Multiple C-C bond formation upon electrocatalytic reduction of CO₂ by a molecular catalyst

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Abstract

Molecular macrocycles show very promising electrocatalytic properties for the reduction of carbon dioxide. Up to now, only C1 products were produced by these catalysts. We show here that iron phthalocyanine, a commercially available molecule based on earth abundant elements, can produce light hydrocarbons upon electrocatalytic reduction of CO₂ in aqueous conditions and neutral pH. When an electrochemical potential of -0.7 to -1.1 V vs. RHE is applied to a glassy carbon electrode modified with iron phthalocyanine, carbon monoxide is generated as main product. An increasing fraction of hydrogen is observed as the potential is decreased and small amounts of C1 to C4 saturated and unsaturated products are evolved. Control experiments in the absence of CO₂ or catalyst does not produce any of these compounds. X-ray spectroscopic analysis of the electrode during catalysis show that the molecular catalyst remains intact and is responsible from the reaction.

Introduction

The electrochemical reduction of carbon dioxide has been proposed as a viable technology to convert this environmentally deleterious gas into valuable chemicals. [1] [2] [3] [4] At present, the most common product of CO₂ reduction is CO, which can be used in industrial processes such as metallurgy or the manufacturing of chemicals. However, great efforts have been directed to further reduce CO₂ to higher value products, particularly those with C-C bonds. Starting from the work of Hori and co-workers [5] in the 80's, copper-based catalysts have shown remarkable activity toward light hydrocarbons. [6] [7] [8] Another strategy involves reducing CO₂ to CO then further converting it into more complex reactions, [9] [10], or use CO as an intermediate to synthesize further reduced products. [11] [12] [13] Regarding the latter approach, one promising CO₂ reduction pathway involves electrochemical Fischer-Tropsch type processes, which are able to convert CO₂ to hydrocarbons with up to six carbons, albeit with modest efficiency [14] [15] [16].

Transition metal macrocycles such as cyclams [17] [18], porphyrins [18] [19] or phthalocyanines [20] [21] [22], have shown very promising results in the electrochemical reduction of CO₂, both as homogeneous [23] and heterogeneous systems [24]. They have been shown to function for several hours in aqueous or organic media without significant alteration of the catalyst, demonstrating the potential of this class of molecules for application. Besides their efficiency and robustness, macrocycles also offer chemical tunability, which allows orienting their reactivity towards higher TONs [19] [25], higher selectivity [26] or the synthesis of a specific compound [10]. However, their main drawback is the fact that they cannot produce any compound beyond C1. A handful of examples have shown that methane [27], or methanol

[21] [22] can be produced by molecular catalysts but to our knowledge, no example of C₂+ products have been reported.

We report here on the electrocatalytic synthesis of light hydrocarbons (C₁-C₄) from CO₂, using a heterogeneous system based on a molecular iron phthalocyanine catalyst (see figure 1a). The reaction takes place in a flow reactor, in which a CO₂-saturated potassium bicarbonate aqueous electrolyte at neutral pH is flown. The distribution of products shows that CO is the main product up to -0.9 V vs RHE, while the amount of hydrogen increases with increasing potential. Starting from -0.9 V and up to -1.1 V, methane, ethylene, ethane, propylene, propane, n-butane along with traces of C₅ products are detected.

Results and discussion

Experimental setup

Based on the design of Ager and co-workers [11], we used an electrocatalytic flow cell consisting in two chambers, for the cathodic and anodic reactions, separated by a Nafion® membrane (see figure 1b and figure S1). The cathode consists of a glassy carbon electrode, on which an ink containing iron phthalocyanine and a carbon powder is dropcasted with a surface concentration of around 80 nmol/cm² (see supplementary information for electrode preparation procedure). A reference electrode is arranged in the cathode chamber and the anode consists of a nickel plate. Two independent reservoirs contain the catholyte and anolyte (KHCO₃ 0.1 M), which are saturated with either Ar or CO₂. The electrolytes are flown independently in the anodic and cathodic chambers using a peristaltic pump, so that they can be circulated in a loop. The headspace of the cathodic compartment is analysed during the experiment by an online gas chromatograph that performs automatic sampling every thirty minutes (see figure S2).

Figure 1. Developed structure of iron phthalocyanine (FePc), the molecular catalyst used in this study (a). Exploded view of the electrocatalytic flow cell in which the FePc-modified working electrode was used (b). WE, RE and CE stand for “working electrode”, “reference electrode” and “counter electrode”, respectively.

The working electrode used at the cathode was characterized by X-ray absorption spectroscopy after ink deposition (see figure 4). The XANES spectrum collected on the electrode before any

catalytic measurements reveals a structure that is essentially identical to the spectrum of the pure molecule, indicating that it remains intact after the drop-casting and drying processes.

Electrocatalytic activity

Figure 2a shows the cyclic voltammograms of the FePc-modified electrode under Ar and CO₂. Under Ar, the catalytic reduction of water starts at *ca.* -0.9 V (2 mA/cm²), while a catalytic process starts already at around -0.7 V (2 mA/cm²) under CO₂. A working electrode onto which a catalyst-free ink was dropcasted did not show any significant catalytic activity towards water or CO₂ reduction before -1.1 V (2 mA/cm²).

Figure 2. Cyclic voltammograms (a), chronoamperometric curves (b) and gas chromatograms (c) of the FePc-modified electrode under Ar (red) and CO₂ (blue) and of the catalyst-free modified electrode under CO₂ (black). Chronoamperometric experiments are performed at -1.1 V vs. RHE for two hours, after which their resulting gaseous products are sampled. The # and * symbols denote the peaks of CO₂ and water vapour, respectively.

Figure 2b shows the chronoamperometric curves of constant potential electrolysis performed at -1.1 V under argon and CO₂ for two hours. As expected from the cyclic voltammograms, the current of the catalyst-free electrode is negligible compared to an FePc-modified electrode in CO₂. One can observe, however, that under Ar, a catalyst-casted electrode exhibits higher current density than in CO₂. This suggests that under adequate overpotential, FePc possesses high activity toward proton reduction to hydrogen in a CO₂-free environment, but this activity is partially suppressed in the presence of CO₂. The ability to produce hydrogen of FePc proves to be beneficial for the formation of hydrocarbon products, which will be discussed later. The noise level in the electrolysis curve under Ar is attributed to the formation of bubbles by the proton reduction process.

Figure 3. Product distribution obtained with FePc-modified electrodes with total amount and current density (a); with faradaic efficiencies and H₂ to CO ratio (b) as a function of applied potential.

The analysis of the electrolysis products was performed by online gas chromatography (GC) using a MicroGC instrument (see figure 2c). Peaks corresponding to ethylene (C_2H_4), ethane (C_2H_6), propene (C_3H_6), propane (C_3H_8), n-butane (C_4H_{10}) and n-pentane (C_5H_{12}) clearly stand out on the chromatogram obtained for an FePc-modified electrode poised at -1.1 V *vs.* RHE under CO_2 atmosphere. Other peaks corresponding to isomers of butane and pentane can also be observed, although with less accuracy. Methane (CH_4) is also clearly observed on another module of the gas chromatograph (see figure S5). Control experiments were performed to ensure that the FePc-modified electrode was responsible for the activity observed. When an FePc modified electrode was set under catalytic conditions (-0.97 V *vs.* RHE) in an Ar-saturated electrolyte, hydrogen was the dominant product detected after two hours of electrolysis, with traces of CO and methane. We attributed the source of these carbon products from CO_2 in equilibrium with the bicarbonate electrolyte. When a catalyst-free modified electrode was poised at -1.1 V in a CO_2 -saturated electrolyte, small amounts of CO and H_2 were detected, while only trace amounts of C2-C3 products were observed (see figure 2c and S5 in SI).

Figure 3 shows the product distribution and total amounts of products generated by an FePc-modified electrode after a 2-hour electrocatalytic experiment at -1.1 V under CO_2 . Above -0.7 V, CO (90% FE) and hydrogen (10% FE) are the only products observed. The amount of hydrogen increases steadily from -0.7 V to -1.1 V up to 65 % FE at the expense of CO. Indeed, figure 3b shows that the amount of CO stays relatively constant, while H_2 increases with increasing overpotential. Noticeable amounts of hydrocarbons can be observed starting from -0.9 V, methane being the main of them with up to 4% at -1.0 V. Ethylene, ethane, propylene, propane and n-butane are produced with faradaic efficiencies of *ca.* 0.5% each. We postulate that the formation of these hydrocarbon products is a consequence of both the applied potential and the H_2/CO ratio. In the Fischer-Tropsch reaction, the ideal H_2/CO ratio is around 2:1, which is about what we observed here as well. It should be noted that the amount of ethylene is likely underestimated because of the high background generated by CO_2 in the chromatograph column. Despite the low amounts of products generated, these results were reproducible, as shown by the replicates performed on three different electrodes. The liquid phase of the reaction was analysed by 1H NMR after two hours of experiments and no products were detected (see figure S3b).

X-ray spectroscopic analysis

In order to determine the structure of the catalyst under operating conditions, we performed *in situ* and *operando* X-ray absorption spectroscopic (XAS) experiments at the iron K-edge. The electrochemical flow cell described above has a window for X-rays to probe the working electrode from the back in a backscattering configuration. In order to obtain a sufficient signal-to-noise ratio, the electrodes prepared for XAS experiments were *ca.* 6 times more concentrated (in catalyst only) than those prepared for electrocatalytic experiments.

Figure 4 shows the X-ray absorption near-edge structure (XANES) spectra of the FePc-modified electrode under resting state and catalytic conditions, with either Ar or CO_2 saturated electrolytes. The spectrum of the electrode under resting state is essentially identical to that of the pure, starting compound, showing the chemical robustness of the FePc catalyst after dropcasting and in the presence of an electrolyte flow. Under Ar and catalytic conditions (-0.97

V vs. RHE), the spectrum keeps a similar shape, but with a drastic shift towards lower energies (*ca.* -1.9 eV) at the edge inflection point. This is clearly indicative of a reduction of the metallic centre in FePc, while the formation of metallic iron can be ruled out (see figure 4 for comparison). When flowing a CO₂-saturated electrolyte, the spectrum recorded under catalytic conditions (-1.1 V) also showed a shift to lower energies (-1.1 eV), albeit less important than under Ar. Whether under Ar or CO₂ saturated electrolyte, the spectra collected under catalytic conditions present the features that are characteristic of phthalocyanines, *i.e.* two pre-edge peaks at 7112 eV and 7119 eV. These features correspond to 1s → 3d and 1s → 4p transitions [28], respectively, and their presence throughout the experiment demonstrate the intactness of the molecular nature of the catalyst. XANES spectra were also recorded *in situ* after performing electrocatalytic experiments with Ar or CO₂ saturated electrolytes and they were identical to those collected on the starting species under open circuit potential (see figure S9). The intensity of the raw fluorescence signal decreased by *ca.* 30% from the start to the end of the experiment, indicating a mechanical erosion of the sample. This phenomenon was only observed in the XAS experiment, likely because of the higher amount of catalyst deposited on the electrode.

Figure 4. *In situ* and *operando* X-ray absorption spectra collected on FePc under argon at open circuit potential (black), argon (red) and CO₂ (blue) at -1.1 V vs RHE are shown in solid curves. *Ex situ* reference spectra collected on pellet of FePc (brown), Fe metal (orange), and FeO(OH) (green) are shown as dashed curves (a); SEM image of a FePc-modified electrode before electrolysis (b); SEM image of a FePc-modified electrode after electrolysis at -1.1 V vs RHE for 2 hours (c).

In order to further characterize the catalyst, we recorded scanning electron microscopy (SEM) images on FePc-modified electrodes, before and after a CO₂ reduction electrocatalytic experiment (see figures 4b and 4c). The images are identical before and after the experiment,

without any evidence for nanoparticles formation. EDX analysis performed on the same electrodes indicate that iron is homogeneously dispersed on the surface (see figures S3 and S4). In addition, infrared spectra were recorded on the FePc catalyst powder and FePc-modified electrodes before and after electrolysis at -1.1 V vs RHE (see figure S10). We can observe from the spectra the characteristic vibrational peaks of the phthalocyanine ligand in a typical metal phthalocyanine species: stretching modes of C=C, C-N=C, isoindole and pyrrole groups from 1800 to 1330 cm^{-1} ; as well as scissoring modes of C-H and isoindole groups from 1330 cm^{-1} to 800 cm^{-1} . [29] [30] The peaks in the stretching region of pure FePc powder are more well-defined since the powder was not affected by the presence of carbon black and Nafion as in the electrodes. However, the IR spectra recorded with modified electrodes before and after electrolysis are identical, agreeing with the XAS results about the high stability of the catalyst during electrolysis.

Discussion

The shifts of the XANES main edge energy position observed under catalytic conditions can be ascribed to changes in the oxidation state of the central metallic ion, suggesting a majority species with an oxidation state below +II under catalytic conditions. This finding is in contrast with what was found by Liu *et al.* on the structure of cobalt phthalocyanine (CoPc) under electrocatalytic CO_2 -reducing conditions [28]. They showed, using *operando* XANES, that the cobalt K-edge position did not significantly change under catalytic conditions very similar to those used in this study. Intrigued by this different spectroscopic behaviour, we performed electrocatalytic CO_2 -reducing experiments using a CoPc-modified electrode in the same conditions that were used for the FePc-modified electrode. We found that no C_2^+ products were formed, while methanol could be observed starting from -1.0 V (see figure S5a and figure S11), as already reported [21] [22]. This difference in catalytic activity can be related to the spectroscopic differences that we observed with respect to Liu's work: FePc shows a shift in its K-edge energy position under catalytic conditions, while CoPc doesn't and FePc produces C_2^+ products while CoPc doesn't. This correlation could tentatively be attributed to differences in the locus of reduction (*i.e.* a metal-centered reduction for FePc and a ligand-centered one for CoPc), but Liu *et al.* convincingly demonstrated that Co is required in CoPc for catalysis and that ZnPc or H_2Pc do not show the same catalytic behaviour. This indicates that the formation of C-C bonds by FePc is clearly occurring on the metal, but also that the nature of the metal, or possibly the electronic structure of the metal-macrocycle system, influences its reactivity towards C-C bond formation.

The demonstration that a molecular electrocatalyst can form several consecutive C-C bonds poses the question of their formation mechanism. Since hydrocarbons only appear when hydrogen is also produced in significant amounts, it is reasonable to assume that the FePc-CO species formed upon reduction of CO_2 further reacts with H_2 . By analogy with what happens during the Fisher-Tropsch Synthesis of long chain hydrocarbons [31] [32] or the electrocatalytic reduction of CO_2 into ethylene by metallic copper [8] [33], we propose that a terminal FePc carbene species is the precursor to all C_2^+ products (see scheme 1). This transient species would be formed by reaction of an FePc-CO adduct with two molecules of H_2 , and further react either with more H_2 to form methane or with another CO to form a C-C

bond. The process could continue a few times and lead to the formation of longer saturated or unsaturated hydrocarbon chains.

Scheme 1. Simplified mechanism proposed for the formation of C-C bonds by FePc and more generally by a mononuclear molecular species.

It is worth mentioning that several iron porphyrin carbene species have been reported, either as transient [34] [35] or stable species [36], and that FePc has been reported as an efficient catalyst for the cyclopropanation of alkenes [37], which involves an FePc-carbene intermediate. This supports the formation of fugacious and minority FePc-carbene species derived from an FePc-CO intermediate, itself generated by the reduction of CO₂. Further mechanistic studies are currently underway to provide clues as to the intermediate species involved in the formation of C-C bonds by FePc-modified electrodes.

Conclusion

We reported in this paper on the electrocatalytic activity of a molecular macrocycle based on earth abundant elements, iron phthalocyanine, towards the reduction of CO₂ into carbon monoxide, hydrogen and light hydrocarbons. This catalyst produces CO as a main product at high potential (-0.7 V vs RHE), while more reduced products ranging from methane to butane and pentane can be produced at lower potentials (starting from -0.9 V). The presence of these hydrocarbons is apparently linked to the increased amount of hydrogen produced. Using *operando* X-ray absorption spectroscopy and SEM, we showed that the catalyst keeps its molecular structure throughout the electrocatalytic process, and that the metallic centre is involved in the reaction. On the basis of literature comparison, we propose the involvement of a carbene intermediate followed by CO insertion for the formation of the C-C bonds that yield C₂⁺ products. These results indicate that the formation of several consecutive carbon-carbon bonds can be catalysed by monomeric transition metal macrocycles under mild electrochemical conditions, at room temperature and low gas pressure. These findings open the way to the design of functional architectures with a better control of C-C bonds formation and selectivity towards C₂⁺ products.

Conflict of interest

The authors have no conflict of interest to declare.

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