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The CO₂-to-CO reduction by carbon monoxide dehydrogenase (CODH) with a [NiFe₄S₄] cluster is considered to be the oldest pathway of biological carbon fixation and therefore may have been involved in the origin of life. Although previous studies have investigated CO₂ reduction by Fe and Ni sulfides to identify the prebiotic origin of the [NiFe₄S₄] cluster, the reaction mechanism remains largely elusive. Herein, we applied *in situ* electrochemical ATR-FTIR spectroscopy to probe the reaction intermediates of greigite (Fe₃S₄) and violarite (FeNi₂S₄). Intermediate species assignable to surface-bound CO₂ and formyl groups were found to be stabilized in the presence of Ni, lending insight into its role in enhancing the multistep CO₂ reduction process.

Understanding how carbon dioxide (CO₂) can be reduced to organic compounds is an important challenge, not only in terms of industrial applications, but also in terms of understanding the chemical processes underlying the biosphere. Of the six known pathways for biological carbon fixation, the Wood-Ljungdahl (W-L) pathway is arguably the simplest due to the absence of autocatalytic cycles and complex multi-carbon compounds.¹ This simplicity, along with its phylogenetic diversity, has led previous studies to suggest the W-L pathway to be the most ancient form of biological carbon fixation which may have been present at the origin of life.² Further, the simplicity of the W-L pathway implies that the underlying physicochemical concepts may be more readily applied towards artificial carbon

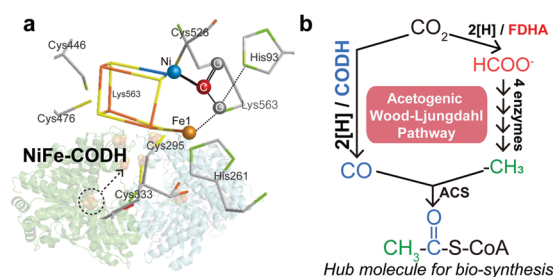
In situ FTIR study of CO₂ reduction on inorganic analogues of carbon monoxide dehydrogenase†

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capture and utilization compared to more complex pathways, such as the Calvin cycle, which is the most widespread carbon fixation pathway in the biosphere today.

Under anaerobic conditions, carbon fixation in the W-L pathway is initiated by the reduction of CO₂ to CO by carbon monoxide dehydrogenase (CODH), which utilizes a highly conserved [NiFe₄S₄] cluster as the catalytic site (Scheme 1a).³ The generated CO can be combined with a methyl group (–CH₃) to form a thioester, acetyl-CoA, which is a central metabolite of biological carbon metabolism (Scheme 1b).^{2,4} The first two-electron reduction of CO₂ is thermodynamically uphill, and therefore, CODH affects the overall efficiency of carbon fixation.^{1a,5} Accordingly, although NiFe-CODH is highly sensitive to O₂, it exhibits superb catalytic properties to generate CO at potentials near the thermodynamic equilibrium with nearly perfect selectivity.⁶ The origin of its high catalytic efficiency remains elusive, but it is likely attributable to the mechanisms by which CODH binds and activates CO₂.^{3,7} Namely, previous crystallographic studies have shown that CODH interacts with the CO₂ molecule in a multi-site conformation through both the Ni and Fe atoms within the [NiFe₄S₄] cluster (Scheme 1a), where a single Ni center associated with the iron-sulfur cluster specifically coordinates to the carbon atom of the CO₂ molecule.³

To identify the prebiotic origin of NiFe-CODH, several research groups have investigated the activity of Fe and Ni



Scheme 1 (a) The CO₂ molecule interacts with the Ni, Fe, and histidine in the [NiFe₄S₄] cluster.³ (b) The acetogenic W-L pathway converts two molecules of CO₂ into CO and formate, which can be combined to yield the acetyl group of acetyl-CoA.^{2b}

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sulfides towards CO₂ reduction under hydrothermal conditions.⁸ Recently, their electrocatalytic activity has attracted attention, due to their ability to catalyze the formation of C₁ and multi-carbon compounds under conditions similar to deep-sea hydrothermal vents.⁹ However, the reaction mechanism remains largely unknown due to the lack of spectroscopic evidence particularly at the conditions where the reactions take place.¹⁰ Herein, we applied *in situ* electrochemical attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to probe the reaction intermediates of NiFe sulfides during CO₂ reduction. The formation of several surface-bound species was promoted in the presence of Ni, highlighting its possible role in enhancing the multistep CO₂ reduction process.

As inorganic analogues of NiFe-CODH, greigite (Fe₃S₄) and violarite (FeNi₂S₄), which share the same crystal structure with the space symmetry group *Fd3m* (spinel), were synthesized following the method reported by Roldan *et al.* (ESI†).^{9d} Ni-doped Fe sulfides were also synthesized on reduced-graphene oxide (rGO) nanosheets modified with polyaniline (PANI), as the amine groups may interact with NiFe sulfides in a similar way with the histidine coordination environment in the natural enzyme. Hereafter, these samples will be referred to as NiFeS-PANI. All peaks in the XRD patterns of the synthesized greigite and violarite were indexed to Fe₃S₄ and FeNi₂S₄, respectively, while the NiFeS-PANI was found to be a mixture of FeNi₂S₄, Fe₃S₄, and NiS₂ (Fig. S1, ESI†). Energy-dispersive X-ray spectroscopy (EDX) imaging of NiFeS-PANI indicated that Ni, Fe, and S were uniformly distributed on the surface of polyaniline-coated rGO with a stoichiometric Ni:Fe ratio of 1:3 (Fig. S2–S4, ESI†). The electrostatic interaction of NiFeS with polyaniline was confirmed based on the shift of the IR bands of amine, benzenoid, and quinonoid rings upon the formation of the NiFeS nanoparticles (Fig. S5, ESI†). The interaction of the amine group of polyaniline with NiFeS was also indicated by X-ray photoelectron spectroscopy (XPS) analysis (Fig. S6 and S7, ESI†).

The activity and selectivity of CO₂ reduction on Fe₃S₄, FeNi₂S₄, and NiFeS-PANI was measured by performing electrolysis for 4 h at different potentials in CO₂-saturated 0.1 M KHCO₃ at 25 °C (Fig. 1). In this study, all potentials are referenced *versus* the reversible hydrogen electrode (RHE). The selectivity was evaluated based on faradaic efficiency (FE) measurements, which were reproducible across three independent sets of experiments (Fig. S8–S13, ESI†).

In the case of Fe₃S₄, hydrogen was the dominant product, and essentially no CO₂ reduction products were detected at all examined potentials (Fig. 1, grey bars: FEs for CO and HCOOH at –1.0 V are 0.05% and 0.014%, respectively). This finding is consistent with previous experiments showing the negligible activity of iron sulfides (FeS and Fe₃S₄) towards CO₂ reduction.^{9a,b} However, upon doping Ni into Fe₃S₄ (Fig. 1, red bars), CO was generated as a major product between –0.4 and –1.0 V, and further reduced products such as CH₄ and C₂H₆ were also observed below –0.7 V. ¹³CO was detected when electrolysis was conducted in ¹³CO₂-saturated 0.1 M KH¹²CO₃, confirming that CO₂ is the substrate for CO production (Fig. S14, ESI†). Introducing PANI into Ni-doped Fe sulfides further increased the CO₂ reduction activity, in terms of

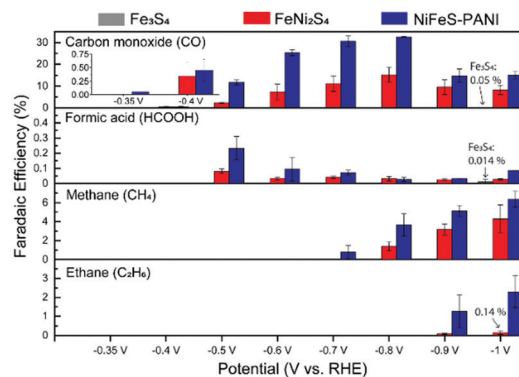


Fig. 1 Performance and analysis of the CO₂ electroreduction products for Fe₃S₄, FeNi₂S₄, and NiFeS-PANI nanostructures after 4 h of constant potential electrolysis. Calculated FEs are shown for the detected products at each potential. Error bars correspond to the standard error of the mean for at least three independent experiments. FE measurements for Fe₃S₄ were performed at –0.4, –0.7, and –1.0 V.

both selectivity and overpotential. Namely, NiFeS-PANI reduced CO₂ to CO from –0.35 V, which corresponds to an overpotential of approximately 250 mV (Fig. 1, blue bars). By applying a more negative potential, the FE for CO production increased to 30% at –0.8 V. The increase in selectivity may be due to the interaction of the PANI amine groups with CO₂, as well as the enhanced hydrophobicity.^{9a,11} The partial current density of all products showed essentially the same potential dependence with the FE (Fig. S15–S17, ESI†). The time course of FEs and product concentrations are shown in Fig. S18 and S19 (ESI†). No liquid products other than formic acid were detected at a concentration higher than 0.1 mM in our experimental conditions.

To determine the mechanism by which Ni doping increases the efficiency of CO₂ reduction on Fe sulfides, electrochemical ATR-FTIR spectroscopy was performed under *in situ* conditions with the catalysts coated on a single internal reflection prism (Ge) as the working electrode. The ATR-IR spectra were collected under the same conditions used for the aforementioned electrochemical CO₂ reduction experiments (Fig. 1), except that H₂O was replaced with D₂O. The use of D₂O enables a high signal-to-noise measurement in the spectral region from 1500 to 1700 cm^{–1}, where CO₂ related species such as adsorbed CO₂ and HCO₃[–], exhibit vibrational bands.¹² The ATR-FTIR spectra of Fe₃S₄, FeNi₂S₄, and NiFeS-PANI measured in CO₂-saturated KDCO₃ (0.1 M) are shown in Fig. 2. All three samples exhibited IR bands at 1363 cm^{–1} at potentials more negative than 0 V. This can be explained by the conversion of DCO₃[–] to CO₃^{2–}, considering that the pD at the electrode surface increases when cathodic reactions such as hydrogen evolution and/or CO₂ reduction are occurring (pK_a of CO₃^{2–}/HCO₃[–] is 10.5). The increase of local pD is consistent with the higher FE of CO relative to HCOOH at more negative potentials (Fig. 1).¹³ In control experiments using Ar-saturated KDCO₃, no change in the IR bands of DCO₃[–] and CO₃^{2–} were observed (Fig. S20, ESI†).

Upon further inspection of the IR spectra, a new band at 1625 cm^{–1} was observed upon the addition of Ni into Fe₃S₄ (Fig. 3a, black and red lines). Although this band was visible



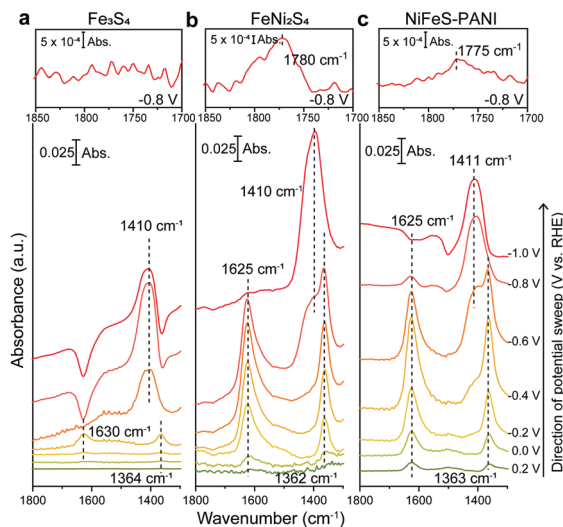


Fig. 2 *In situ* ATR-FTIR spectra of (a) Fe_3S_4 , (b) FeNi_2S_4 , and (c) NiFeS-PANI were recorded during electrochemical CO_2RR in CO_2 -saturated 0.1 M KDCO_3 . The insets in the upper panel of (a–c) show magnification of the 1700–1850 cm^{-1} region at -0.8 V vs. RHE were used as the reference.

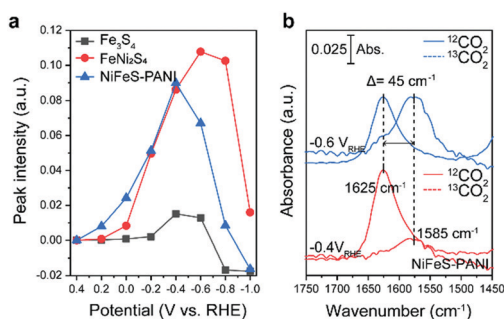


Fig. 3 Analysis of the chemical species observed at 1625 cm^{-1} . (a) The potential dependence of the absorption intensity at 1625 cm^{-1} relative to the baseline absorption value taken at 1700 cm^{-1} . Adding Ni and PANI enhanced the formation of this species. (b) *In situ* ATR-FTIR spectra of NiFeS-PANI . An isotope shift of the species with ^{13}C -labeled CO_2 at 1625 cm^{-1} was observed at -0.4 and -0.6 V vs. RHE.

even in the case of Fe_3S_4 at -0.4 V, the intensity was an order of magnitude lower and also appeared across a smaller potential range. This band was also observed on NiFeS-PANI and exhibited a similar potential dependence (Fig. 3a, blue lines). Furthermore, exchanging $^{12}\text{CO}_2$ with ^{13}C -labeled CO_2 resulted in a clear isotopic shift from 1625 to 1580 cm^{-1} on both FeNi_2S_4 and NiFeS-PANI (Fig. 3b and Fig. S21, ESI[†]). Therefore, the band at 1625 cm^{-1} is attributable to a reaction intermediate derived from the CO_2 molecule.^{7a,12,14}

The observed spectral position and isotopic shift value of 45 cm^{-1} are consistent with the asymmetric vibration of metal-associated CO_2 .^{7a,14,15} Considering that the intensity of the 1625 cm^{-1} band was largely increased upon Ni doping, a possible assignment to this species is adsorbed CO_2 on the doped Ni site. Although bicarbonate also shows a vibrational band at a similar wavenumber,¹⁶ the intensity of the 1625 cm^{-1}

band is independent of the bicarbonate bands at 1362 and 1410 cm^{-1} , indicating that this band is not due to bicarbonate. The absence of the 1625 cm^{-1} band in the case of Fe_3S_4 , despite clearly observable bicarbonate peaks, also supports that the 1625 cm^{-1} band is not due to bicarbonate.

In addition to the IR band at 1625 cm^{-1} , another potential-dependent IR band was detected at 1780 cm^{-1} (inset of Fig. 2b and c). The formation of this band becomes evident at potentials more negative than -0.8 V and showed a clear isotopic shift to 1763 cm^{-1} upon exchanging $^{12}\text{CO}_2$ with $^{13}\text{CO}_2$ (Fig. S22, ESI[†]). This band is absent for Fe sulfide without Ni doping (inset of Fig. 2a). The observed band is located in the spectral region of the C=O stretching of carbonyl, and close to that of surface-bound formyl, CHO, formed by electrochemical CO_2 reduction.^{13,17} The possibility of assigning the band to the C=O stretching of HCOOH can be ruled out because the deprotonated form is expected to become dominant under the reaction condition ($\text{p}K_a$ of $\text{HCOO}^-/\text{HCOOH}$ is 3.74).

Based on the electrochemical analysis and *in situ* ATR-FTIR observations, we propose a multistep reaction depicted in Fig. 4 as a possible mechanism for CO_2 reduction on the surface of Ni-doped Fe sulfide. As seen from the evolution of the 1625 cm^{-1} band from $+0.4$ V, a surface-bound CO_2 species forms on Ni-doped Fe sulfide prior to the initiation of CO_2 reduction. The coverage of this species increases upon scanning the potential negatively, likely due to the enhanced nucleophilicity of the Ni site to coordinate to the carbon atom of CO_2 . The Fe site may act as an electrophilic center to interact with the oxygen atom of CO_2 .^{7a,18} The role of the Ni center to facilitate CO_2 adsorption is consistent with recent DFT calculations by Posada-Pérez *et al.*,¹⁹ where the weak interaction of Fe_3S_4 with CO_2 was attributed to the repulsion between the lone pair electrons of the oxygen atoms within the CO_2 molecule and the spatially extended electronic clouds of the surface sulfur atoms.¹⁹ Posada-Pérez *et al.* also demonstrated that the partial substitution of Fe atoms by Ni strengthens the CO_2 binding on Fe sulfides.¹⁹ Upon further scanning the potential negatively, the surface-bound CO_2 species are reduced to CO, which is accompanied with the formation of a surface-bound formyl species (H–C=O). This species has been proposed as an intermediate to facilitate the downstream reaction of CO to form CH_4 and C_2H_6 compounds.^{13,17a,20} As a support for this hypothesis, when electrolysis was conducted in a CO saturated solution, CH_4 and C_2H_6 productions were confirmed (Fig. S23, ESI[†]). Thus, the potential dependent formation of the carbonyl species, together with the concomitant production of CH_4 and C_2H_6 , suggests that surface-bound formyl species plays a role in facilitating the multi-electron reduction of CO on Ni-doped Fe sulfide.

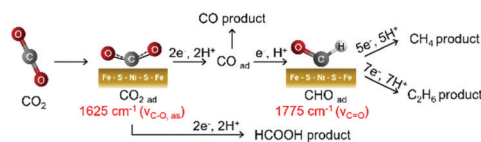


Fig. 4 Proposed pathway for electrochemical CO_2 reduction to CO, HCOOH , CH_4 , and C_2H_6 on Ni-doped Fe sulfide.



In summary, we have identified the role of Ni during the electrochemical reduction of CO₂ to CO by Fe sulfides. Ni enhances the formation of an intermediate assignable to surface-bound CO₂, which leads to a substantial increase in the electrochemical selectivity. This intermediate is further reduced to surface-bound formyl species, which leads to products such as CH₄ and C₂H₆. Recent studies have intensively argued the possibility that CO formation by NiFe-CODH is the oldest pathway of biological carbon fixation and was therefore involved in the origin of life.^{8a,b,9a-c,21} In this scenario, the reduction of CO₂ to CO is proposed to proceed on the surfaces of metal sulfide minerals, either electrochemically¹⁵⁻¹⁷ using geochemically generated pH and temperature gradients as the driving force^{21,22} or hydrothermally, using H₂ or metals as the electron source.^{8b} Several Ni-containing Fe sulfides, such as violarite (FeNi₂S₄),^{9a} pentlandite (Fe_{4.5}Ni_{4.5}S₈),^{9c} and awaruite (Ni₃Fe),^{8b} have been tested as possible prebiotic catalysts, but there is a lack of understanding of how CO₂ can be converted to CO and multi-carbon compounds. The present study is the first to provide molecular level insight into the origin of the marked increase in CO₂ reduction activity on iron sulfides by Ni doping. This will not only promote the development of biomimetic catalysts, but also yield a clue to identify prebiotic carbon fixation reactions.

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Conflicts of interest

There are no conflicts to declare.

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