CO₂ Reduction

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Metal-Doped Nitrogenated Carbon as an Efficient Catalyst for Direct CO_2 Electroreduction to CO and Hydrocarbons

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Abstract: *This study explores the kinetics, mechanism, and active sites of the CO_2 electroreduction reaction (CO2RR) to syngas and hydrocarbons on a class of functionalized solid carbon-based catalysts. Commercial carbon blacks were functionalized with nitrogen and Fe and/or Mn ions using pyrolysis and acid leaching. The resulting solid powder catalysts were found to be active and highly CO selective electrocatalysts in the electroreduction of CO_2 to CO/H_2 mixtures outperforming a low-area polycrystalline gold benchmark. Unspecific with respect to the nature of the metal, CO production is believed to occur on nitrogen functionalities in competition with hydrogen evolution. Evidence is provided that sufficiently strong interaction between CO and the metal enables the protonation of CO and the formation of hydrocarbons. Our results highlight a promising new class of low-cost, abundant electrocatalysts for synthetic fuel production from CO_2.*

In the past few years direct electrochemical CO_2 reduction has attracted renewed attention as an alternative atom-efficient and process-intensified method to directly produce synthetic fuels using waste CO_2 as a chemical feedstock.[1] Ideally, renewable electricity would be used to drive the conversion of CO_2 into hydrocarbons, alcohols or CO-rich feeds of high interest for industry.[2] The viability of this process, however, is currently limited by prohibitively high electrochemical overpotentials required to achieve practical current densities and by the low product selectivities.

To date, metals have been the preferred group of heterogeneous electrocatalysts for the CO2RR.[3] Earlier work has repeatedly shown that the selectivity of CO_2 electroreduction greatly depends on the detailed nature and geometry of the metallic surface as well as the working electrolyte.[4] Copper was found to be the one and only metal capable of producing hydrocarbons in considerable amount.[5] However, on Cu, hydrocarbons are formed in complex mixtures of C_1, C_2, and C_3 products and only at large negative overpotentials, which imply significant kinetic reaction barriers. More recent work investigated the CO2RR on size selected Cu particles, evidencing a characteristic particle size effect of the hydrocarbon selectivities.[6] The high kinetic barriers are partly attributed to the complexity of the reaction that requires multiple electron transfer steps.[7] In particular, the coupled protonation/reduction of CO is a critical step for hydrocarbon formation. In contrast to hydrocarbon formation, the electroreduction of CO_2 to CO requires only the transfer of two electrons and two protons, which makes it a substantially less hindered reaction process.

Moreover, the 2-electron reduction of CO_2 to CO on metals is accompanied by the 2-electron hydrogen evolution reaction (HER) resulting in a mixture of H_2 and CO. This mixture, also known as syngas, is an attractive feedstock for the chemical industry. Coupling the electrochemical CO_2 reduction to syngas to a subsequent gas phase-catalytic Fischer–Tropsch process step constitutes an alternative strategy to produce synthetic fuels from waste CO_2.[8]

To realize the coupled electrochemical/gas-phase chemical CO_2 reduction to synthetic fuels, a suitable and efficient catalyst is critically required. Hori and co-workers found that gold reduces CO_2 to CO at low overpotentials, with a faradaic selectivity of 87 % making it the most efficient CO_2-to-syngas electrocatalyst in its polycrystalline form.[9] Gold, however, is not an appropriate catalyst to be used in large scale given its high cost and low abundance. For this reason it is crucial to find catalytically active materials with activities, stabilities, and selectivities comparable to, but substantially less expensive and more abundant than gold.[10] With this purpose Lu et al. recently studied a nanoporous silver catalyst. They reported that this material is highly active and selective for CO_2 reduction with a 92 % faradaic efficiency towards CO.[11]

Ultimately, however, use of earth-abundant solid catalyst materials for the electrocatalytic reduction CO_2 to CO will be inevitable. Among them, hybrid catalyst materials based on carbon have largely remained unexplored to date for the CO2RR. While porphyrin-type macrocycles have repeatedly been shown to be reactive for the reduction of CO_2 to CO, either as homogenous catalyst[12] or as immobilized molecular catalysts on solid substrates,[13] they generally show poor stability. Recent studies have reported the use of metal-free N-doped carbon nanotubes for CO_2 reduction into formate[14] and N-doped carbon nanofibers for the reduction of CO_2 to CO.[15] The use of N-doped high surface area porous carbons containing N-coordinated non-precious metal ions, however, are a novel and highly attractive path forward in CO_2 electroreduction research.

Here, we explore the use of metal-containing N-doped porous carbon black-based solid catalysts (here also referred to as "M-N-C catalysts") for the CO_2 electroreduction to CO and hydrocarbons. We show that PANI-derived N-doped and

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metal-doped porous carbons—in the past studied as an alternative for Pt-based catalyst[16] for the oxygen reduction reaction (ORR)[17]—are exceptionally promising materials for the CO2RR. While numerous reports on the ORR electroactivity of metal and nitrogen-doped carbons exist, this is the first report of their use for the CO2RR. Our results indicate that, in analogy to the 4-electron ORR, the activity of PANI-derived N-doped carbons is greatly improved by the incorporation of non-precious metal ions. Our study provides evidence that this class of materials is a cost efficient alternative to carbon-supported Au catalysts for CO2RR to CO/H_2 mixtures at low overpotentials, both in terms of mass activity and selectivity. We also show that, given sufficiently strong interaction between CO and the metal ion, the M-N-C catalysts are capable to protonate CO associated with the formation of hydrocarbons.

At the outset of our study, we synthesized three different mono- and bimetallic N-doped solid carbon catalysts, referred to as Fe-N-C, Mn-N-C and FeMn-N-C, by processing Fe and/or Mn chloride salts, polyaniline (PANI) and Ketjenblack carbon powder[17a,18] in consecutive annealing and acid leaching cycles. The metal loadings of the final catalysts ranged between 4 and 6 wt % (Table S1 in the Supporting Information), while the nitrogen content was between 6 and 7 wt %. For reference, we prepared a metal-free catalyst, N-C. Figure 1 a shows the powder X-ray diffraction patterns of the four materials. All XRD profiles evidence broad reflections characteristic of ordered graphitic domains, yet lack any metal-related crystalline phases. TEM imaging (Figure S1) corroborated the absence of crystalline metallic particles, pointing to an ionic chemical state of the incorporated metal. BET was used to estimate the catalyst surface area while capacitance measurements were used to compare the electroactive surface area (Figure S2). X-ray photoemission spectroscopy (Figure S3) revealed the presence of a variety of nitrogen species (Figure 1 b) in agreement with earlier findings for this materials.[15] Time and again denied and defended, a widely reiterated structural metal site hypothesis for this class of materials consists of a central transition metal ion multiply coordinated to edge nitrogen atoms at the perimeter of graphene di-vacancies or micropores.[19]

The overall electrocatalytic performance of the N-C, Fe-N-C, Mn-N-C, and FeMn-N-C catalysts was initially evaluated by linear sweep voltammetry (LSV) in presence and absence of CO_2 (Figure 2). The Faradic currents observed in CO_2-free electrolyte were entirely attributed to the HER, while the Faradaic currents in CO_2-saturated bicarbonate solutions split between the HER and the CO2RR. Comparing Figure 2 a with Figure 2 b–d, it is evident that the catalytic activity of both HER (dashed line) and CO2RR (solid line) is substantially improved in presence of metal ions in the carbons. As the BET and capacitance measurements (Table S1, Figure S2) suggest similar active areas, we attribute this higher activity to an enhancement of the intrinsic activity by the addition of metal ions. Importantly, during sweep voltammetry the M-N-C catalysts show a clearly more positive onset potential for the CO2RR compared to a polycrystalline Au foil catalyst (Figure S4).

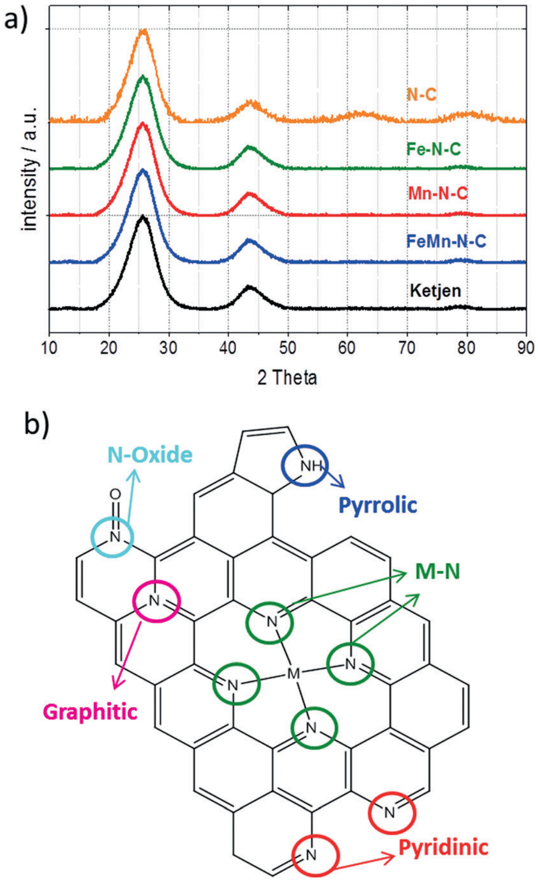

Figure 1. a) XRD patterns of mono- and bimetallic nitrogen-doped catalysts, Fe-N-C (green), Mn-N-C (red), FeMn-N-C catalyst (blue) compared to Ketjenblack carbon (black) and the metal-free catalyst, N-C (orange). b) Structural models of nitrogen atoms in various chemical environments in the N-C catalyst.

Closer inspection of Figure 2 reveals a number of interesting experimental observations with important mechanistic implications. First, the onset potential of the HER shifts from $-0.72\ V_{RHE}$ for the N-C catalyst to $-0.5\ V_{RHE}$ for the M-N-C catalysts (Table S2). Obviously, the presence of metal either induces the formation of new and more active HER sites, or else it activates HER active sites already present in the N-C metal-free catalyst. Second, while all three M-N-C catalysts exhibited a more positive onset potential in CO_2-saturated bicarbonate electrolyte compared to the CO_2-free electrolyte (Table S2), there appears to be no significant difference in their overall faradaic current potential characteristics. This could point to metal-insensitive catalytic active sites, possibly nitrogen functionalities, with high specificity toward the electroreduction of CO_2. Recent work, however, showed an enhancement of the HER activity by the mere presence of CO_2 or CO.[20] Clearly, deeper insight requires detailed product analysis. This is why stationary bulk electrolysis and stationary product selectivity analysis was performed at constant electrode potentials between -0.5 V and $-1.0\ V_{RHE}$ with gold catalysts used as benchmark.

Stationary reductive bulk electrolysis of CO_2 on the carbon catalysts and Au is presented in Figure 3. The activity of the N-C catalyst was substantially lower compared to Au,

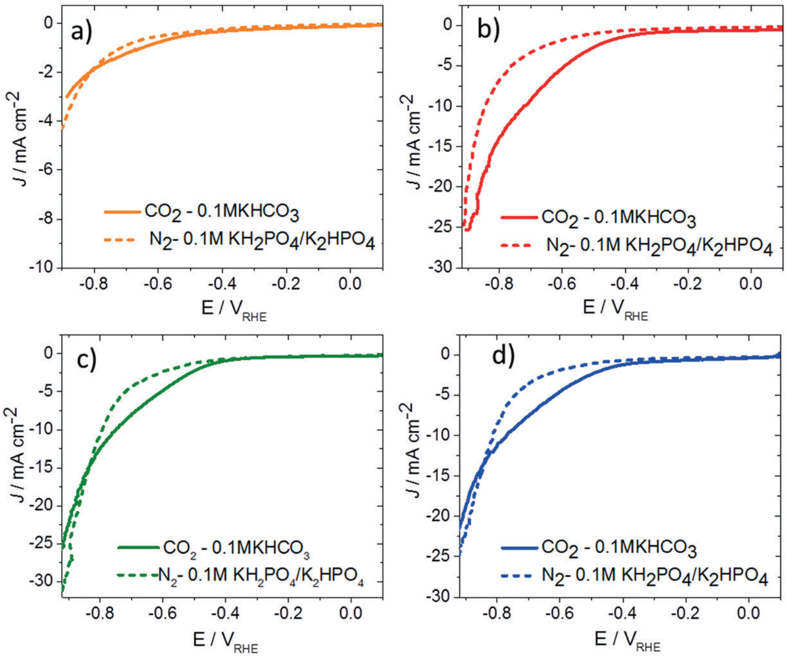

Figure 2. Linear sweep voltammetry (LSV) of a) N-C catalyst, b) Mn-N-C, c) Fe-N-C, d) FeMn-N-C in CO_2-saturated 0.1 M $KHCO_3$ (solid lines) and in N_2-saturated 0.1 M KH_2PO_4/K_2HPO_4 (dashed lines) with a catalyst loading of 0.785 mg cm^{-2} at 5 mV s^{-1} in cathodic direction.

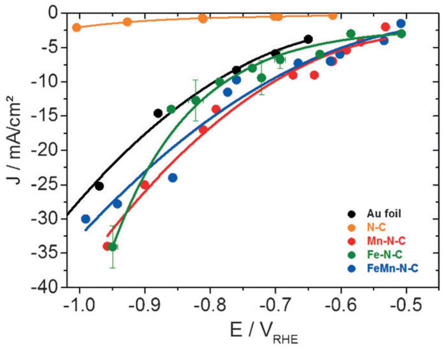

Figure 3. Stationary CO_2 electroreduction current densities after 10 min of bulk electrolysis of a low-area polycrystalline gold foil, compared to N-C, Mn-N-C, Fe-N-C, FeMn-N-C catalysts. Conditions: CO_2-saturated 0.1 M $KHCO_3$, 0.785 mg cm^{-2} catalyst loading. Lines to guide the eye.

while the incorporation of Fe and Mn in the N-doped carbon structure caused a dramatic increase of the stationary CO_2 reduction activity outperforming the low-area Au benchmark.

Along with the stationary Faradaic currents the product yields and Faradaic selectivities of the major reaction products were monitored and are plotted in Figure 4. The measurements confirmed that the main reaction products were H_2 and CO formed in 2-electron coupled proton/electron transfer reactions according to:

$$2\,H^+_{(sol)} + 2\,e^- + CO_{2(sol)} \rightarrow H_2O_{(l)} + CO_{(g)} \tag{1}$$

$$2\,H^+_{(sol)} + 2\,e^- \rightarrow H_{2(g)} \tag{2}$$

Liquid reaction product analysis by HPLC revealed traces of formate as the only detectable CO_2 reduction product in the electrolyte (Figure S6).

Inspection of product analysis in Figure 4 reveals striking similarities and differences with profound mechanistic implications. All M-N-C catalysts show a similar non-monotonic stationary CO production dependence on the applied potential, peaking, for instance, around $-0.7\,V_{RHE}$ for the Mn containing catalysts (formation rate of 14.8 L m^{-2}h^{-1}). Au, in contrast, displays a monotonic increase in CO formation rate with overpotential. This could be attributed to either limitations in the CO_2 mass transport to the catalytic active sites on the porous carbon electrodes, or else could reflect a competition between the H_2 and CO formation processes for specific catalytically active sites. Future CO_2 pressure-dependent experiments may elucidate this issue further. H_2 production, on the other hand, increases on both M-N-C and Au with more negative overpotential, with the carbon catalysts offering a more efficient HER catalysis. Selectivity towards CO increased monotonically with more positive overpotentials displaying ca. 80% at $-0.5\,V_{RHE}$. The potential range between $-0.5\,V_{RHE}$ and $-0.7\,V_{RHE}$ appeared to be the preferred operation conditions for CO and synthesis gas (CO/H_2) production, as the M-N-C catalysts met and exceeded the low-area Au benchmark.

This comparison however, is based on geometric current densities and does not reveal information about the intrinsic activity of the materials. Herein, we compare a low-area gold with high-area carbon-based materials. By contrast, in comparison with high surface area pre-oxidized gold, the M-N-C catalysts have much lower geometric currents, given the higher intrinsic activity of gold.[21]The mass activities (Figure 4c,b), however, reveal that the partial current density towards CO (≈ 6 mA g^{-1}) meets or exceeds that of carbon-supported Au catalyst,[22] making the M-M-C a promising cost efficient alternative for syngas production.

To confirm that any of the observed C_1 fuel products, such as CO, are indeed generated from CO_2 rather than from the carbonous catalysts, we performed stationary product analysis of the M-N-C catalysts during electrolysis in a CO_2-free electrolyte (Figure S7, red symbols). Detection of H_2 as the only reaction product discarded any possibility of decomposition or transformation of the carbon structure into CO.

To arrive at mechanistic conclusions we note that the CO and H_2 selectivities seemed largely independent of the specific nature of the metal ion incorporated in the N-C structure. In fact, even the N-C catalyst, at vastly different absolute activities, showed a similar selectivity trend as the M-N-C catalysts. These observations hint at an important role of the nitrogen moieties as active surface sites for the reduction of protons and CO_2. Indeed, earlier work by Kumar et al., in which N-doped carbon nanofibers efficiently produced CO in

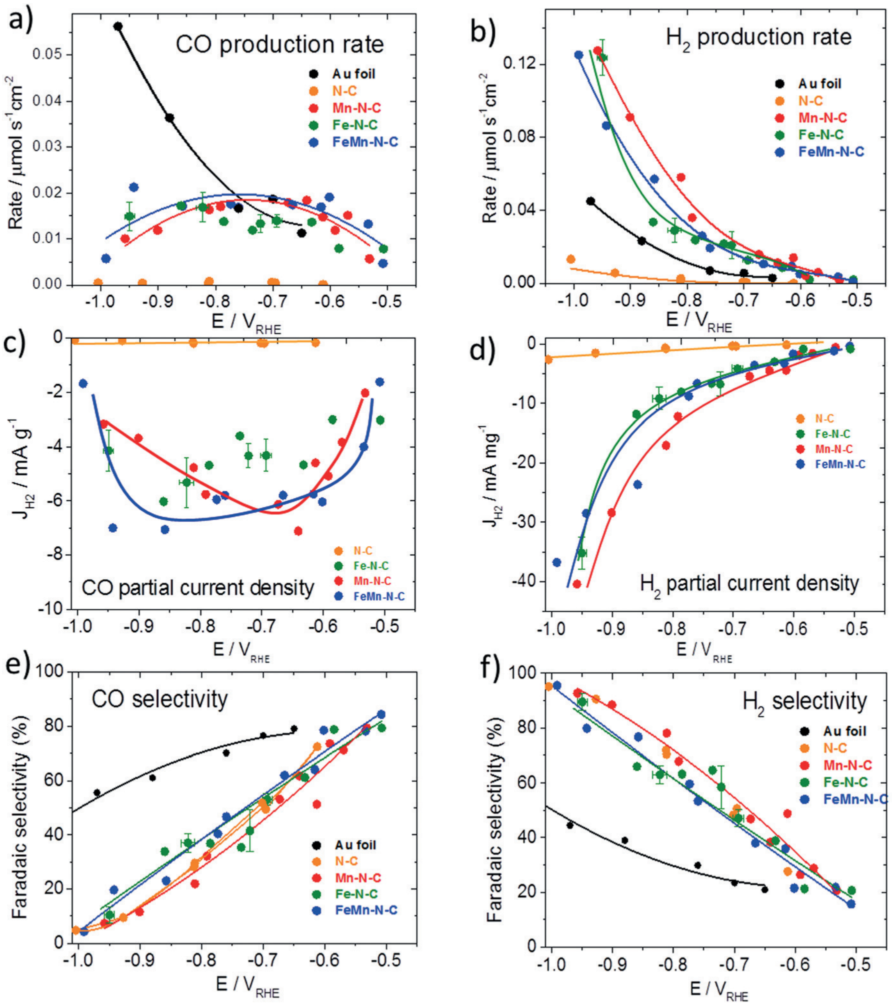

Figure 4. Stationary product yields (production rate), partial current densities and faradaic selectivities of CO (a,c,e) and H_2 (b,d,e) for gold (black), N-C (orange), Mn-N-C (red), Fe-N-C (green) and FeMn-N-C (blue). Conditions: 10 min at constant electrode potential in CO_2-saturated 0.1 M $KHCO_3$ at 0.785 mg cm^{-2} catalyst loading. Lines to guide the eye. The CO/H_2 ratios are shown in Figure S5.

EMIM-BF_6,[15] confirmed that metal ions are in principle not needed for the reductive processes, yet offer a drastic enhancement for both. Furthermore, we note that the catalyst surface area, the N content, the nature of the metal and CO uptake (Table S1, Figure S2), as a measure of the metallic sites active sites towards CO, have no clear correlation with the catalyst activity. Thus, it is reasonable to assume that nitrogen moieties determine the selectivity of the reaction. This is also consistent with theoretical calculations by Rossmeisl and co-workers, which predicted that the metal centers in ideal M-N-C moieties should have negligible activity towards CO2RR to CO.

Another important observation with important mechanistic implication is the detection of methane gas formed at electrode potentials more negative than $-0.8\ V_{RHE}$ (Figure 5), evidencing that an electron/proton transfer to CO is possible on this type of materials [Eq. (3)] according to:

$$6\,H^+_{(sol)} + 6\,e^- + CO_{(sol)} \rightarrow H_2O_{(l)} + CH_{4(g)} \qquad (3)$$

Interestingly the formation of methane was invariably limited to the Fe-containing catalysts, suggesting that this particular metal ion does play a critical role in the mechanism of reduction/protonation of adsorbed CO. Temperature-programmed CO desorption studies (Figure S9) indeed evidenced that the CO desorption energy on Mn was much lower than that on Fe centers. Furthermore, we observed that FeMn-N-C binds stronger to CO than Fe-N-C, consistent with the observed trends in CH_4 formation.

We conclude that methane formation correlates with CO–metal interaction strength. Accordingly, once CO is formed on Mn-N-C, it would be more likely to desorb from the surface (Figure 5a). In contrast, CO could be reabsorbed on the Fe containing catalysts and undergo further reduction when adsorbed on the metal center (Figure 5b). Our observations are also consistent with model calculations by Rossmeisl and co-workers. Despite predicting little activity of the metal sites towards CO2RR, they found that, depending on the metal, CO can be reduced to CH_4 and CH_3OH In particular the Fe-N-C moieties are predicted to form CH_4 at 0.93 V overpotential ($-0.76\ V_{RHE}$).[23]

In conclusion, this study has introduced N-doped carbon materials are promising catalysts for the electrochemical reduction of CO_2 to CO, syngas and hydrocarbons. In addition to their low cost, metal-N-C catalysts showed a 100 mV reduced onset potential in comparison to the low-area polycrystalline gold benchmark. Furthermore the M-N-C catalysts meet or exceed the mass activity of carbon-supported Au catalyst at comparable high CO selectivity of up to 80 % at $-0.5\ V_{RHE}$.[22] Experimental CO selectivity and methane formation trends combined with CO adsorption studies provided firm mechanistic evidence of nitrogen moieties as active sites for CO production, while the metal centers act as active sites for hydrocarbon formation. From a more practical point of view, the possibility of substituting doped carbons for Au constitutes an important step towards sustainable CO_2 electrocatalysis to syngas, CO, and other synthetic fuels.

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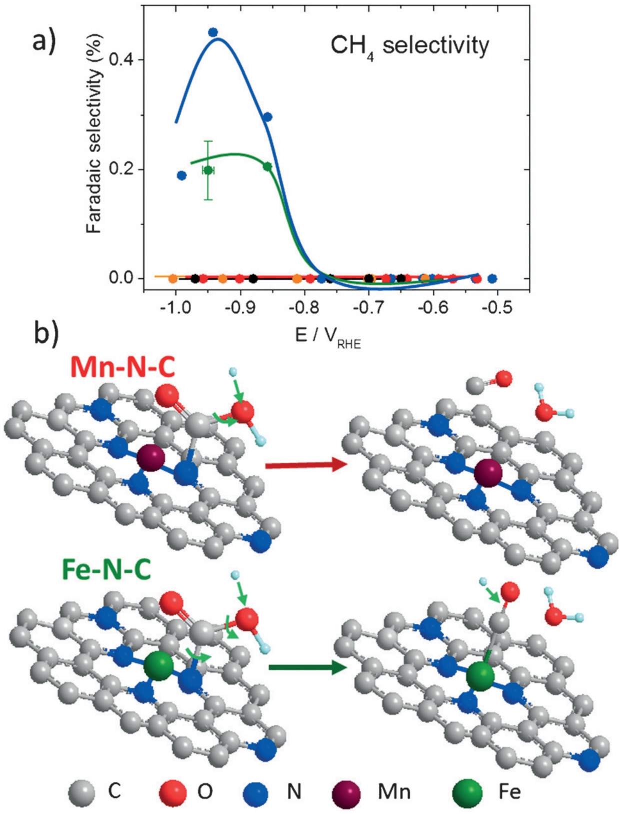

Figure 5. a) Methane faradaic selectivity of N-C (orange), Mn-N-C (red), Fe-N-C (green), and FeMn-N-C (blue) catalysts during CO$_2$ electroreduction. Conditions: 0.1 M KHCO$_3$, 0.785 mg cm^{-2} catalyst loadings and 10 min reaction. b) Proposed mechanisms for the CO2RR on Mn-N-C and Fe-N-C. Fe centers, with their enhanced CO interactions (Figure S9), are able to hydrogenate CO to hydrocarbons.

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