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Repurposing a Bio-Inspired NiFe Hydrogenase Model for CO₂ Reduction with Selective Production of Methane as the Unique C-based Product

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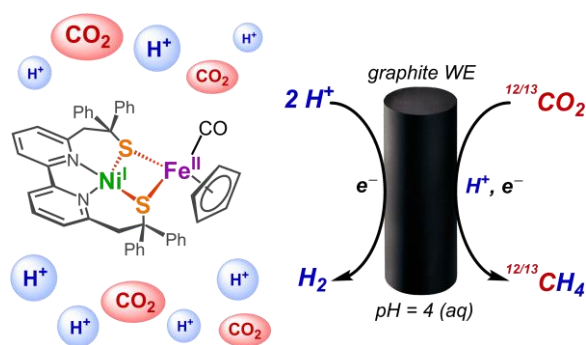
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Abstract

In the current environmental and economical context, there is an urgent need to conceive catalytic systems to efficiently activate and transform abundant small molecules while demonstrating selectivity when multielectron processes are involved. This is especially true for catalytic production of CH₄ from CO₂, as a limited number of active photo- or electro-catalysts have been described so far. Herein, we report the unprecedented reactivity of a molecular electrocatalyst physisorbed on a graphite electrode: the bioinspired [L^{N₂S₂}Ni^IFe^{II}Cp(CO)]⁺ (L^{N₂S₂} = 2,2'-(2,2'-bipyridine-6,6'-diyl)bis(1,1'-diphenylethanethiolate) complex selectively and catalytically reduces CO₂ in acidic aqueous solution to produce a mixture of CH₄ and H₂. Under optimized conditions, at pH 4, faradaic yields of 12% and 66% for CH₄ and H₂ production (TOF_{CH₄} = 214 s⁻¹, TOF_{H₂} ~5.1×10³ s⁻¹), are measured, respectively. We demonstrate that this binuclear NiFe catalyst is stable for hours under controlled potential electrolysis conditions.

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Main text

The exponential increase in energy demand with an overwhelming dependence on fossil fuels leads to an uncontrolled growth in the CO₂ concentration in the atmosphere. Although CO₂ is the greenhouse gas that contributes most to global warming, it also represents a potential feedstock for the synthesis of value-added fine chemicals and fuels thanks to its high abundance and low cost.¹ However, chemical conversions of CO₂ are difficult because of its high kinetic inertness. Consequently, the development of efficient, and stable catalysts for CO₂ reduction remains one of the key challenges in the energy conversion domain, especially when multielectron processes involving more than two electrons are involved.² In this context, selectivity becomes another crucial parameter, since diverse products can be generated as a function of the number of electrons implicated during the reduction process.

Homogeneous CO₂ reduction electrocatalysts have so far demonstrated selectivity for the production of either CO or formate in aprotic solvents. Based on structure/function and mechanistic investigations carried out on series of first-row transition metal catalysts, including polypyridinyl Mn and N-based macrocyclic Fe and Co complexes, rational design of selective and efficient catalytic systems has become possible.³⁻¹¹ Their implementation in future devices now requires improving their stability and transitioning to aqueous solution. A promising strategy, developed by several groups, relies on surface immobilization to take full advantage of the benefits of heterogeneous catalysis. Overall, this approach has already demonstrated a considerable improvement to the stability of the electrocatalysts, and the modified electrodes can work in aqueous conditions at various pHs.¹²⁻²¹

Intriguingly, in Nature, two enzymes with active sites displaying key structural analogies can either produce H₂ or reduce CO₂; both contain a heterobinuclear FeNi complex with sulfur-rich coordination spheres (Figure 1). While the [NiFe] hydrogenase generates H₂ from the reversible reduction of H⁺,²² the CO dehydrogenase reversibly reduces CO₂ to CO.²³⁻²⁴ Recently, we have reported an electrocatalytic system based on a NiFe model of the [NiFe] hydrogenase, [L^{N2S2}Ni^{II}Fe^{II}Cp(CO)]⁺ (L^{N2S2} = 2,2'-(2,2'-bipyridine-6,6'-diyl)bis(1,1'-diphenylethanethiolate), named **NiFeCp** (Figure 1, right) physisorbed on a graphite electrode, active in acidic aqueous solutions for H₂ production and robust for hours.²⁵ In this context, the capability of the same modified edge-plane graphite (EPG) electrode to reduce CO₂ was evaluated. Remarkably, we found that this electrocatalytic system can activate CO₂ and selectively generate CH₄, as the unique carbon-based product. Production of H₂ is still observed, and under optimal conditions, faradic yields (FY) of 70 and 13 % for H₂ and CH₄ production can be obtained, respectively. We have thus developed a molecular complex modeling common structural features of both the [NiFe] hydrogenase and the CO dehydrogenase, which functions as part of a unique electrocatalytic system that, in the presence of CO₂ and protons, can generate a mixture containing only H₂ and CH₄.

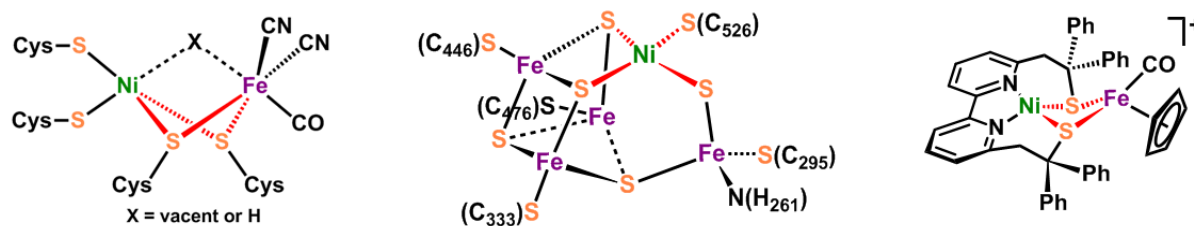


Figure 1. Active site structures of [NiFe] hydrogenase (left) and Ni-CODH (middle), and the chemical structure of **NiFeCp** (right).

Modified electrodes have been prepared by physisorption by dropcasting a dichloromethane solution of the binuclear **NiFeCp** complex on EPG electrodes. A previous investigation based on X-ray photoelectron (XPS) and attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopic data performed on these electrodes, demonstrated that the structure of the heterobinuclear complex is preserved after physisorption.²⁵ The cyclic voltammogram (CV) of the modified electrode in a 100 mM KPF₆ aqueous solution (pH 5.5) displays an irreversible cathodic signal (mid-wave potential at -0.75 V vs. SHE), assigned to the reduction of [LNi^{II}Fe^{II}Cp]⁺ to [LNi^IFe^{II}Cp] and an irreversible anodic process ($E_{pa} = 0.45$ V vs. SHE; $E_{pc} = 0.18$ V vs. SHE) attributed to the one-electron oxidation of [LNi^{II}Fe^{II}Cp]⁺ (Figure S1). The catalyst surface loading was determined to be 6×10^{-12} mol·cm⁻².²⁵

When the pH value is dropped to 4, the cathodic wave becomes catalytic in nature, this process corresponding to hydrogen evolution (HER).²⁵ Interestingly, when the same solution is saturated with CO₂ ([CO₂] ~3.9 mM), the catalytic wave displays a clear 150 mV anodic shift indicative of the fact that a new electrocatalytic process occurs (Figure 2).

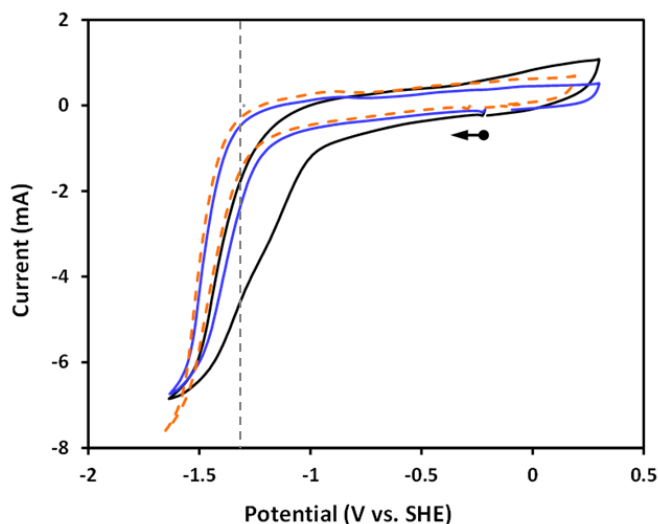


Figure 2. CVs of **NiFeCp**-modified EPG electrodes (3.5 mm diameter) in aqueous (pH = 4, phosphate buffer 0.1 M) 100 mM KPF₆ electrolyte at 50 mVs⁻¹ under either Ar (blue line) or CO₂ (black line) with an Ag/AgCl (satd. KCl) reference and Pt counter electrodes. CV

of pristine EPG electrode (3.5 mm diameter) in aqueous (pH = 4, phosphate buffer 0.1 M) 100 mM KPF₆ electrolyte at 50 mVs⁻¹ under CO₂ (dashed orange).

Controlled potential electrolysis (CPE) has been carried out at -1.3 V vs. SHE at pH 4 to identify the products. The headspace gas of the CPE cell was then analyzed by gas chromatography (GC). Only two products, H₂ and CH₄, were detected with a H₂/CH₄ molar ratio of 23:1 (Table 1, entry 1); the corresponding FY for CH₄ evolution is 12%. No other gaseous product is formed, and analysis of the liquid phase failed to detect methanol or formaldehyde by ¹H NMR, or formate by ion chromatography. In the absence of CO₂ or when unmodified EPG electrodes are used, no CH₄ is generated (Table 1, entry 2).

CPE experiments conducted in the presence of various partial pressures of CO₂ show that the CH₄ production increases linearly as a function of the square root of the concentration of CO₂ (Figure S4), consistent with the fact that CH₄ originates from CO₂. The H₂/CH₄ ratio is slightly affected, with a larger production of H₂, when the CO₂ partial pressure decreases (Table 1, entry 1, and Table S1, entry 1). This ratio is also sensitive to the pH at which the CPE is run (Table 1, entries 1, 6-7). While a ratio of 23:1 is obtained at pH 4, it rises notably when the pH is either increased or decreased, i.e., the H₂/CH₄ ratios are 30:1 and 50:1 at pH 5 and 3, respectively (Figure S2). This ratio is also slightly affected by the applied potential of the CPE, but to a lesser extent (Table 1, entries 1, 8-10). It remains around 20:1 in the range -0.8 V to -1.3 V vs. SHE and starts to increase at more negative potential (H₂/CH₄ ratio of 28:1 at -1.4 V vs. SHE) (Figure S3).

Table 1. Faradic yields and H₂/CH₄ ratio as a function of the experimental conditions in CO₂ saturated aqueous buffer.

entry	Catalyst	Applied potential (vs. SHE)	pH	Time (h)	H ₂ /CH ₄ ratio	Faradic yield (H ₂)	Faradic yield (CH ₄)
1	NiFeCp -EPG	-1.3	4	3	23	62	11
2	EPG	-1.3	4	3	only H ₂	46	N/A
3	Ni-EPG ^a	-1.3	4	3	only H ₂	36	N/A
4	Fe-EPG ^b	-1.3	4	3	only H ₂ ^c	35	N/A
5	(S4)NiFeCp-EPG ^d	-1.3	4	3	only H ₂ ^c	34	N/A
6	NiFeCp -EPG	-1.3	3	3	50	62	6
7	NiFeCp -EPG	-1.3	5	3	30	64	8
8	NiFeCp -EPG	-0.8	4	3	19	64	13
9	NiFeCp -EPG	-1.0	4	3	22	66	12
10	NiFeCp -EPG	-1.4	4	3	28	61	8

^{a)} [NiL^{N2S2}] was immobilized instead of NiFeCp, ^{b)} [CpFe(CO)(CH₃CN)₂]⁺ was immobilized instead of NiFeCp, ^{c)} a negligible amount of CH₄ was detected, which was below the quantification limit. ^{d)} a NiFeCp complex with

a different N2S2 ligand was used: $[(xbsms)Ni^{II}Fe^{II}Cp(CO)]^+$, $H_2xbsms = 1,2\text{-bis}(4\text{-mercapto-}3,3\text{-dimethyl-}2\text{-thiabutyl)benzene}$.²⁶

CPE run at -1.3 V vs. SHE in pH 4 phosphate buffer 0.1 M displays constant catalytic current at a value of $\sim 9 \text{ mA/cm}^2$ (Figure S5), with a relatively constant H_2/CH_4 ratio during the first few hours. (Figure S6). The increase of the H_2/CH_4 ratio observed during a 6-hour experiment could be related to the slight increase in pH that was measured after 3 hours (0.3 pH unit). After a CPE experiment carried out under the reference conditions (Table 1, entry 9), faradaic yields of 12% and 66% for CH_4 and H_2 , respectively, were measured (current density at -1.3 V vs. SHE with $CO_2 = 8.8 \text{ mA}\cdot\text{cm}^{-2}$, and current density at -1.3 V vs. SHE with Ar = $0.95 \text{ mA}\cdot\text{cm}^{-2}$. After $\sim 1650\text{s}$ of CPE, $TON_{CH_4} \sim 3.5 \times 10^5$ and $TON_{H_2} \sim 8.2 \times 10^6$; $TOF_{CH_4} = 214 \text{ s}^{-1}$, $TOF_{H_2} \sim 5.1 \times 10^3 \text{ s}^{-1}$; see SI for detailed calculations, Figure S7).

Gas chromatography coupled to mass spectrometry analysis (GC-MS) confirms that methane is generated during the electrolysis ($m/z = 16$ with expected mass profile). Interestingly, isotope-labeling experiments were performed with $^{13}CO_2$ that confirmed that $^{13}CH_4$ methane ($m/z = 17$ with expected mass profile) arises from CO_2 reduction (Figure 3).

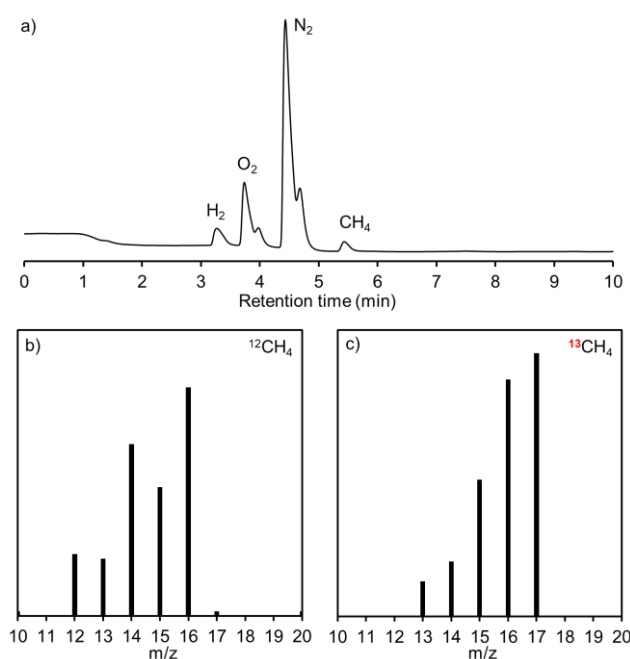


Figure 3. GC-MS analysis of the gaseous headspace in the cell following CPE. The gas chromatogram (a), and the mass spectra of the methane product for solutions pre-saturated with $^{12}CO_2$ or $^{13}CO_2$ showing $^{12}CH_4$ (b) and $^{13}CH_4$ (c). The $^{13}CH_4$ mass spectrum has been corrected to eliminate water vapor contaminant, based on the NIST spectral database ($m/z(H_2O) = 18, 17$) (See SI for details).

The stable electrolysis current combined with a quasi-constant H_2/CH_4 ratio suggests that the **NiFeCp** catalyst is stable under CPE conditions. To provide additional support that the molecular nature of **NiFeCp** is retained during catalysis under such highly acidic conditions, XPS and ATR-FTIR experiments were performed on the modified EPG electrodes before and after electrolysis. The ATR-FTIR spectra are similar (Figure 4, left), both displaying a single CO ligand vibration at $\bar{\nu}_{\text{CO}} = 1916 \text{ cm}^{-1}$, previously assigned to the Fe-bound CO in immobilized **NiFeCp** (1926 cm^{-1} in an ATR-IR spectrum of the powder sample of **NiFeCp**).²⁵ Additionally, both XPS spectra recorded before and after electrolysis are characterized by a single peak at 854.4 eV in the Ni 2p core region (Figure 5, top), which was previously unambiguously assigned to **NiFeCp**.²⁵ In the same vein, the two XPS spectra recorded in the Fe 2p core region display a similar single peak at 708.9 eV , in agreement with the presence of a single Fe-based species (Figure 5, bottom). Finally, the CVs of the modified EPG electrode recorded before and after a CPE experiment under the reference conditions are comparable, indicating that the adsorbed complex still displays the redox properties of the molecular **NiFeCp** complex (Figure 4, right). The small current shift between the two CVs can be explained by the modification of the pH occurring during the CPE experiment.

We have also tested another known binuclear NiFe HER electrocatalyst, $[(\text{xbsms})\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}\text{Cp}(\text{CO})]^+$,²⁶ which also contains a NiFeS₂ core, but the Ni ion is in a S₄ environment instead of an N₂S₂ one, as in **NiFeCp**. Interestingly, the corresponding modified EPG electrode displays only HER catalytic activity, but no product arising from CO₂ reduction is generated (Table 1, entry 5). Taken together, these experiments confirm that the reactivity of **NiFeCp** is specific to its molecular structure, which is entirely retained after electrolysis when immobilized onto an EPG electrode.

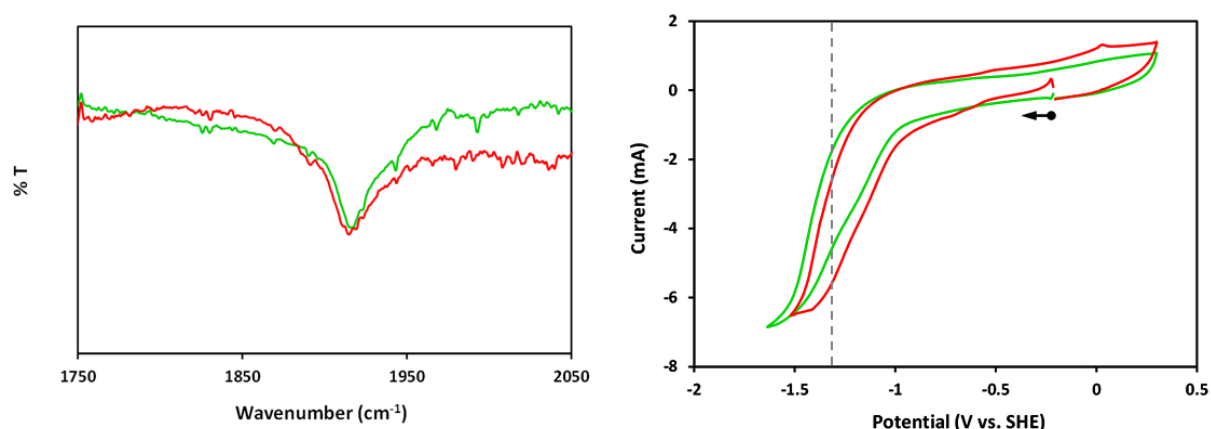


Figure 4. ATR-FTIR spectra (left) and CVs (right) of electrodes drop-cast with $[\text{LNi}^{\text{II}}\text{Fe}^{\text{II}}\text{Cp}]^+$ as prepared (green traces) and after 2 h electrolysis at -1.3 V vs. SHE (red traces), in degassed pH 4 phosphate buffer 0.1 M with 100 mM KPF_6 electrolyte.

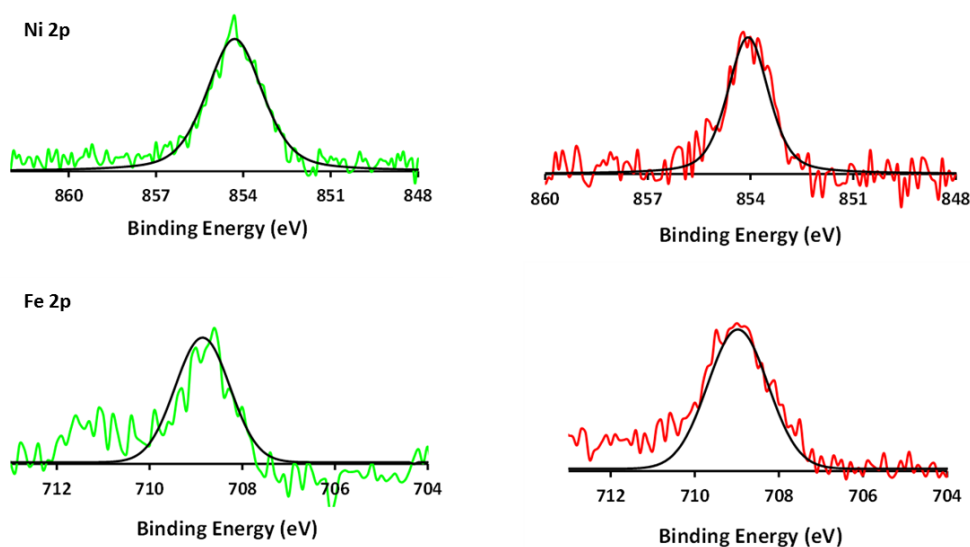


Figure 5. XPS spectra at the Ni 2p and Fe 2p core level of electrodes drop-cast with $[\text{LNi}^{\text{II}}\text{Fe}^{\text{II}}\text{Cp}]^+$ as prepared (left) and after 2 h electrolysis at -1.3 V vs. SHE in degassed pH 4 phosphate buffer with 100 mM KPF_6 electrolyte (right).

The molecular catalyst described here distinguishes itself from almost all known systems by producing CH_4 as the only carbon-based product, rather than mixtures of CO, short chain alkanes, and/or HCOOH . In the literature, the number of reported catalytic systems capable of generating products such as long-chain (C_2+) alkanes²⁷⁻²⁸ or alcohols^{18, 29} is limited, and they generally display modest efficiency. In the specific case of CH_4 production, only two main families of catalysts have been described based on two different approaches: (i) molecular metal-based porphyrins and derivatives either via photocatalytic processes in aprotic solvents or via electrocatalysis in aqueous solutions when immobilized on modified electrodes,^{20-21, 30-32} and (ii) metallic Cu-based materials working in aqueous solution.³³⁻³⁹ In general, the electrochemical production of methane from aqueous CO_2 is observed for overpotential values higher than 0.8 V.⁴⁰⁻⁴¹ Physically adsorbed **NiFeCp** mediates CH_4 evolution (apparent standard potential is 0.17 V vs. the Reversible Hydrogen Electrode) from -0.8 V vs. SHE in pH 4 aqueous buffer, corresponding to ~ 0.75 V onset overpotential requirement. At the mid-wave potential (-1.2 V vs. SHE) of the catalytic wave (Figure 2), for a more accurate description of the performance of a molecular electrocatalyst,⁴² the overpotential for CH_4 evolution is 1.13 V. Our molecular catalyst thus compares well with previously reported heterogeneous catalysts including immobilized molecular complexes.^{20, 32}

Electrochemical methane production on metallic (M) surfaces generally involves a M-CO intermediate,⁴³⁻⁴⁵ although such an intermediate can be overcome for single-atom catalysts.⁴⁶ In the case of physically adsorbed **NiFeCp**, CO_2 reduction is inhibited in the presence of external CO, and only hydrogen is detected as the product (Table S1, entry 2). These observations indicate that CO is not involved as an intermediate during the CO_2 reduction process. Based on experimental data and DFT calculations, it has been

previously proposed that under homogeneous conditions, CO terminally binds at the Fe site of the reduced [LNi^IFe^{II}Cp] complex.⁴⁷ However, the electrocatalyst remains active for H₂ production, though to a lesser extent, with hydride species being generated at the Ni site.⁴⁸⁻⁴⁹ We can thus propose that a similar process takes place here, with CO blocking the Fe site, preventing the CO₂ activation, but leaving the Ni site available for HER activity.

Overall our data suggest that production of CH₄ proceeds through a mechanism involving two sites acting in a concerted manner, where CO₂ is activated and transformed at one metal site, while the second metal site delivers hydride to the first site until CH₄ is formed and released. Similar mechanisms have been proposed with Cu-based electrodes,⁴⁴ and also for bimetallic nanoalloy catalysts, in which each metal plays a distinct role: one to activate the C-based intermediate products, and the second to stabilize the hydride species.³⁴

The selectivity of this present molecular catalyst, which can go beyond a 2-electron CO₂ reduction process, is unique even when compared with the best metal-based materials described so far. Further studies are in progress in our laboratories to decipher the unique reaction mechanism underlying such a behavior. In parallel, ligand design is underway to tune the reactivity of physisorbed **NiFeCp** complexes and increase the selectivity for CH₄ production over proton reduction.

Supporting Information Available: Experimental methods (preparation of the modified electrodes, description of the spectroscopic techniques and of the electrochemical techniques), additional data (redox properties of the modified electrodes, catalytic performance under different experimental conditions).

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