Single-Atom Electrocataylsts from Multivariate Metal–Organic Frameworks for Highly Selective Reduction of CO\textsubscript{2} at Low Pressures

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Abstract: Single-atom catalysts (SACs) are of great interest because of their ultrahigh activity and selectivity. However, it is difficult to construct model SACs according to a general synthetic method, and therefore, discerning differences in activity of diverse single-atom catalysts is not straightforward. Herein, a general strategy for synthesis of single-atom metals implanted in N-doped carbon (M\textsubscript{1}-N-C; M = Fe, Co, Ni and Cu) has been developed starting from multivariate metal–organic frameworks (MOFs). The M\textsubscript{1}-N-C catalysts, featuring identical chemical environments and supports, provided an ideal platform for differentiating the activity of single-atom metal species. When employed in electrocatalytic CO\textsubscript{2} reduction, Ni\textsubscript{1}-N-C exhibited a very high CO Faradaic efficiency (FE) up to 96.8\% that far surpassed Fe\textsubscript{1}, Co\textsubscript{1}, and Cu\textsubscript{1}-N-C. Remarkably, the best-performer, Ni\textsubscript{1}-N-C, even demonstrated excellent CO FE at low CO\textsubscript{2} pressures, thereby representing a promising opportunity for the direct use of dilute CO\textsubscript{2} feedstock.

Introduction

Single-atom catalysts (SACs), as a new frontier of heterogeneous catalysis, have witnessed their great superiority in diverse reactions.\textsuperscript{[1–9]} With the active sites dispersed at atomic level, SACs possess ultrahigh catalytic activity and selectivity and facilitate the understanding of the structure-performance relationship at atomic/molecular scale.\textsuperscript{[1–9]} Generally, the catalytic performance of SACs is highly dependent on intrinsic properties of metal active sites and their surrounding microenvironment as well as physicochemical characteristics of supports, the latter of which pose great challenges to the nature identification of catalytic sites.\textsuperscript{[10–12]} Specifically, single-atom metal decorated N-doped carbon (M\textsubscript{1}-N-C) materials, an important subclass of SACs, have been recognized as excellent electrocatalysts for CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR).\textsuperscript{[13–20]} However, the carbon supports of the reported M\textsubscript{1}-N-C materials always display various characteristics (pore structure, surface area, morphology, etc.), making the activity of M\textsubscript{1}-N-C tends to vary considerably even with the same metal center.\textsuperscript{[21,22]} On account of this, the general synthesis of M\textsubscript{1}-N-C with a wide variety of metal species but similar microenvironment and supports is highly desired to identify the intrinsic activity of single-atom active sites.

Multivariate metal-organic frameworks (MTV-MOFs), an important subclass of MOFs incorporating multiple linkers of different functionalities within a single crystal, creating complexity within a skeleton in a controlled manner, have attracted growing attentions in many applications.\textsuperscript{[23–26]} The diversity of constituent units in MTV-MOFs create huge opportunities for the general construction of M\textsubscript{1}-N-C with various metal centers. Meanwhile, it is ready for MTV-MOFs to control the variables of their derivatives, such as morphology, pore structure, surface area, elemental content, etc. Therefore, MTV-MOFs are ideal candidates to construct SACs and exclusively identify the intrinsic activities of different metal centers for CO\textsubscript{2}RR. Meanwhile, the porous feature of MOFs can be largely inherited to their derivatives, which will benefit the exposure of active sites and thereby CO\textsubscript{2}RR performance.\textsuperscript{[27–29]}

In addition to the active site identification, another critical issue in CO\textsubscript{2}RR is the energy-consuming capture and purification process of CO\textsubscript{2}. Specifically speaking, to achieve high selectivity, the currently reported CO\textsubscript{2}RR are generally performed in pure CO\textsubscript{2}.\textsuperscript{[30–42]} However, the actual concentration of CO\textsubscript{2} feedstock available from industrial processes such as coal power plant (5–15\% CO\textsubscript{2}) and steel/petrochemical industry (14–33\% CO\textsubscript{2}) is relatively low.\textsuperscript{[43–45]} Given the thermodynamic stability of the C=O bond (≈806 kJ mol\textsuperscript{-1}) of CO\textsubscript{2} and its limited solubility in aqueous solution, low CO\textsubscript{2} concentration will significantly affect the activity, setting great barriers for the direct CO\textsubscript{2} utilization.\textsuperscript{[46–47]} Therefore, the development of efficient electrocatalysts for direct
conversion of CO$_2$ at low pressures is extremely significant. However, such technology remains in its infancy and therefore this is rarely achieved.

With all of the aforementioned points in mind, a series of isostructural porphyrinic MTV-MOFs constructed from M-TCPP (M = Fe, Co, Ni and Cu; TCPP = tetrakis (4-carboxyphenyl)porphyrin) and H$_2$-TCPP were selected as precursors. Thanks to the isomorphism of MTV-MOFs and spatial isolation of metal centers in M-TCPP, four kinds of M$_1$-N-C (M = Fe, Co, Ni and Cu) materials, featuring single metal atoms with a very similar carbon support environment, have been obtained upon pyrolysis and serve as model catalysts to compare the intrinsic activity of diverse single-atom metal species (Scheme 1). Among all four M$_1$-N-C (M = Fe, Co, Ni and Cu) model catalysts for electrocatalytic CO$_2$RR, Ni$_1$-N-C exhibits the highest CO Faradic efficiency (FE) of 96.8% with a turnover frequency (TOF) up to 11315 h$^{-1}$ at −0.8 V in pure CO$_2$. Theoretical calculations reveal that Ni$_1$-N-C possesses the most positive value of the limiting potential difference between CO$_2$ reduction and H$_2$ evolution among all four M$_1$-N-C catalysts, elucidating its high CO$_2$RR selectivity in experiments. Remarkably, the best-performer—the Ni$_1$-N-C catalyst—is able to catalyze the reduction of diluted CO$_2$, though a very challenging task, and it presented excellent CO FE even at 30% and 15% CO$_2$ concentrations. These results strongly prove the great superiority of Ni$_1$-N-C toward selective CO$_2$ reduction under practical conditions.

![Scheme 1. Illustration showing the general fabrication of single-atom M$_1$-N-C catalysts based on MTV-MOFs for electrocatalytic CO$_2$ reduction.](image)

Results and Discussion

Synthesis and characterization of M$_1$-N-C

A family of isostructural porphyrinic MTV-MOFs, named M-PCN-222 (M = Fe, Co, Ni and Cu), have been successfully constructed by M-TCPP (M = Fe, Co, Ni and Cu) and H$_2$-TCPP via the mixed ligand strategy (Supporting Information, Figure S1).[28] With the general synthetic approach, the obtained M-PCN-222 involving different M-TCPP ligands present uniform rod-like shape with similar particle sizes, surface area and pore structure (Figure 1a; Figures S2 and S3). Upon the pyrolysis of M-PCN-222 followed by ZrO$_2$ removal, M$_1$-N-C (M = Fe, Co, Ni and Cu) can be finally obtained. Taking Ni$_1$-N-C as a representative, it shows a rod-like shape with a diameter of ≈200 nm, similar to those of Fe$_1$-, Co$_1$- and Cu$_1$-N-C (Figure 1b; Figure S4). In addition, no obvious metal nanoparticle is found in the TEM images of M$_1$-N-C (Figure 1b; Figure S4). Ni$_3$ absorption measurements indicate that all M$_1$-N-C possess similar surface area and pore size distribution (Supporting Information, Figure S5, Table S2). Powder X-ray diffraction (XRD) patterns of all M$_1$-N-C catalysts present two broad peaks corresponding to the (002) and (101) planes of carbon and no peaks of metallic phase can be observed, in accordance with TEM results (Figure S6). In the Raman spectra of all M$_1$-N-C catalysts, the intensity ratios of D band (1345 cm$^{-1}$) and G band (1590 cm$^{-1}$) are subject to small oscillation from 0.92 to 0.94, illustrating their similar graphitization degree (Figure S7, Table S2).

X-ray photoelectron spectroscopy (XPS) was adopted to investigate the chemical compositions and electronic states of M$_1$-N-C catalysts. The fitted N 1s XPS spectrum of Ni$_1$-N-C clearly shows five characteristic peaks including pyridinic N (398.7 eV), Ni-N moieties (399.4 eV), pyrrolic N (400.2 eV), graphitic N (401.1 eV) and oxidized Ni (402.6 eV) species (Figure S8a), confirming the existence of Ni-N bonding.[28,48] The Ni 2p$_{3/2}$ of Ni$_1$-N-C presents a binding energy (855.4 eV) located between Ni$^0$ (853.0 eV) and Ni$^{2+}$ (857.5 eV), measuring the partially oxidized Ni species originated from Ni-N species (Figure S9a).[50,51] Moreover, the N K-edge near-edge X-ray absorption fine structure (NEXAFS) analysis has been further conducted. For the metal-free N-doped carbon (N-C) derived from PCN-222 involving H$_2$-TCPD linker only, two π* peaks corresponding to pyridinic N (peak a) and graphitic N (peak b), as well as a broaden peak (peak c) related to C=N π* bond, are detected (Figure S10a).[50,51] In contrast, peak a broadens and splits into double peaks (a$_1$ and a$_2$) in Ni$_1$-N-C, suggesting the existence of Ni atoms stabilized by pyridinic N (Figure 2a).[51] Supportive results of XPS and N K-edge NEXAFS spectra are also obtained for Fe$_1$-, Co$_1$- and Cu$_1$-N-C catalysts, all demonstrating the formation of corresponding M-N species (Figures S8, S9 and S10a). Quantitatively, the N content and Ni loading in Ni$_1$-N-C are
determined to be 4.94 and 1.75 wt%, similar to the other M$_2$-N-C (M = Fe, Co and Cu) catalysts (Table S2). In the aberration-corrected high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) images, all M$_2$-N-C catalysts are featured with bright dots randomly dispersed in the selected area, clearly presenting the full of atomically dispersed metal species in the domain of each M$_2$-N-C (Figures 1c–f).

**Atomic structure analysis by X-ray absorption spectroscopy (XAS)**

To gain more information on the chemical environments of single metal atoms in M$_2$-N-C, X-ray absorption spectroscopy (XAS) was carried out. Taking Ni$_2$-N-C as an example, the adsorption edge of Ni$_2$-N-C in the Ni-K edge XANES spectra locates between Ni foil and Ni$_2$O$_3$, manifesting the positive charge state of Ni in Ni$_2$-N-C, in consistence with the XPS result (Figure 2b; Figure S9a). In the Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectrum of Ni$_2$-N-C, only one dominated peak at 1.4 Å associated to the Ni-N scattering path is presented and no Ni-Ni bond ($\approx 2.07$ Å) can be observed, verifying the formation of single-atom Ni sites in Ni$_2$-N-C (Figure 2c). The EXAFS fitting suggests that the Ni is coordinated by four N atoms (Figure 2d, Table S3). The XAS analyses have been performed on Fe$_2$-, Co$_2$- and Cu$_2$-N-C as well and the results illustrate that all M$_2$-N-C possess similar metal coordination environment, featuring single-atom M coordinated by four N atoms (Figures S10 and S11, Table S3).

**Electrocatalytic performance for CO$_2$RR in pure CO$_2$**

Encouraged by the above results, the M$_2$-N-C materials indeed feature almost identical structures except for different single metal atom sites. Therefore, they are ideal model catalysts to decode the intrinsic properties of these single-atom metals, by deducing their similar microenvironment and support factors, in electrochemical CO$_2$ reduction. As revealed by the linear sweep voltammetry (LSV) curves, Ni$_2$-N-C offers a much larger current response in pure CO$_2$ stream than the other M$_2$-N-C catalysts, indicating the significantly higher activity of Ni$_2$-N-C toward CO$_2$RR (Figure 3a; Figures S12–S14). Furthermore, the Faradaic efficiencies (FEs) for M$_2$-N-C catalysts at different potentials have been investigated. The Ni$_2$-N-C shows the best CO selectivity with a highest CO FE of 96.8% at $-0.8$ V among all M$_2$-N-C catalysts (Figure 3b). Meanwhile, the high CO FE (over 90%) of Ni$_2$-N-C can be maintained in a wide potential range from $-0.65$ V to $-0.95$ V with H$_2$ as the only byproduct (a detectable liquid product), manifesting the excellent selectivity of Ni$_2$-N-C for CO$_2$RR (Figure 3b; Figures S15 and S16). The Fe$_2$-N-C catalyst is the second most active catalyst with a highest CO FE of 86.5%. In comparison, the remaining two catalysts, Co$_2$-N-C and Cu$_2$-N-C, display much lower CO FE caused by the very competitive HER process (Figure 3b; Figure S15). Moreover, the TOF and CO partial current density ($J_{CO}$) of Ni$_2$-N-C reach 11 315 h$^{-1}$ and 27 mA cm$^{-2}$ at $-0.8$ V, far surpassing those of the other three M$_2$-N-C catalysts (Figure 3c; Figure S17). In fact, Ni$_2$-N-C shows a smaller Tafel slope (98 mV/decade) than that of Fe$_2$- (104 mV/decade), Co$_2$- (142 mV/decade) and Cu$_2$-N-C (118 mV/decade), indicating the more favorable kinetics of Ni$_2$-N-C (Figure 3d). Meanwhile, Ni$_2$-N-C also shows smaller charge transfer resistance and larger electrochemical active surface area (ECSA) than other M$_2$-N-C catalysts, further supporting its much higher catalytic activity (Figures S18 and S19). In addition, the best performed Ni$_2$-N-C exhibits a long-term stability at $-0.8$ V for 10 h without obvious decay in current density and FE of CO (Figure 3e). The distinctly different performance of M$_2$-N-C model catalysts not only...
reveals that the catalytic activity and selectivity are strongly dependent on active metal species, but also unambiguously demonstrates that single-atom Ni site far exceeds the other metal sites in M$_1$-N-C. This conclusion is of significant yet being achieved previously, given the complexity of different SACs with different structural parameters such as metal loading, surface area, pore structure, coordination environment, etc. For better comparison, the metal-free N-C prepared from the PCN-222, with similar structural characteristics as M$_1$-N-C, has also been synthesized (Figures S1–S7, Tables S1 and S2). It can be seen that N-C shows much lower current response, CO$_2$ and turnover number (TON) and larger Tafel slope than Ni$_1$-N-C for CO$_2$ reduction, further supporting the importance role of single Ni atoms (Figures 3b,d; Figures S20 and S21). Furthermore, Ni$_1$-N-C also shows better current response and CO FE than mix-Ni-N-C, the latter of which is derived from the mixture of Ni-TCPP and H$_2$-TCPP, further demonstrating the superiority of MOFs as precursors (Figure S22).

**Theoretical study of M$_1$-N-C in CO$_2$RR**

The above control experiments clearly demonstrate that all structural parameters in M$_1$-N-C catalysts are almost identical except for different metals. Therefore, M$_1$-N-C virtually provide ideal models for density functional theory (DFT) calculations to achieve reliable mechanism of diverse single-atom metal centers toward CO$_2$RR. Generally, the generation of CO by CO$_2$RR takes place in the following steps: (i) the CO$_2$ adsorption; (ii) the formation of *COOH; (iii) the formation of *CO and (iv) the CO desorption (* represents adsorbed intermediates; Figure 4a). Among the four elementary reaction steps, the formation of *COOH is calculated to be the rate-determining step (RDS) for all M$_1$-N-C catalysts (Figure 4b; Figures S23 and S24). In all investigated M$_1$-N-C catalysts, Ni$_1$-N-C and Fe$_1$-N-C present much lower energy barriers for *COOH formation than Co$_1$-N-C and Cu$_1$-N-C, manifesting the much higher activity of Ni$_1$-N-C and Fe$_1$-N-C for CO$_2$ reduction (Figure 4b; Figure S25). In addition, Ni$_1$-N-C also shows much lower energy barrier for CO desorption than Fe$_1$-N-C, illustrating the faster CO release from Ni$_1$-N-C (Figure 4b; Figure S25). All above support the highest activity of Ni$_1$-N-C for CO$_2$ reduction. Given the existence of competitive HER process, the limiting potential difference between CO$_2$RR and HER (U$_{L(CO_2)}$-U$_{L(H_2)}$; U$_L = -\Delta G/e$) has been further calculated and employed as the descriptor of CO selectivity, where more positive value of U$_{L(CO_2)}$-U$_{L(H_2)}$ represents a higher CO$_2$RR selectivity than hydrogen evolution. As shown in Figure 4c, the U$_{L(CO_2)}$-U$_{L(H_2)}$ values for Fe$_1$-, Co$_1$-, Ni$_1$- and Cu$_1$-N-C are $-1.15$, $-1.98$, $-1.19$ and $-2.33$ eV,

![Figure 3. Electrochemical performances in pure CO$_2$. a) LSV curves of Ni$_1$-N-C in pure Ar- and CO$_2$-saturated 0.5 m KHCO$_3$. b) FE and c) TOFs of M$_1$-N-C for CO in pure CO$_2$-saturated 0.5 m KHCO$_3$. d) Tafel plots of M$_1$-N-C for CO$_2$RR. e) Durability test of Ni$_1$-N-C at a constant potential of $-0.8$ V vs. RHE in pure CO$_2$.](https://www.angewandte.org/doi/10.1002/anie.202005922)
Electrocatalytic performance in CORR at low pressures

On the basis of the experimental evidences and theoretical calculations above, Ni-N-C incorporated with Ni-N$_2$ sites is highly efficient in selective CO$_2$ reduction. Inspired by this, the electrocatalytic performance of Ni-N-C toward low-concentration CO$_2$ reduction, which is a very challenging target in CO$_2$RR, has been further investigated. Prior to electrocatalytic measurements, the concentrations of protons ([H$^+$]) and dissolved CO$_2$ ([CO$_2$(aq)]) in aqueous solution under different CO$_2$ concentrations are calculated in detail based on dissociation equilibrium theories and Henry’s law (Figure S26). Obviously, the [H$^+$] and [CO$_2$(aq)] concentrations decrease significantly under lower CO$_2$ pressures, making CO$_2$ reduction more difficult according to the reaction equilibrium (CO$_2$(aq) + 2H$^+$ + 2e$^-$ = CO + H$_2$O). Moreover, the equilibrium potentials are calculated based on the Nernst equation to be negatively shifted by 46 and 73 mV when CO$_2$ partial pressure decreased from 1 atm to 0.3 and 0.15 atm (Figure S27). The calculations conclude that the CO$_2$RR will be much more difficult at low CO$_2$ partial pressures from the viewpoint of thermodynamics. Therefore, this raises a higher demand for both activity and selectivity of the electrocatalysts, toward addressing this challenging goal.

In the experimental results, the LSV curves of Ni-N-C in CO$_2$/Ar mixed gas containing 30% and 15% CO$_2$ reasonably present higher current responses than that in pure Ar, indicating the evident CO$_2$ reduction activity under diluted CO$_2$ (Figure 5a). Using 30% CO$_2$ as the feed gas, the maximal CO FE of Ni-N-C reaches 91.6% with J$_{CO}$ and TOF values of 6.69 mA cm$^{-2}$ and 1395 h$^{-1}$ at −0.8 V (Figure 5b and S28). Even though the concentration of CO$_2$ lowers to 15%, a high CO FE (83.2%) can still be observed at −0.75 V with J$_{CO}$ and TOF of 2.91 mA cm$^{-2}$ and 607 h$^{-1}$ (Figure 5b; Figure S28). It can be seen that even though the CO partial current density goes down with decreased CO$_2$ concentration, the CO FE still reaches above 80% under 15% CO$_2$ (Figure 5b; Figure S29). In addition to the main product of CO, a small amount of H$_2$ as the only byproduct (no liquid product) can be detected at low CO$_2$ concentrations (Figures S30 and S16), similar to that in pure CO$_2$. Furthermore, Ni-N-C possesses stable current densities and CO FEs over 10 h at 30% and 15% CO$_2$ concentrations (Figure 5c). The results above clearly demonstrate the great potential of Ni-N-C for highly selective CO$_2$ reduction by using dilute CO$_2$ feedstock from industrial processes.

Conclusion

In summary, a series of single-atom catalysts (M$_x$-N-C, M = Fe, Co, Ni and Cu), exhibiting almost identical pore structures and compositions, were constructed from isosstructural porphyrinic MTV-MOFs. The obtained M$_x$-N-Cs, featuring a very similar microenvironment and support effect for metal active sites, were employed as ideal model catalysts to identify the intrinsic properties of single-atom metal species in electrochemical CO$_2$ reduction. Under pure CO$_2$ conditions, Ni-N-C, with single-atom Ni as the active center, manifests the most satisfactory CO$_2$RR performances with the highest CO selectivity up to 96.8%, followed by Fe$_x$-N-C, Co$_x$-N-C and Cu$_x$-N-C. DFT calculations support the activity trend and illustrate that the best performing catalyst, Ni$_x$-N-C, with the most positive value of U$_i$(CO$_2$)-U$_i$(H$_2$), can efficiently promote CO$_2$RR and suppress the competitive HER. Given the ultrahigh selectivity of SACs, Ni$_x$-N-C has also been employed to catalyze the reduction of CO$_2$ at low pressures, which is more challenging and rarely reported. Strikingly, Ni$_x$-N-C maintains high selectivity even at 30% and 15% CO$_2$, which are practical concentrations that are directly available from industrial processes, further suggesting the superiority and ultrahigh selectivity of Ni$_x$-N-C for CO$_2$RR. This work provides a general route to a broad class of model SACs, which can eliminate the interference of microenvironment and support effects, thereby unambiguously unveiling the superior intrinsic performance of single Ni atoms compared to Fe, Co and Cu in M$_x$-N-C for CO$_2$RR.
Moreover, the preliminary results herein highlight the great potential of Ni-based SACs for direct electrocatalytic CO$_2$ conversion at low concentrations.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO$_2$ reduction · electrocatalysis · low pressure · metal–organic frameworks

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Figure 5. Electrochemical performances of CO$_2$ at low pressures. a) LSV curves and b) CO FE of Ni$_1$-N-C in 0.5 m KHCO$_3$ saturated with 30% and 15% CO$_2$. c) Durability tests of Ni$_1$-N-C at a constant potential of $-0.8$ V under 30% CO$_2$ concentration and $-0.75$ V under 15% CO$_2$ concentration, respectively.


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