nanotubes would produce CH\(_4\) at lower potential than Cu catalysts. While low curved nanotube would produce CO as a major product. These results highlight the complexity of these MNC materials and that multiple factors control their catalytic activity and selectivity. The role of the carbon support is one that has yet to be experimentally studied and can be key for finding the most suitable catalysts for the process.

Furthermore, similar to other catalytic materials, the reaction conditions are also expected to play an important role in determining the activity and selectivity of MNC materials. Therefore, Varela et al. studied the catalytic performance of a polyaniline derived Fe–N–C material in different electrolytes.[108] We observed that the electrolyte's pH can be used to tune the reaction's selectivity. In particular, at high local pH (low proton concentration), the HER and CH\(_4\) formation are favored, while CO production is not dependent on pH on the NHE scale. As a result, higher CO faradaic efficiencies are observed at higher pH values. The HER and CH\(_4\) formation dependency on pH (in the NHE scale) is consistent with a reaction mechanism in which the rate limiting step involves a proton transfer. In particular, for CH\(_4\) formation, this step has been proposed to be the CO protonation.[97,99] By contrast, the independency of the CO\(_2\) reduction to CO on pH suggests a decoupled proton electron transfer mechanism, similar to that observed on immobilized metal N–C macrocyclic complexes. In particular, we proposed that the CO2RR on FeNC materials occurs via the formation of a (Fe–N–C)–CO\(_2\)− intermediate, as shown in Figure 15, showing that these FeN\(_x\) functionalities introduced to the carbon support behave similar to the FeN\(_4\) sites on metal macrocycle complexes.

5. Metal-Free Heterodoped Carbon Materials

Incorporating nitrogen and metal atoms into carbon structures typically results in carbon-based catalysts with a high activity and tunable selectivity for the electroreduction of CO\(_2\) to CO. Several studies, however, have shown that the presence of metal is not needed to create an active CO2RR catalyst. Consistent with the observation of Leonard et al. that pyridinic species are involved in the catalytic process, it has been reported that nitrogen doped carbon (NCs) materials are also promising catalyst for the CO2RR.

In 2013, Kumar et al. reported the use of low-priced and metal-free carbon nanofibers (CNFs) as highly active catalyst for CO2RR in ionic liquid (EMIM–BF\(_4\)).[109] The CNFs were prepared via pyrolysis of electrospun nanofiber mats and PAN. After the heat treatment, the incorporation of nitrogen was confirmed via XPS. For the electrocatalytic testing, EMIM–BF\(_4\) was chosen as the electrolyte given its high CO\(_2\) capture capability and its ability to lower the CO\(_2\) reduction overpotential for metal based catalysts. Constant potential CO\(_2\) electrolysis at −0.57 V versus SHE showed that the CNFs are highly selective for the CO2RR, producing CO with a faradaic efficiency of 98%. A total current of −1.5 mA cm\(^{-2}\) was maintained during 9 h of CO\(_2\) electrolysis. Despite the current being low for technological applications, this work shows that the N functionalities without metal present are active toward the CO2RR.

In order to get further insight on the role of the different functionalities on the N doped carbon materials, the potential electrolysis experiments need to be accompanied by material characterization. In this regard, the authors looked in to the XPS N1s spectrum before and after reaction (Figure 16). The unchanged concentration of the pyridinic N leads the authors to believe that the CO2RR is taking place on the positive carbon atoms next to the pyridinic N. The authors proposed that the positive carbon atoms are first reduced and then formed an intermediate complex with [EMIM–CO\(_2\)]. This hypothesis suggests an important role of the N containing ionic liquid in stabilizing the key intermediate and facilitating the reaction. As it has been observed on different catalysts materials, carrying out the CO2RR in ionic liquids has a beneficial effect for the
process, suggesting an involvement of the electrolyte itself during the CO2RR.\[39,80\] As we will discuss later in this section, the role of ionic liquids is important but not crucial for the CO2RR on NC materials, as there are also several examples of their activity in aqueous electrolytes.

5.1. Formate Producing N–C Materials

The study by Kumar et al. showed promising activity of N doped carbon materials for the CO2RR. However, despite some of the advantages of ionic liquids such as high CO2 solubility, they also have some drawbacks such as their elevated price. Therefore, working in aqueous electrolytes is still desired. In that regard, Zhang et al. tested nitrogen-doped carbon nanotubes (NCNT) in aqueous media and observed that such nanotubes are selective and robust electrocatalysts for CO2 reduction to formate.\[110\] The NCNTs were prepared by an ammonia plasma treatment of multiwalled carbon nanotubes deposited onto a glassy carbon electrode. Later, the incorporation of nitrogen was monitored by XPS. For these materials, it is crucial to ensure that no metal impurities are present, since even small amounts could have an important impact on the CO2RR. Therefore, for this study, the authors purified the nanotubes by electrochemical oxidation. Electrocatalytic testing was evaluated by controlled potential electrolysis in CO2-saturated 0.1 M KHCO3 followed by product analysis using NMR and gas chromatography. Contrary to the studies of Kumar, herein formate was found to be the main reaction product (59% FE) from the CO2RR accompanied by small amounts of CO. The important role of the incorporated N on the CO2RR was confirmed by comparing the catalytic performance of NCNT with that untreated carbon nanotubes and on the oxygen plasma treated carbon nanotubes. In both cases, a lower activity was accompanied by a lower formate faradaic efficiency (5 and 7% respectively), suggesting that the presence of N enhanced the activity of the nanotubes toward the CO2RR. Analogous to what has been observed in the presence of ionic liquids, Zhang et al. also investigated the effect of polyethyleneimine (PEI) as a cocatalyst and found that it significantly reduces the catalytic overpotential and increases formate selectivity which reaches 85%. The authors suggest that the PEI acts as a cocatalyst helping in stabilizing the CO2•− intermediate, showing once again that N functionalities are beneficial for the CO2RR.

Formate was also observed as a main product of the CO2RR in KHCO3 electrolyte using N doped graphene by Wang et al.\[111\] The nitrogen-doped graphene was prepared via pyrolysis of graphene oxide and melamine under an N2 atmosphere. The incorporation of N was confirmed by XPS, which is commonly used when studying these materials to quantify the different types of N present. In this study, pyridinic N was found to have a higher concentration with 3% atomic content, followed by graphitic (1.6%) and pyrrolic N (0.9%). In addition, scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to characterize its morphology, revealing that the N-graphene sheets are folded and layered structures. Finally, Raman spectroscopy analysis revealed a local distortion in graphitic sheets which is caused by the difference in atomic masses and chemical bond lengths of carbon and nitrogen. Constant electrolysis experiments in CO2-saturated 0.5 M KHCO3 solution in the potential range from −0.3 to −1.3 V versus RHE showed H2 and formate as the only reaction products. The faradaic efficiency toward formate reached a maximum of 73% at −0.84 V which is higher than that observed on the study by Zhang et al. in the absence of cocatalysts (Table 6). The reason behind this difference is still unclear. One could elucidate that the concentration of the different N functionalities could be playing a role on the catalysts selectivity. In the study by Zhang et al., most of the incorporated N correspond to pyrrolic N while the catalysts prepared by Wang et al. had more pyridinic N. This could be an indication that pyridinic N is facilitating the CO2RR.

**Figure 15.** Proposed mechanism by Varela et al. for the CO2RR on Fe–N–C catalysts.
Nevertheless, more systematic studies looking into the role of the N functionalities are needed to draw such a conclusion. In addition, with the aim of gaining insight on the possible CO₂ reduction mechanism of N-graphene, Wang et al. presented a Tafel analysis obtaining a slope of 135 mV dec⁻¹. Based on this value, the authors proposed that the CO₂ reduction mechanism goes through a rate-determining transfer of one electron, in particular the reduction of the adsorbed CO₂ to generate the surface adsorbed CO₂⁻, similar to what has been proposed for Fe–N–C and Co-porphyrins.

5.2. CO Producing N–C Materials

In contrast to the observation of Zhang et al. and Wang et al., other groups have observed CO as a main reaction product of the CO₂RR in aqueous electrolyte using N doped carbon materials as catalyst. That is the case of Wu et al. who investigated the catalytic activity of a NCNT array in aqueous media. These NCNTs were prepared by liquid chemical vapor deposition, spraying a precursor solution of acetonitrile and dicyandiamide with ferrocene in Ar/H₂ atmosphere at 850 °C, leading to a homogeneous NCNT deposition. SEM and TEM revealed the formation of well-aligned multiwalled NCNTs arrays with a mean tube diameter of ≈30 nm. In addition, the obtained XRD spectra were consistent with a high crystallinity and a graphitic nature of NCNTs. Finally, XPS was used to calculate the N content which was estimated to be 5.0 at%. In this case, graphitic N was identified as the major N functionality (2.4 at%) followed by pyridinic and pyrrolic with 1.5 and 1.1 at%, respectively. The catalytic activity of the NCNTs was tested via electrolysis in CO₂-saturated 0.1 m KHCO₃. The authors found that this is a selective catalyst for the CO₂ reduction to CO reaching of 80% FE at −0.78 V and that the catalyst was stable for 10 h. These results indicate that the NCNTs are competitive catalyst for the CO₂RR in terms of selectivity and stability, however their current density was only 0.75 mA cm⁻² and therefore the activity needs to be improved to compete with metal catalysts and MNC materials.

An alternative approach for preparing active N–C catalyst has been explored by Lu et al., who prepared N doped carbon nanotubes by covalently attaching graphitic carbon nitride onto multiwall carbon nanotubes (g-C₃N₄/MWCNTs). This composite was prepared from a strong acidic solution containing dicyandiamide and MWCNTs. According to TEM images, the resulting composite consists of a g-C₃N₄ layered structure in which MWCNTs act as the separator. The g-C₃N₄/MWCNTs composite was also characterized with XRD, the resulting pattern shows a strong diffraction peak at 2θ = 27.3° which is attributed to the π-conjugated layers for graphitic materials and confirms the presence of a graphic phase. The composition of the resulting composite was analyzed with XPS, showing the presence of both carbon and nitrogen. The electrocatalytic tests were carried out in 0.1 m KHCO₃, forming CO as a major reaction product.
product. Its detection starts at $-0.45$ V versus RHE, with a faradaic efficiency of 41%. As observed for other materials, the CO faradaic efficiency increases up to a maximum, in this case 60% at $-0.75$ V versus RHE. The authors compared the catalytic g-C$_3$N$_4$/MWCNTs with that of pure MWCNTs and found that MWCNTs alone exhibit negligible CO$_2$ reduction activity, suggesting an important role of the N species on the CO2RR. In addition, the authors claimed that both types of nanotubes should have similar amounts of metal impurities, and therefore, the high catalytic activity of the N containing nanotubes is not attributed to any metal present on the catalysts. Nevertheless, to exclude the involvement of a metal in the catalytic process, it would be necessary to analyze the catalyst composition to ensure there is no metal present. One could hypothesize, for example, that the metal impurities can coordinate to N creating a metal active site for the CO2RR which is not present on the N free catalysts.

To gain further insight in the nature of the active sites, Lu et al. also evaluated the catalytic performance of physically mixed as-prepared g-C3N4 and MWCNTs with a 1:1 mass ratio. They found that in this case HER was the predominant process. The authors attribute this difference to the absence of covalent C--N bond between g-C3N4 and MWCNTs, which were not observed in the XPS of the physical mixture. Therefore, they proposed that these covalent C--N bonds formed between the g-C3N4 and MWCNT are the active sites for CO2RR.

Interestingly, Jhong et al. achieved much higher CO selectivity also using a composite made of carbon nitride (g-C3N4) and MWCNTs. This material was prepared by heat pyrolysis of g-C$_3$N$_4$ supported on MWCNTs at 1000 °C. Elemental analysis of the resulting material revealed a low N content of 0.39%, which is due to the fact that the pyrolyzed g-C$_3$N$_4$ forms only a thin layer on the surface of the MWCNT. Furthermore, the N 1s peak from the XPS analysis showed the presence of the following N functionalities: pyridinic (33.4%), pyrrolic (26.3%), tertiary/graphite-like (27.6%), and amine (12.7%). For electrocatalytic testing, the g-C$_3$N$_4$/MWCNT composite was sprayed onto a carbon paper gas diffusion electrode and assembled into the cell containing 1 M KCl as electrolyte. In this case, as Cl$^-$ is present in the electrolyte, the anodic reaction was Cl$_2$ evolution. Analysis of the reaction products showed the formation of only CO and H$_2$ after the reaction. Interestingly, CO was obtained with a remarkably high faradaic efficiency of 98% with a current density of 90 mA cm$^{-2}$ at a potential of $-1.62$ V versus Ag/AgCl. These values are notably higher than those reported for other N-doped carbon catalysts, which could partially be attributed to the use of gas diffusion electrode. Furthermore g-C$_3$N$_4$/MWCNTs composite outperforms Ag nanoparticles tested on the same system. These are encouraging results to explore N doped carbon materials as a viable alternative to state-of-the-art metal catalyst for the CO2RR.

The reason behind the superior catalytic performance of these g-C$_3$N$_4$/MWCNTs composite with respect to other N-doped carbon catalysts, however, is not yet clear. The authors claim that more experimental and theoretical work is needed to gain insight into the catalysis active site, which will help to understand how the catalyst structure and composition affect the performance. Furthermore, we believe that the experimental conditions might also play an important role in the high CO selectivity observed by Jhong et al. For instance working with gas diffusion electrode facilitates the transport of CO$_2$ to the active site enhancing the CO2RR resulting in higher currents. In addition, the use of a nonbuffer electrolyte with high current densities will cause an important shift on the local pH. It is known that the local pH can play an important role in the selectivity of Cu catalyst. In electrolyte with low buffer capacity, the alkaline pH limits the reactions that are pH dependent such as the HER, whereas the reactions in which the rate limiting step does not involve a proton transfer, as CO formation, are not affected. In the study of Jhong et al., the nonbuffer electrolyte as well as the high current density would shift the pH to alkaline resulting in inhibition of the competing process of the hydrogen evolution reaction which could partially explain the high CO selectivity.

5.3. Production of Hydrocarbon and Other Oxygenates

Besides the 2 electron reduction to CO and formate, different groups have reported that N doped carbon material can work as catalysts for the multistep reduction of CO$_2$ to hydrocarbons and oxygenates. That is the case of the work by Sun et al. who observed the formation of CH$_4$ on N-doped carbon (graphene-like) material (NGMs) on a carbon paper electrode in ionic liquids. Different NGMs were prepared using the following N containing compounds 3-pyridinecarbonitrile, 3-hydroxypyridine, 4-dimethylaminopyridine, benzimidazole, and 1-vinylimidazole by mixing each of them with equimolar sulfuric acid in solution. Then the solvent was removed and the solid was adhered to one side of the carbon paper and then heat treated at 1000 °C under inert atmosphere. The resulting materials were tested as electrocatalyst for the CO2RR in [Bmim]BF$_4$. Interestingly, besides CO and H$_2$, CH$_4$ was also found as one of the gas products after constant potential electrolysis at $-1.4$ V versus RHE. The CH$_4$ faradaic efficiency varied from 20.8 to 93.5% among the studied catalyst being the one prepared with 3-pyridinecarbonitrile most selective. The authors correlate the ability of these materials to directly reduce CO$_2$ to CH$_4$ with a high concentration of the pyridinic and pyridonic/pyrrolic species (Table 5). In addition, as we have previously discussed the ionic liquid might also be playing a role on the catalytic process, as it has been suggested that the pyridinic ion acts as a cocatalyst for the CO2RR facilitating the stabilization of the reaction intermediates.

Despite the key role of the ionic liquid in the direct reduction of CO$_2$ to hydrocarbons, methane has also been detected as a reaction product in an aqueous electrolyte using S,N-nanoporous carbon as electrocatalysts. For this study, Li et al. prepared their S,N carbon (CPS) material from the carbonization of poly (4-styrenesulfonic acid-co-maleic acid) at 800 °C. The addition of N to this S containing carbon was achieved by heat treatment in the presence of urea. The electrocatalytic activity of CPS and CPSN toward the CO2RR was evaluated by constant potential electrolysis in CO$_2$-saturated aqueous KHCO$_3$. Once again, the importance of the N functionalities was confirmed by control experiments using the N free material. In this case, the CPS faradaic efficiency toward CO was only 2%. While these results indicate some activity of the sulfur containing materials...
Table 5. Characteristics of the different NGMs with the total current densities ($j_{\text{tot}}$) and faradaic efficiencies (FE) for each product over the different NGM/CP electrodes at an applied potential of −1.400 V in bulk [Bmim]BF$_4$ with an electrolysis time of 5 h. NT stands for the total N content. NS is the surface N content detected by XPS. SBET stands for the specific surface area (table from ref. [103]).

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>N-containing base</th>
<th>NT [%]</th>
<th>NS [%]</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$j_{\text{tot}}$ [mA cm$^{-2}$]</th>
<th>FECH$_4$ [%]</th>
<th>FECO [%]</th>
<th>FEH$_2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.65</td>
<td>0</td>
<td>29.4 ± 0.4</td>
<td>70.3 ± 0.7</td>
</tr>
<tr>
<td>Graphene/CP</td>
<td>–</td>
<td>0</td>
<td>0</td>
<td>–</td>
<td>0.87</td>
<td>0</td>
<td>32.4 ± 1.9</td>
<td>67.5 ± 1.4</td>
</tr>
<tr>
<td>NGM-1/CP</td>
<td>3-pyridinecarbonitride</td>
<td>9.46</td>
<td>6.52</td>
<td>1.28</td>
<td>1.42</td>
<td>93.5 ± 1.2</td>
<td>4.2 ± 0.2</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>NGM-2/CP</td>
<td>3-hydroxypyridine</td>
<td>6.07</td>
<td>4.34</td>
<td>1.24</td>
<td>1.36</td>
<td>81.6 ± 1.5</td>
<td>5.7 ± 0.6</td>
<td>12.5 ± 0.7</td>
</tr>
<tr>
<td>NGM-3/CP</td>
<td>4-dimethylaminopyridine</td>
<td>4.71</td>
<td>3.74</td>
<td>1.09</td>
<td>1.32</td>
<td>67.2 ± 0.4</td>
<td>8.6 ± 1.3</td>
<td>24.6 ± 0.2</td>
</tr>
<tr>
<td>NGM-4/CP</td>
<td>Benzoimidazole</td>
<td>4.03</td>
<td>3.34</td>
<td>0.88</td>
<td>1.27</td>
<td>49.3 ± 0.2</td>
<td>24.5 ± 0.4</td>
<td>26.1 ± 1.5</td>
</tr>
<tr>
<td>NGM-5/CP</td>
<td>1-vinylimidazole</td>
<td>3.63</td>
<td>3.17</td>
<td>0.64</td>
<td>1.26</td>
<td>20.8 ± 1.6</td>
<td>56.2 ± 0.3</td>
<td>23.1 ± 0.8</td>
</tr>
</tbody>
</table>

Table 6. Summary table of the catalytic performance toward CO2RR on NC catalysts materials.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Working potential [V]</th>
<th>Product efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI-N-Doped-CNT</td>
<td>GC</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−1.8 V vs SCE</td>
<td>−1.53</td>
<td>−1.13</td>
</tr>
<tr>
<td>N-Doped-CNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT</td>
<td></td>
<td></td>
<td>−0.4 V vs RHE</td>
<td>−1.27</td>
<td>−0.84</td>
</tr>
<tr>
<td>N-doped Graphene</td>
<td>5 ± 0.2 mg cm$^{-2}$</td>
<td>0.5 M KHCO$_3$ pH = 7.3</td>
<td>−0.8 V vs RHE</td>
<td>−0.8</td>
<td>−0.4</td>
</tr>
<tr>
<td>N-doped CNT</td>
<td>0.5 mg cm$^{-2}$</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−0.8 V vs NHE</td>
<td>−0.8</td>
<td>−0.4</td>
</tr>
<tr>
<td>g-C$_3$N$_4$/MWCNT</td>
<td>0.36 mg cm$^{-2}$</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−0.75 V vs RHE</td>
<td>−1.15</td>
<td>−0.75</td>
</tr>
<tr>
<td>S,N-doped polymer-derived carbon (CPSN)</td>
<td>2.5 mg cm$^{-2}$</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−0.99 V vs RHE</td>
<td>−1.4</td>
<td>−0.99</td>
</tr>
<tr>
<td>N-doped graphene quantum dots (NGQDs)</td>
<td>0.5 ± 0.1 mg cm$^{-2}$</td>
<td>1 M KOH pH = 13.48</td>
<td>−0.86 V vs RHE</td>
<td>−1.65</td>
<td>−0.86</td>
</tr>
<tr>
<td>metal-free cylindrical mesoporous N-doped carbon (c-NC)</td>
<td>0.5 mg cm$^{-2}$</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−0.4 to −0.56 V vs RHE</td>
<td>−0.8 to −0.96</td>
<td>−0.4 to −0.56</td>
</tr>
<tr>
<td>N-doped Graphene doped at 800 °C (NG8000)</td>
<td>0.3−0.5 mg cm$^{-2}$</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−0.58 V vs RHE</td>
<td>−0.98</td>
<td>−0.58</td>
</tr>
<tr>
<td>Nitrogen doped carbons (NCNT-3700)</td>
<td>0.5 mg cm$^{-2}$</td>
<td>0.5 M NaHCO$_3$ pH = 7.3</td>
<td>−0.9 V vs RHE</td>
<td>−1.33</td>
<td>−0.9</td>
</tr>
<tr>
<td>Carbon nanofiber (CNF)</td>
<td></td>
<td>Emim-BF4 0% H$_2$O pH = 5.54</td>
<td>−0.573 vs SHE</td>
<td>−0.573</td>
<td>−0.25</td>
</tr>
<tr>
<td>Nitrogen doped CNT Arrays</td>
<td>0.5 mg/cm$^{-2}$</td>
<td>0.1 M KHCO$_3$ pH = 6.8</td>
<td>−1.05 V vs SHE</td>
<td>−1.05</td>
<td>−0.65</td>
</tr>
<tr>
<td>ACN 850</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>g-C$_3$N$_4$/MWCNT</td>
<td>2.39 mg cm$^{-2}$</td>
<td>CO$_2$ Sat. 1 M KCl pH = 5</td>
<td>−1.4 to −1.6 V vs Ag/AgCl</td>
<td>−1.18 to −1.38</td>
<td>−0.88 to −1.08</td>
</tr>
</tbody>
</table>

Table 6. Summary table of the catalytic performance toward CO2RR on NC catalysts materials.
of small pores in which the CO can be strongly adsorbed and reduced, suggesting that the carbon structure is also playing an important role in the selectivity of the CO2RR of N doped carbon materials. Despite the ability of this material to directly reduce CO2 to CH4, its selectivity toward the CO2RR is still too low for actual applications. Therefore, further studies on the how the product selectivity can be tuned by the material properties and the reaction conditions are still needed.

In addition to the formation of CH4, other carbon based products have also been reported as products of the CO2RR on N doped carbon materials. For example, Wu et al. reported that nanometer-size N-doped graphene quantum dots (NGQDs) reduce CO2 into multicarbon hydrocarbons and oxygenates (NGQDs).117] The authors prepared NGQDs with a thickness between 0.7 and 1.8 nm through exfoliating and cutting graphene oxide (GO) precursor followed by N doping with DMF. Electrocatalytic testing was carried out in CO2-saturated 1 M KOH using a gas diffusion electrode. Product analysis of the gaseous and liquid phase showed a variety of products from the CO2RR. At low overpotentials (∼0.26 V vs RHE) only CO and HCOO− were detected, while at more negative potentials hydrocarbons and oxygenates are produced. Ethylene was shown to be the major hydrocarbon product with a maximum FE of 31% at −0.75 V versus RHE, CH4 was also formed but the FE reached only 15% at −0.86 V. Remarkably, oxygenates, mainly EtOH, were also formed, reaching a 26% FE at −0.78 V. To confirm that these remarkable results are due to the CO2RR activity of the NGQDs, the authors performed different control experiments. Reduction under Ar and using isotope labeled 13CO2 confirmed that the products are indeed formed from the reduction of CO2. Finally, catalytic testing on undoped graphene carbon dots and N doped reduced graphene oxide primarily yield CO and HCOO− as products of the CO2RR. As we have mentioned before, in addition to the N functionalities one must also consider that metal impurities could also be involved in the catalytic process. In this case, the authors found that the NGQDs contained 1.02 ppm of Cu. This metal is a well-known catalyst for the CO2 reduction into hydrocarbons. The authors claim, however, that the low amount of Cu present on the NGQDs is too low to produce the quantities of carbons and oxygenates generated during the electrolysis experiments. Certainly, metal N doped carbon materials have at least 1000 times higher metal content than the Cu present in NGQDs, suggesting that in fact the observed activity toward the CO2RR is due to the N functionalities. The authors attribute the remarkable catalytic performance of NGQDs to their unique nanostructure in combination with utmost exposure of edge sites and heteroatom N doping. Suggesting that there are several factors that are needed to have a good CO2RR catalyst. Not only the composition is important but the carbon structure seems to play a role.

To ensure the availability of N carbon materials toward the formation of multicarbon products, it would be crucial to have different studies that confirm this result. In this regard, a recent study by Song et al. also reported the direct reduction of CO2 to ethanol using N doped carbon catalysts.118] This is a second example of the possibility of using N doped carbon materials in the direct reduction of CO2 to hydrocarbons and for the formation of C−C bond. In particular, they reported the use of a cylindrical mesoporous N doped carbon c-NC, prepared via the soft template method, using resol as carbon precursor, a soft template (F127), and dicyandiamide as the N precursor. In addition, a noncylindrical N doped carbon was prepared for comparison (i-NC). Both materials had similar N content (7% for c-NC and 7.2% for i-NC). However, the small angle X-ray scattering pattern suggests a larger unit cell parameter for i-NC while RAMAN analysis suggests a higher concentration of defects on i-NC. The catalytic activity of these materials was tested via CO2 electrolysis in 0.1 M KHCO3 in a potential range between −0.4 and −1.0 V versus RHE. Interestingly, ethanol was observed as the main product of the CO2RR. In particular, the c-NC reaches a remarkably high faradaic efficiency toward ethanol of more than 70% at low overpotential (−0.4 to −0.56 V vs RHE). At higher overpotentials, however, HER becomes the favored process lowering the selectivity toward EtOH. As in the work by Wu et al.,117] control experiments using Ar and isotope labeled 13CO2 confirmed that the observed EtOH comes from the CO2RR. In addition, no metallic impurities were detected using inductively coupled plasma excluding the contribution of metal impurities in the catalytic process. Finally, using DFT calculations, the authors proposed that the ethanol formation occurs via the coupling of two adsorbed *CO molecules which are formed from the reduction of CO2 on pyridinic and pyrrolic sites. The absence of C1 products, however, results puzzling, as adjacent active sites are needed to form the observed C2 product. The authors attribute the high EtOH faradaic efficiency to a stabilization of the *CO and a high electron density which favors the C=C coupling and the subsequent reduction, the possible activity of isolated N sites, however, is not discussed.

Another C2 product that can be formed from the CO2RR is acetate and it was reported as a major reaction product by Liu et al. when using N-doped nanodiamond/Si rod array (NDD/Si RA) as catalysts.119] This material was prepared by photolithography, using Si rod array as substrate. The N-doped nanodiamond film was deposited by microwave plasma enhanced chemical vapor deposition. The resulting NDD/Si RAs were evaluated by constant-potential electrolysis in CO2-saturated NaHCO3 solution. It was found that the main reaction products were formate and acetate, with the last one being the preferred product reaching a faradaic efficiency of 77.6%. The authors also looked into the influence of N content on the CO2 reduction activity, by investigating NDD/Si Ra with different N content (from 0.93 to 3.68 N at%). It was found that the production rates for acetate and formate are significantly enhanced as the N content increases from 0.93 to 2.12 at%, suggesting an involvement of N in the catalytic process. However, the enhancement is not obvious when N content is further increased. The authors attributed the low selectivity toward the CO2RR on the high N content catalyst to an enhanced HER. Nevertheless, these results could also be attributed to mass transport limitations. Suggesting that when increasing the N content from 2.12% to 3.68%, the rate of the CO2RR is not limited by the number of the active sites but rather by the amount of CO2 that reaches the catalyst surface. This result shows that the selectivity of the CO2RR is not only controlled by the properties of the catalyst material and that reaction conditions are also playing an important role. In particular, at high current densities which can be achieved by...
high over potentials or by a high number of active sites, the mass transport of CO2 to the catalyst might be the limiting factor for the CO2RR.

In order to understand the mechanism for the formation of acetate, Liu et al. also performed in situ infrared experiments to identify the reaction intermediates. Based on these results, the authors propose that the CO2 is first reduced to CO2•−, followed by a protonation and a further reduction to form *HCOO, leading to the production of formate. The formation of the C–C bond is proposed to occur via the combination of a CO2•− radical and a CO2 molecule generating the OOC–COO– intermediate which was observed in the infrared spectrum. The OOC–COO is then protonated and further reduced to produce acetate (Figure 17).

5.4. Theoretical–Computational Simulations for Mechanistic Insights

In the previous sections, we have discussed different experimental studies showing that a variety of products can be obtained from the CO2RR on N doped carbon materials. Nevertheless, it is not yet fully understood how the structural composition of the material affects its catalytic performance. To clarify this point and to elucidate the reaction mechanism toward different reaction products, it is necessary to combine theory and experimental studies to understand the role of the N functionalities on the CO2RR. This, however, is not an easy task, on one hand, a variety of N functionalities are present in the material resulting different possible active sites. Furthermore, the CO2RR is a complex process affected also by the reaction conditions, in which many products can be formed. In this section, we will discuss the recent input from theoretical simulations in the understanding of the catalytic performance of N doped carbon materials.

With the aim of understanding the role of distinct nitrogen groups in the CO2RR, Wu et al. presented an experimental study combined with DFT modeling on the catalytic activity of N doped 3D graphene. Using chemical vapor deposition of CH4 on a Ni foam, the authors prepared a carbon foam which was graphitic-C3N4, at various temperatures. Finally, the Ni skeletons were removed using HCl solution. This synthesis allowed to prepare different materials, which, according to the XPS, contained different concentrations of pyridinic, pyrrolic, and graphitic N. The authors found that the catalyst with the highest concentration of pyridinic N forms CO at a lowest overpotential and with the highest faradaic efficiency (85%).

Interestingly, this catalyst also reaches the highest selectivity toward formate (15%) but a higher overpotential. The role of the different N moieties was then investigated using DFT simulations. Consistent with their experimental results, the authors found that the most likely active site is a triple pyridinic N, which is the site with the lower free energy barrier for the first reaction step, the formation of *COOH. In comparison with pristine graphene, the presence of N lowers dramatically the barrier for the adsorption of *COOH facilitating the CO2RR. Interestingly, the formation of *COOH is exergonic on pyrrolic N, in this case the rate limiting step becomes the CO desorption which is a nonelectrochemical step with a barrier of 0.6 eV (Figure 18a).

Similar observations were done by Sharma et al. who used nitrogen doped carbon nanotubes as electrocatalysts for the CO2RR. In their study, they used three different N precursors, acetonitrile (ACN), DMF, and triethylamine, and various growth temperatures, 750, 850, and 950 °C to vary the N content and configuration. According to TEM images, the synthesized nanotubes present a bamboo like structure, whereas the Raman spectroscopy presents the signals consistent with a graphitic structure with some disorder introduced by the N atoms. For the catalytic testing, gas diffusion electrodes containing the NCNTs were used as cathode. Product analysis after constant potential electrolysis showed CO and HCOO− as the only products for the CO2RR. Among these products, CO was clearly the predominant one, but its maximum faradaic efficiency varied from 14 to 80% depending on the material used as catalysts. Interestingly, the authors found that the onset potential for CO formation and the maximum CO FE correlate with the pyridinic and graphitic nitrogen contents. This observation indicates that both pyridinic and graphitic N are involved in the CO2 reduction to CO. The catalytic activity of these individual N moieties, however, could not be distinguished with the experimental data. Therefore, the authors also present DFT calculations in order to elucidate the role of the different N functionalities in the CO2RR. Considering the formation of adsorbed *COOH as the rate limiting step for CO formation, pyridinic N is found to be the site with the lowest overpotential. Graphitic N exhibits a 0.7 eV higher barrier than pyridinic N, however, this value is still lower than pristine carbon nanotubes, suggesting that they can also be involved in the catalytic process (Figure 18b).

By contrast, in a study by Xu et al., the most likely active sites are predicted to be quaternary nitrogens, followed by pyridinic and pyrrolic nitrogens. For their study, they looked
into the catalytic activity of NCNTs synthesized via calcination at different temperatures of composites of poly (di-allyl-dimethyl ammonium chloride) and oxidized CNTs. By analyzing the N1s signal of XPS, they found that the content of pyridinic N, pyrrolic N, quaternary N, and N oxide changed with the synthesis conditions resulting in materials with different catalytic behaviors. The performances of the NCNTs toward the CO2RR were evaluated by controlled potential electrolysis. CO and H2 were the only products detected by gas chromatography, while no liquid products were detected using nuclear magnetic resonance. A maximum FE toward CO was clearly dependent on the catalyst material changing from 15 and 90% NCNTs, whereas only 2% CO FE was obtained on the N free CNTs. To understand the different catalytic performances of different NCNTs, the authors performed DFT calculations considering decoupled proton electron transfer mechanism in which the reduction of CO2 to CO is the rate limiting step. The authors found that the N moieties stabilized the CO2− with respect to pristine CNTs. Contrary to previous studies, however, the quaternary nitrogen was found to be the most active site followed by pyridinic and pyrrolic nitrogen (Figure 18c). The discrepancy between these results and previous simulations can be explained by the consideration of a different reaction mechanism. Therefore, it is crucial to elucidate if the CO2 reduction to CO on N doped materials occurs via a proton transfer as proposed by Wu et al. [121] and Sharma et al. [122], or if it is the reduction of CO2 to CO−, as proposed by Liu et al. [124]

In addition to the multiple possible active sites on N doped C materials considered in the previous studies, it is also important to consider the variety of products that can be formed during the CO2RR. This presents the second challenge in elucidating the reaction mechanism and in understanding the structural and composition effects that control the reaction’s selectivity. Liu et al. performed DFT simulations to investigate the electrochemical reduction of CO2 into CO and HCOOH on N-doped graphene [124]. They suggested that for the formation of both products, the CO2 molecule can be first hydrogenated by coupled proton electron transfer to form COOH. Consistently with previous studies, they found that the formation of this intermediate is an uphill step in the free energy profile for most N sites except pyrrolic N. Once COOH is formed on pyridinic and graphitic N, its reduction to CO or HCOOH is energetically favored suggesting that both products can be formed during the CO2RR. By contrast, on the pyrrolic N, the rate limiting step comes after the formation of COOH. In this case, the formation of HCOOH is favored over CO production, indicating that there is a potential range in which on pyrrolic N only formate could be formed (Figure 18d). These results suggest that the presence of different N moieties can affect the reaction selectivity, and could explain the different product distribution observed in different experimental studies. In particular, these simulations suggest that an N doped carbon material...
Containing a high content of pyrrolic N should be highly selective for the reduction of CO₂ to formate instead of CO.

Most of the previous studies suggest that the reason for the good catalytic performance of NC materials toward the CO₂RR relies on the stabilization of the *COOH intermediate by the presence of N moieties on the carbon structure. In addition, Siahrostami et al. found that the adsorption energies of *COOH and *CO do not follow the linear scaling relationship, which could also contribute to the activity of the CO₂RR on this class of catalysts. Metal surfaces present a linear scaling relation between the *COOH and the *CO adsorption energies, which means that the metals with weak binding energy toward COOH also bind weakly to CO.

As result, on weak binding metals, such as Ag and Au, once CO is form it desorbs from the surface becoming the main product of the CO₂RR. By contrast, metals that bind strong to *COOH also bind strongly to CO and in this case CO formation becomes limited by its desorption from the surface. Siahrostami et al. used DFT calculation to study the adsorption energies of the key reaction intermediates of the CO₂RR. Interestingly they found that N moieties on graphene do not follow the scaling relationship observed for the transition metals because they do not bind CO. As a result, the catalytic activity of the different N functionalities depends only on the binding energy of *COOH. A high biding energy results in a stabilization of the key intermediate *COOH, which is later reduced to CO and easily desorbed from the surface. Consistent with previous studies, N pyridinic was found to be the most active site for the CO₂RR in N doped carbon materials, surpassing the catalytic activity of Ag and Au. In addition, the authors studied the selectivity of the reaction by comparing the thermodynamic limiting potentials (UL) of the two possible processes, CO₂RR and HER. This is also a parameter to consider, since in general a highly active catalyst toward the HER shows poor selectivity toward the CO₂RR. According to their simulations, pyridinic N also presents the larger difference between the UL(CO₂) − UL(H₂) suggesting that in addition of being a highly active site it should also be the most selective one for the CO₂RR.

As we discussed previously, hydrocarbons and oxygenates can also be formed during the CO₂RR on NC materials. These products, however, were only observed on some of the tested catalysts such as NGQDs. The structural and composition requirements to allow the multistep reduction are not clear yet. Therefore, Zou et al. performed first-principles simulations to investigate CO₂RR on NGQDs. Consistent with previous studies, they found that incorporating N atoms to the carbon structure facilitates the formation of *COOH intermediate, promoting the reduction of CO₂ to CO. Once CO is formed it can be further reduced to hydrocarbons. The authors consider first the formation of C₁ species, namely CH₄ and CH₃OH. It was found that the formation of *CHO is favored over *COH by 1.9 eV leading to the formation of the formaldehyde intermediate which is reduced to *CH₂OH. Thermodynamic analysis suggests that at this point the following hydrogenation takes place on the C atom, forming CH₂OH. Experimental studies, however, showed CH₄ as the only C₁ species during the CO₂RR on NGQDs. This selective formation of CH₄ over CH₃OH is attributed to lower kinetic barrier for the formation of *CH₂ via water molecule mediated proton shuttling. In addition to CH₄, the experimental studies by Wu et al. showed that NGQDs can reduce CO₂ to C₂ compounds such as ethylene and EtOH.

The authors acknowledge that the NGQDs do not provide enough adjacent active sites for the formation of C–C bond through *CO dimerization as on Cu surfaces. Therefore, they proposed that adsorbed *CH₂ provides active sites for the coupling with CO forming *CH₃CO. The carbon from the CO can also coordinate to nearest-neighbor zigzag edge C atom allowing the stabilization of the CH₂CO intermediate which can later be reduced to EtOH or ethylene (Figure 17b). These results suggest an involvement not only of the N atoms on the catalytic process but also the C atoms. Furthermore, this study indicates that the C structure is also an important factor in controlling the reaction’s selectivity. In this case, it is suggested that the presence of carbon edges is crucial for formation of C₂ compounds. In other to understand the role of the carbon structure on the formation of C₂ products, however, it is important to analyze other NC materials that reduce CO₂ to C₂ products and their ability to stabilize the CH₂CO intermediate by interaction with a C atom.

Whereas most studies consider N atoms as the active sites, there are groups that consider the involvement of C atoms. In particular a study from Chai and Guo used DFT and ab initio molecular dynamic calculations to look in the interplay of N-doping and curvature of NCNTs on their activity and selectivity toward the CO₂RR. They found that undoped graphene surface does not possess a stable CO₂ adsorption state. The CO₂ adsorption barrier on the carbon, however, is reduced with the presence of a neighboring N atom. In particular, it was found that a carbon edge next to graphitic N was the most likely active site. This result highlights the complexity of these catalyst materials as not only N atoms could be involved in the catalytic process. In order to design an optimal catalyst, it would be necessary to understand the role of all the possible active sites. In addition to the effect of the N dopants, the reaction selectivity in two different graphene structures was also investigated. By comparing a graphene without curvature, and carbon nanotubes with a significant degree of curvature, the authors found that graphene sheets with weak bounding sites favored the 2 electron reductions to form CO/HCOOH. While, the curvature on the CNTs results in a stronger binding energy between the catalyst and the reaction intermediates facilitating the multielectron reduction to form HCHO and CH₂OH. These theoretical results also point toward an important role of the carbon support on stabilizing reaction intermediates in the reduction of CO. This effect, as well as the other parameters that control the selectivity of NC materials, still needs to be further investigated in order to design an optimal metal free catalysts for the CO₂RR.

6. Summary and Outlook

A number of different strategies have been used to prepare solid nitrogen-containing carbon-based materials as heterogeneous electrocatalysts for the CO₂RR. Recent research has repeatedly demonstrated that these materials constitute a very promising alternative to metallic CO₂ reduction electrocatalysts. Carbon-based materials have been shown to be efficient in the reduction of CO₂ to CO, formate, and even alcohols and hydrocarbons. Despite these promising results, the catalytic performance still needs to be optimized, especially in terms of current densities and catalyst's
stability. Furthermore, the reaction mechanism as well as the different parameters that control the catalytic performance of these materials are still unclear. Therefore, further studies directed to a deeper understanding of the catalytic process in order to find an optimal catalyst and reaction conditions are still needed.

One of the first approaches to have heterogeneous nitrogen containing carbon-based catalysts was to immobilize metal N–C macrocyclic complexes, which have been shown to be selective homogeneous catalysts toward the CO2RR. In particular, immobilized Fe and Co complexes have been reported as selective catalysts for CO production, reaching faradaic efficiencies as high as 95%. Formate was observed as a main reaction product using complexes of other metal centers such as Mn and In. More interestingly, Co protoporphyrin was shown to be able to further reduce CO to CH4 and a Cu porphyrin complex was shown to reduce CO2 to hydrocarbons with high selectivity. The use of these metal complexes has the advantage of having well-defined active sites that can be used as model system to gain further insight on the factors that control the activity of these metal centers coordinated to N atoms. For instance, it has been shown that the addition of different functional groups to the metal complexes affects the catalytic performance. This observation could be attributed to the resulting electronic density on the metal centers. Further systematic studies using different functional groups would help to understand the effect of the metal electronic density in controlling the activity and selectivity of metal complexes. This knowledge can lead to rational design of new catalysts. The catalytic performance of these immobilized complexes, however, is not only dependent on the structure of the complex. Other parameters such as the effect of the support and electrolyte also need to be understood in order to find an optimal catalyst. One main drawback of these immobilized complexes has to do with the low overall current densities which could be attributed to the low number of surface active sites.

In order to increase the availability of metal–Nx surface sites, other materials such as MOFs have been explored as CO2RR catalysts. These highly porous materials can have similar active sites as those in immobilized N macrocycle complexes, but with a higher density of available active sites, which could lead to higher current densities. Furthermore, as MOFs can be made from a diversity of organic ligands and inorganic building blocks, they can be tailored to have the optimal properties for the catalytic process. Therefore, in recent years, MOFs have also been studied as electrocatalysts for the CO2 reduction reaction, showing promising results, especially when it comes to their CO selectivity. Nevertheless, their activity and selectivity still need to be improved, as low turnover frequencies have been observed, which can partially be attributed to the general low conductivity of MOFs. To overcome this challenge is possible to work with other reticular materials such as COFs. In order to design an optimal MOF or COF based CO2 reduction electrocatalyst, the structural factors that control the activity and selectivity of such materials need to be further studied. For this purpose, the knowledge from the work on immobilized complexes can help to understand the role of electron donor and electron attractor groups to better select the organic ligand. In addition, the length of the organic building blocks can also be tuned to find the optimal pore size to allow an efficient transport of the reactants.

In recent years, solid carbon materials doped with N and transition metals (MNCs) have emerged as a less expensive alternative of preparing heterogeneous CO2RR catalysts containing MNx sites, without the conductivity limitations. These MNC materials are commonly prepared from inexpensive precursors such as carbon, organic N containing molecules, and inorganic transition metal salts. Such MNC materials have been proven to be highly selective catalysts for the CO2RR. In particular, Ni catalysts exhibit CO faradaic selectivities up to 99% with currents densities of 26.8 mA cm−2, making NiNC an extremely promising low cost alternative for the direct CO2 reduction to CO. Another promising metal is Fe on which an early onset potential for CO production is observed. In addition, Fe containing MNC materials have been shown to be able to reduce CO to CH4. The selectivity toward CH4, however, remains low, showing another opportunity for improving the catalytic performance of this class of materials. To increase the CH4 selectivity on Fe containing catalysts, one can try to find optimal reaction conditions. For instance, working on ionic liquids on different catalysts has shown to favor the CO2RR and hydrocarbon formation, which is an approach that has not been used on FeNC catalysts.

The good catalytic performance, as well as their relative low cost, makes MNC materials a great alternative as future CO2RR catalysts. Nevertheless, another key challenge needs to be addressed: Most of MNC materials are stable only for a few hours, which is not enough for industrial applications. Therefore, it is critical to understand the reason for catalyst deactivation in order to design an optimal catalyst. Furthermore, the nature of the active site is still under debate. In fact, as these MNC materials contain different functionalities, it is possible to have more than one active site. Both metal coordinated to N and metal coordinated to C have been proposed as active sites. In addition, some N functionalities as pyridinic N are also believed to be involved in the catalytic process. In order to understand the role of the different functionalities, it is necessary to carry out studies on the relationship between the catalysts structure and its performance. In addition, the knowledge from well-defined catalysts such as immobilized complexes can complement these studies.

Finally, metal free N carbon materials have also been reported as efficient CO2RR catalysts. The reaction products from the CO2RR range from CO and formic acid to hydrocarbons and alcohols. For some of the studies, showing CO as the main reaction product, it was observed that the selectivity toward CO depends on the N content and the concentration of different N functionalities. In particular pyridinic N seems to correlate with the formation of CO2, while other studies have suggested pyrrolic N as the site for formate production. The presence of different N functionalities might be one of the reasons behind the distinct product distribution of the different materials. Nevertheless, more experimental and theoretical studies are needed to understand how the catalysts structure and composition control its selectivity and to clarify the reaction mechanism. In particular, it would be important to gain insight on the reaction mechanism for the direct CO2 reduction into hydrocarbons to be able to design an efficient and selective metal free catalyst. It has been suggested that the carbon structure is also playing an important role in facilitating the reduction of CO to hydrocarbons and
alcohols in N doped carbon materials. Further studies dedicated to the understanding of how the structure of catalysts affects its reactivity, however, are still needed to fully comprehend the CO2RR in NC materials. For instance, it is important to reach a consensus on the role of the different N functionalities and on the involvement of the carbon atoms in the catalytic process. Furthermore, the reaction mechanism is still under debate as both coupled and decoupled electron proton transfers have been suggested. Experimental studies can help bring insight in this matter by determining if a proton transfer is involved in the rate limiting step. A final challenge when working with these materials arises from their low current densities and, therefore, strategies to achieve higher current densities such as increasing the concentration of active sites and facilitating the CO2 transport remain necessary.

Despite the promising catalytic performance of heterogeneous nitrogen containing carbon-based catalysts toward the CO2RR, several aspects need to be addressed to optimize their catalytic performance. As we have discussed, how the structure and composition of these catalysts affect their catalytic performance is not yet fully understood. This is particularly crucial for carbon doped materials in which a variety of active sites seems to be involved in the CO2RR. Nevertheless, even in immobilized metal N–C macrocyclic complexes, in which the active sites seemed to be well defined, it is not clear how parameters, such as the support and ligand substituents, control the catalytic performance. Furthermore, it has also been observed that the reaction conditions, such as the working electrolyte and mass transport, play a crucial role in determining the catalytic performance of N containing carbon-based catalysts. Therefore, the future technological viability of these materials as CO2RR catalysts relies on both, catalyst design based on the understanding of how the structure and material composition affect its reactivity and in optimizing the reaction conditions.

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Conflict of Interest

The authors declare no conflict of interest.

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carbon, CO2, CO2 electroreduction, electrocatalysis, M–N–C catalysts, single site metal–nitrogen doped carbons

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