Manganese Carbonyl Complexes as Selective Electrocatalysts for CO2 Reduction in Water and Organic Solvents

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CONSPECTUS: The electrochemical reduction of CO2 provides a way to sustainably generate carbon-based fuels and feedstocks. Molecular CO2 reduction electrocatalysts provide tunable reaction centers offering an approach to control the selectivity of catalysis. Manganese carbonyl complexes, based on [Mn(bpy)-(CO)3]Br and its derivatives (bpy = 2,2′-bipyridine), are particularly interesting due to their ease of synthesis and the use of a first-row earth-abundant transition metal. [Mn(bpy)(CO)3]Br was first shown to be an active and selective catalyst for reducing CO2 to CO in organic solvents in 2011. Since then, manganese carbonyl catalysts have been widely studied with numerous reports of their use as electrocatalysts and photocatalysts and studies of their mechanism. This class of Mn catalysts only shows CO2 reduction activity with the addition of weak Brønsted acids. Perhaps surprisingly, early reports showed increased turnover frequencies as the acid strength is increased without a loss in selectivity toward CO evolution. It may have been expected that the competing hydrogen evolution reaction could have led to lower selectivity. Inspired by these works we began to explore if the catalyst would work in protic solvents, namely, water, and to explore the pH range over which it can operate. Here we describe the early studies from our laboratory that first demonstrated the use of manganese carbonyl complexes in water and then go on to discuss wider developments on the use of these catalysts in water, highlighting their potential as catalysts for use in aqueous CO2 electrolyzers.

Key to the excellent selectivity of these catalysts in the presence of Brønsted acids is a proton-assisted CO2 binding mechanism, where for the acids widely studied, lower pKa values actually favor CO2 binding over Mn−H formation, a precursor to H2 evolution. Here we discuss the wider literature before focusing on our own contributions in validating this previously proposed mechanism through the use of vibrational sum frequency generation (VSFG) spectroelectrochemistry. This allowed us to study [Mn(bpy)(CO)3]Br while it is at, or near, the electrode surface, which provided a way to identify new catalytic intermediates and also confirm that proton-assisted CO2 binding operates in both the “dimer” and primary (via [Mn(bpy)(CO)3]−) pathways. Understanding the mechanism of how these highly selective catalysts operate is important as we propose that the Mn complexes will be valuable models to guide the development of new proton/acid tolerant CO2 reduction catalysts.

KEY REFERENCES

• Walsh, J. J.; Neri, G.; Smith, C. L.; Cowan, A. J. Electrocatalytic CO2 reduction with a membrane supported manganese catalyst in aqueous solution. Chem. Commun. 2014, 50, 12698−12701.1 This work used a simple approach to immobilize the Mn complex on a carbon support allowing for its study in aqueous solvent for the first time, demonstrating that CO2 reduction selectivity was retained.

• Walsh, J. J.; Neri, G.; Smith, C. L.; Cowan, A. J. Water-Soluble Manganese Complex for Selective Electro-catalytic CO2 Reduction to CO. Organometallics 2019, 38, 1224−1229.2 Here we showed the activity and selectivity of a carboxylic acid derivative in water across a wide pH range.

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This study used vibrational sum-frequency generation spectroscopy to follow the reaction mechanisms of the Mn catalyst transiently at an electrode during carbon dioxide reduction.

Neri, G.; Donaldson, P. M.; Cowan, A. J. In situ study of the low overpotential “dimer pathway” for electrocatalytic carbon dioxide reduction by manganese carbonyl complexes. *Phys. Chem. Chem. Phys.*, 2019, 21, 7389–7397. Here we examined the surface behavior of the Mn catalyst as it arrives at the electrode and also explored the mechanism of the less studied lower overpotential reaction pathway.

1. INTRODUCTION

Electrochemical CO$_2$ reduction will be needed to enable a circular carbon economy and it is proposed to play an important role in managing CO$_2$ emissions. Electrochemical CO$_2$ conversion at scale is expected to make use of point...
sources of CO2, such as flue gas from heavy industries. Metal electrodes and metallic electrocatalysts2 deposited onto high surface area supports have demonstrated that reduction of pure CO2 feeds can achieve high current densities (up to 1 A cm\(^{-2}\)) in CO2 electrolyzers.9 However, as the CO2 concentration is decreased and impurities such as O2, NOx, and SOx are added to simulate a typical flue gas stream, changes in selectivity have been reported.10,11 Molecular catalysts12−15 provide an opportunity to achieve desired reactant and product selectivity by altering the ligands surrounding the metal center to tune the reaction center’s electronics and steric bulk. Therefore, they are particularly interesting as both models of how CO2 selectivity can be controlled and potential practical-scale catalysts for application in an immobilized configuration.

A widely studied class of molecular electrocatalysts is those based on [fac-Re(bpy)(CO)3Cl] (bpy = 2,2′-bipyridine, hereafter the fac- is assumed for all tricarbonyl structures unless otherwise stated). This catalyst was first reported in the 1980s to produce CO both photocatalytically and electrochemically from CO2, displaying high Faradic efficiencies for CO and good stability under electrocatalytic conditions.10,17 Despite these promising results, Re has low natural abundance.15 Early on, [Mn(bpy)(CO)3Br] was examined as a possible alternative high-abundance catalyst, but initial reports in organic solvents noted a lack of activity toward CO2.19 It was not until 2011 in a breakthrough study by Deronzier and co-workers20 that [Mn(bpy-R)(CO)3Br] (R = H or alkyl group at the 4,4′ position) was shown to be an active electrocatalyst for CO2 reduction in organic solvents, but only when a Brønsted acid was added. A typical cyclic voltammogram of [Mn(bpy)(CO)3Br] in acetonitrile, similar to that measured in those first reports, is shown in Figure 1a, and a proposed catalytic cycle is shown in Figure 1b. Under N2, initial reduction at −1.2 V\text{SCE} results in the loss of Br and then dimerization to form [Mn(bpy)(CO)3]2+. This dimer complex is reduced at −1.5 V\text{SCE} to form the main catalytically active species [Mn(bpy)(CO)3]− as indicated by the large increase in current under CO2 and in the presence of a proton source. In competition with CO evolution is H2 production, which occurs via the formation of [Mn(bpy)(CO)3H].

The initial study by Deronzier and colleagues20 led to a large number of follow-on works on this class of catalyst, of which several reviews exist.13,21−24 In this Account, we discuss one of the most interesting aspects, the need for a Brønsted acid for any measurable CO2 reduction to occur.16,17 This finding was confirmed in a study by the Kubik group in 2013, on a derivative, [Mn(bpy′Bu)3(CO)Br], in acetonitrile with the addition of the weak acids water, methanol, and 2,2,2-trifluoroethanol (TFE), where higher turnover frequencies were achieved than with the parent complex.25 Also, the turnover frequency of the Mn catalyst was shown to increase with acid strength, and in general with higher concentrations of acid, without a loss in selectivity toward CO2 reduction. These experiments on the complex in aprotic solvents with an acid source led us to ask in 2014,14 could the performance of [Mn(bpy)(CO)3Br] be further improved by use in a protic solvent, in particular water?

Developing CO2 reduction catalysts that are selective in water is important; in a practical electrolyzer, the CO2 reduction reaction will need to be coupled to a sustainable oxidation reaction, presumably water oxidation. In particular, there is current interest in understanding how to develop systems that can selectively reduce CO2 in an acidic environment26 as operating CO2 electrolyzers at high pH leads to carbonate formation with consequential decreased CO2 conversion efficiencies.27 With conventional metal catalysts (e.g., Ag, Au, or Cu) operating at low pH is challenging due to competitive hydrogen evolution as a result of the high proton concentration. Therefore, the development and mechanistic study of molecular electrocatalysts that show high selectivity to CO2 reduction in the presence of high proton concentrations is of great interest to the field. Here we describe in section 2 the use of this class of Mn catalysts for CO2 reduction in water, focusing on early work from our own laboratory before discussing wider developments in the field. In section 3, we discuss mechanistic studies on the role of the acid source in the CO2 reduction mechanism in an effort to understand how these catalysts achieve selectivity. In particular, we introduce the use of vibrational sum frequency generation (VSFG) spectroscopy, which confirmed a previously proposed proton-assisted CO2 binding mechanism for the main catalytic pathways, rationalizing why these catalysts can operate even in proton-rich environments.

2. [Mn(bpy)(CO)3Br] AND ITS DERIVATIVES AS CO2 REDUCTION CATALYSTS IN WATER

To test how [Mn(bpy)(CO)3Br] behaved in the presence of aqueous electrolytes, we initially applied a simple approach previously described for a range of catalysts including [Re(bpy)(CO)3Cl],29 where we deposited the Mn complex directly onto a glassy carbon electrode (GCE) using a Nafion ionomer support.1 Direct study of the mechanism of the catalyst within the Nafion membrane is challenging but CVs indicated that despite being immobilized and used at pH 7, the catalyst showed very similar behavior to that observed when it is dissolved in aprotic solvents with the largest current enhancement under CO2 occurring following the formation of [Mn(bpy)(CO)3]−. Intriguingly in the Nafion membrane, dimerization is believed to still occur following initial reduction of [Mn(bpy)(CO)3Br], prior to the formation of the active [Mn(bpy)(CO)3]− catalyst, as indicated by the oxidation peak of [Mn(bpy)(CO)3]3+. A linear dependence of peak current with scan rate for the reduction of [Mn(bpy)(CO)3Br] indicated that the complex was not solubilized in the polymer, and no evidence of Mn loss into the electrolyte was found suggesting that dimer formation was the result of electroactive aggregates; however definitive evidence of the mechanism of dimerization within Nafion is still missing. Regardless of the possible mechanisms of dimerization the most important outcome of this first study was that once formed [Mn(bpy)(CO)3]2− displayed good selectivity for CO2 reduction in water at pH 7 with a CO/H2 ratio of 2.1 being achieved at −1.4 V\text{Ag/AgCl}, and TON of up to 470. This demonstrated the viability of using this complex in protic solvents and indicates that CO2 reduction selectivities on par with those seen in aprotic solvents could be achieved.

In the first studies of GCE/[Mn(bpy)(CO)3Br]/Nafion electrodes, current densities were low (0.3 mA cm−2) due to the majority of the catalyst present being electro-inactive. The addition of multiwalled carbon nanotubes (MWCNTs), increasing the electroactive content, led to a large increase in current density under CO2 (up to 3 mA cm−2, Figure 2), albeit with a partial loss in CO/H2 selectivity (dropping to ~1:2).1 A subsequent study investigated a wider range of Mn complexes that contained modifications to the 4,4′ positions of the 2,2′-bipyridine ligand immobilized in a similar manner with
Among the complexes studied $[\text{Mn(bpy(tBu)$_2$)(CO)$_3$Br}]$, which was first reported by Kubiak and colleagues, gave the highest level of selectivity toward CO ($\text{CO}/\text{H}_2 \approx 1$); however the CO partial current density was lower than the original unmodified bipyridine complex. Also studied were $[\text{Mn(bpy(OH)$_2$)(CO)$_3$Br}]$ and $[\text{Mn(bpy(COOH)$_2$)(CO)$_3$Br}]$, but both complexes gave disappointing levels of selectivity when immobilized, with $\text{CO}/\text{H}_2 \approx 0.28$ and 0.33, respectively. The initial studies of the Mn catalysts deposited on GCE made use of the low solubility of $[\text{Mn(bpy)(CO)$_3$Br}]$ in water; however relatively low electroactive contents were achieved, and the current densities reported above are $\sim 30$ times lower than is required for application in a practical electrolyzer ($>100 \text{ mA cm}^{-2}$).

Subsequent studies have reported more advanced approaches to immobilize manganese carbonyl catalysts with several achieving notably higher current densities. Reisner and colleagues developed a derivative where the catalyst was anchored to carbon nanotubes through a pyrene-modified MWCNTs. Among the complexes studied $[\text{Mn(bpy(tBu)$_2$)(CO)$_3$Br}]$, which was first reported by Kubiak and colleagues, gave the highest level of selectivity toward CO ($\text{CO}/\text{H}_2 \approx 1$); however the CO partial current density was lower than the original unmodified bipyridine complex. Also studied were $[\text{Mn(bpy(OH)$_2$)(CO)$_3$Br}]$ and $[\text{Mn(bpy(COOH)$_2$)(CO)$_3$Br}]$, but both complexes gave disappointing levels of selectivity when immobilized, with $\text{CO}/\text{H}_2 \approx 0.28$ and 0.33, respectively. The initial studies of the Mn catalysts deposited on GCE made use of the low solubility of $[\text{Mn(bpy)(CO)$_3$Br}]$ in water; however relatively low electroactive contents were achieved, and the current densities reported above are $\sim 30$ times lower than is required for application in a practical electrolyzer ($>100 \text{ mA cm}^{-2}$).

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bipyridine ligand, which was found to show a stable current density of 0.5 mA cm$^{-2}$ ($-1.1$ V$_{SHL}$) with a good selectivity for CO production (maximum Faradaic efficiency of 34%) at pH 7.4.\textsuperscript{28} Interestingly this system also produced appreciable concentrations of formate, which is not a common observation in other electrocatalytic studies in water described below. Excellent selectivity for CO production (>80% Faradaic efficiency) and a stable current density of 5 mA cm$^{-2}$ were reported from a polymerized manganese carbonyl complex on MWCNTs in a pH 7 electrolyte when K$^+$ ions were present at high concentrations.\textsuperscript{31} Of great relevance is also the work of Vizza and co-workers who prepared [Mn(apbpy)(CO)$_3$Br] (apbpy = 4-(4-aminophenyl)-2,2′-bipyridine), which can be electrochemically grafted onto carbon cloth.\textsuperscript{32} In this way, electrodes with the catalytic center covalently bound onto the support can be prepared and achieved Faradaic efficiencies of ~60% for CO production at $-1.4$ V$_{Ag/AgCl}$ in CO$_2$ saturated KHCO$_3$. Very recently, studies of this catalyst bound onto a gas diffusion electrode showed that the mass normalized turnover frequencies of the catalyst exceeded those of a benchmark Au catalyst.\textsuperscript{33} Another strategy to achieve higher electroactive concentrations of catalytic centers, and therefore potentially higher current densities, is to incorporate the Mn catalytic center directly within a high surface area porous framework. Examples that use a Mn catalytic center for CO$_2$ reduction in water include a conjugated microporous polymer\textsuperscript{34} and a covalent organic framework\textsuperscript{35} with the latter achieving an impressive CO partial current density of 11 mA cm$^{-2}$ and selectivity (55% Faradaic efficiency) at pH 7.4.\textsuperscript{33}

The examples of [Mn(bpy)(CO)$_3$Br] derivatives immobilized onto and into electrode supports for CO$_2$ reduction in water have demonstrated that a good level of selectivity (typically $\geq 1:1$ CO/H$_2$) can be achieved at pH $\sim$7. However, it is difficult to quantify the intrinsic selectivity of the catalyst due to the possibility of hydrogen being evolved from the carbon support or impurities within. In order to better understand the behavior of the Mn catalyst in a wide pH range, we also developed a water-soluble Mn diimine CO$_2$ reduction complex [Mn(bpy(COOH)$_2$)(CO)$_3$Br], where bpy(COOH)$_2$ = 4,4′-dicarboxy-2,2′-bipyridine. The solubility of the catalyst allowed for experiments using a Hg amalgam electrode, which has a high overpotential for hydrogen evolution making it ideal for analytical electrochemistry in water at a range of pH values.\textsuperscript{2} UV/vis spectroscopy showed a pH dependence due to the changing protonation state of the carboxylate groups and also indicated that the bromide ligand was readily displaced by water at open circuit. In contrast to the equivalent Re complex\textsuperscript{36} where the displacement of the aqua ligand by bicarbonate led to a loss in solubility at some pH values under CO$_2$, the Mn analogue retained solubility under CO$_2$, and no evidence of carbonate/bicarbonate ligation was observed.\textsuperscript{12} CVs of [Mn(bpy(COO)$_2$)(CO)$_3$]$^{3-}$ under Ar and CO$_2$ at a range of pH values were similar to other complexes from this class in conventional organic solvents with an initial reduction between $-1.0$ and $-1.1$ V$_{Ag/AgCl}$ depending upon pH, leading to loss of a solvent ligand and dimer formation, and a further reduction between $-1.4$ and $-1.3$ V$_{Ag/AgCl}$ formed the active [Mn(bpy(COO)$_2$)(CO)$_3$]$^{3-}$ (Figure 3a). At the highest pH values studied (>9), minimal CO$_2$ reduction occurs, presumably due to a combination of low concentrations of available CO$_2$ and H$. Bulk electrolysis was only carried out at a single pH in this initial communication but notably between pH 9 and 2.5 a large enhancement in catalytic current occurred under CO$_2$ with the greatest increases in current under CO$_2$ occurring at the lowest pH values (Figure 3b). This indication of CO$_2$ catalysis even at the lowest pH values studied is of particular interest because at pH $< 4$ bicarbonate formation is no longer a significant process; therefore the development and study of catalysts that can operate selectively toward CO$_2$ reduction under these conditions may provide a way to enable acid CO$_2$ electrolyzers.\textsuperscript{26}
were the original work of Deronzier and colleagues who noted in protic environments. As noted in section 1, two key studies group also represented the from the Kubiak group on the behavior of \[\text{Mn(bpy(tBu)2)}\]−. The Mn follows by the barrierless, strongly exergonic protonation of CO2 binding was endergonic. But once phenol was added, CO2 binding to \[\text{Mn(bpy(CO)3)}\]− is the acid source, which showed a dual role for the acid, stabilizing the Mn–CO2 species or facilitating the cleavage of a C–O bond. DFT calculations following on from this work by Carter and colleagues confirmed that without an acid present CO2 binding was endergonic. But once phenol was added, the process became exergonic, and initial CO2 binding was followed by the barrierless, strongly exergonic protonation of the Mn–CO2 adduct. This finding has since been further validated and expanded upon in DFT calculations where TFE is the acid source, which showed a dual role for the acid, stabilizing the Mn–CO2 adduct with subsequent rapid protonation and exergonic carbonation of the conjugate base providing additional driving force for the overall generation of a Mn–CO3H intermediate. The DFT studies of the Carter group also represented the first report of the presence of two catalytic pathways for CO evolution following proton assisted CO2 binding to \[\text{Mn(bpy)}(\text{CO})_2\]−, labeled the “protonation first” and “reduction first” pathways in Figure 1b. These calculations provided a rationale for the excellent selectivity and improved turnover frequency in the presence of stronger acids, and a framework by which we can understand the selectivity of the catalysts in water. However, direct detection of many of the short-lived intermediates proposed has historically been a challenge with conventional spectroscopies where the need to electrochemically generate high concentrations of species in the bulk inevitably makes the detection of short-lived transient species at the electrode surface difficult.

Our own contribution has focused on using vibrational sum frequency generation (VSFG) spectroscopy to study Mn catalysts at the electrode surface in the presence of a range of acids, with the aim of validating the calculated role of the Brønsted acid in CO2 reduction. In a VSFG experiment, two incident, short laser pulses are overlapped on the sample interface (in this case the working electrode surface), and the light is generated at the sum of the frequency of the two input pulses (Figure 4a,b). In our experiments, we use a broad-band (typically 500 cm−1 fwhm, 50 fs) tunable mid-infrared (mIR) laser and a fixed wavelength visible (800 nm) laser that has a picosecond pulse duration and a time asymmetric shape. Both of these are transmitted through a thin-layer of electrolyte to the electrode surface (Figure 4c,d; for full details of the experimental apparatus, see ref 40). When the mIR laser frequency is resonant with a sum-frequency active vibrational mode, the VSFG light intensity is significantly increased and a vibrational spectrum of the species can be recorded. VSFG is often described as surface selective because signals are only generated in a non-centrosymmetric environment under the electric dipole approximation. However, it is important to note that across the electrical double layer structure ordering can occur giving rise to VSFG signals and contributions from third order nonlinear polarization terms can also arise from molecules throughout the double layer; therefore this statement is not strictly correct. Nonetheless VSFG spectroscopy provides a powerful way to study molecular electrocatalysts while they are near (within the double layer structure) or at the electrode surface, as sufficient ordering can occur due to the large electric fields present and the use of catalysts with nonzero dipole moments. A detailed review on the application of the technique to molecular electrocatalysts, which describes in more detail the experimental considerations and the route by which spectra are assigned and fitted, is available.

Figure 5. CV (a) of \[\text{[Mn(bpy)}(\text{CO})_3\text{Br)}\] in CH3CN in the presence of 1.5 M TFE under Ar and VSFG spectra (b, c) recorded in situ of the complex at the working electrode. Panel c is an expansion (z-axis, VSFG intensity) of panel b. The numbers on the right correspond to the spectral assignments. (1) \[\text{[Mn(bpy)}(\text{CO})_3(\text{solv})]^{-}\]; (2) \[\text{[Mn}_2\text{bpy}_2(\text{CO})_6\text{]}\]; (4) \[\text{[Mn(bpy)}(\text{CO})_3\text{H}]\]. Adapted from ref 3 with permission from Springer Nature.
Initially we have carried out experiments in acetonitrile with added Bronsted acids as the need for IR transmission through the electrolyte prevents the study of aqueous electrolytes. VSFG data recorded during a CV of [Mn(bpy)(CO)3Br] in CH3CN with TFE using a static Hg/Au amalgam electrode under an Ar atmosphere is shown in Figure 5. In the VSFG experiments, we focus on the metal carbonyl stretching modes as they act as excellent reporter groups on the state of the metal center and prior bulk SEC-FTIR studies1,45−47 provide a way to assign known species at the electrode surface. At open circuit, no ν(CO) bands were observed, but as the potential of the electrode was swept reductively from +0.1 V to −0.4 V (all potentials in the VSFG experiments in this section are versus a Ag pseudoreference electrode), a strong (∼2043 cm−1) ν(CO) band increased in intensity (Figure 5c). A second broad, much weaker band around 1940 cm−1 could also be observed upon careful inspection of individual spectra (not shown here) with both bands assigned to [Mn(bpy)-(CO)3(CH3CN)]+ (the solvent can displace the bromide ligand). The ν(CO) bands shifted in frequency with applied potential, giving a Stark shift of ∼35 cm−1 V−1, demonstrating that the vibrational spectra were occurring from [Mn(bpy)-(CO)3(CH3CN)]+ experiencing a large electric field, which therefore must be at or near the electrode surface.

As expected from the past FTIR reports25,48 the reduction of [Mn(bpy)(CO)3(CH3CN)]+ leads to formation of [Mn(bpy)2(CO)]0 (species 2, Figure 1b), and this in turn could be reduced at potentials negative of −0.9 VAg. The IνFG of the ∼1970 cm−1 resonant mode of [Mn2(bpy)2(CO)6]− is very intense (Figure 5b) as the visible laser pulse is resonant with an electronic transition of this complex.20 We were unable to observe the anticipated active catalyst, [Mn(bpy)(CO)3]2−, at the electrode surface. Instead, [Mn(bpy)(CO)3H]+ formed rapidly (Figure 5) in the absence of CO2. Using VSFG spectroscopy, we found, in both the absence of a deliberately added acid and the presence of a number of acids (methanol, TFE, phenol), at the electrode surface [Mn(bpy)(CO)3H]+ formation in the absence of CO2.3,49 It is clear that at the electrode surface [Mn(bpy)(CO)3H]+ formation occurs very rapidly even in the absence of a deliberately added Bronsted acid (trace water is likely present), and the cause of the high selectivity of this complex toward CO2 is not the lack of hydride formation. This is an interesting observation as FTIR spectroelectrochemistry had monitored the formation of [Mn(6,6′-dimesityl-2,2′-bipyridine)(CO)3]− in the bulk electrolyte indicating its stability50 and DFT calculations38,39 predicted a ∼13−15 kcal mol−1 barrier to binding of H+ to [Mn(bpy)(CO)3]−. One possible rationale of the VSFG result may be the presence of the large electric field at the electrode interface, which can have a profound effect on the relative stability of the species,51 or due to preferential orientation/accumulation of protons at the electrode surface, with both situations highlighting the need to monitor the surface species.

Under CO2 with TFE present, in the potential region where CO2 reduction begins, [Mn(bpy)(CO)3H]+ is not detected; instead several new ν(CO) bands due to CO2 reduction intermediates appear, Figure 6.3 The intensity of the VSFG bands of the CO2 reduction intermediates was greatest with respect to CO2,2.0 V SCE, phenol were the acid sources at 1.7 and 2.0 V SCE, respectively.57 However, isotopic labeling experiments and DFT calculations of the Stark tuning rates of the ν(CO) modes of the CO2 intermediate ruled out assignment to [Mn(bpy)-(OCO)]+, and the VSFG bands at ∼1376 and 1600 cm−1
were assigned to \([\text{Mn(bpy})(\text{CO})_3]^+\), a later intermediate in the catalytic cycle of the "protonation first" pathway. The VSFG data did support the proposed potential dependent switching between a protonation first and reduction first pathway, with an additional band at \(\sim 1875 \text{ cm}^{-1}\) possibly being due to \([\text{Mn}(\text{bpy})(\text{CO})_2]^+\). The availability of the lower-overpotential protonation first pathway catalysis had also been demonstrated to occur elsewhere in several studies with derivatives of the Mn complex, and its accessibility offers a further reason for the typically lower overpotentials and increased activity for CO\(_2\) reduction using this class of Mn complexes in the presence of stronger acids.

With \([\text{Mn(bpy})(\text{CO})_3\text{Br}]\), a CO\(_2\) reduction current is also observed at potentials positive of \([\text{Mn}(\text{bpy})_2(\text{CO})_3](\text{CO}_2\text{H})\) reduction, demonstrating the presence of an additional low-overpotential pathway to produce CO. The catalytic studies outlined in section 2 show that this "dimer pathway" (Figure 1b) also retains high selectivity toward CO production even in water. The mechanism of catalysis via the dimer was first studied through a combination of pulsed-EPR and UV/vis spectroscopy, where it was shown that in a 5% water/95% CH\(_3\)CN solution CO\(_2\) purging led to loss of electrochemically generated dimer in the bulk electrolyte. Further UV/vis and FTIR studies of immobilized Mn catalysts also explored the reactivity of the dimer complex in the presence of water and showed that it was decreased within seconds of the electrolyte being exposed to CO\(_2\).

However, the behavior of the dimer using different acid sources had not been previously studied in detail and VSFG spectroscopy also offered a way to analyze the possible role of surface specific species in the "dimer mechanism".

In a homodyne experiment, it can be approximated that VSFG signal intensities scale quadratically with the density of vibrational modes in the interface region. Therefore, a plot of the square root of the VSFG intensities versus electrode potential provides a semiquantitative measure of the surface/double layer concentration of the species. VSFG experiments looking at the behavior of \([\text{Mn}(\text{bpy})_2(\text{CO})_3]\) in CH\(_3\)CN with a range of acids added showed that the dimer accumulated and reached a plateau concentration at \(-0.7 \text{ V}_{\text{Ag}}\) (Figure 7a) in the presence of TFE. Under Ar, the surface population of \([\text{Mn}(\text{bpy})_2(\text{CO})_3]\) remained constant regardless of the acid used (TFE, phenol, no acid) until reduction occurred, and this led to the formation of \([\text{Mn}(\text{bpy})(\text{CO})_3\text{H}]\). Identical behavior was observed under CO\(_2\) in the absence of an added acid, with \([\text{Mn}(\text{bpy})_2(\text{CO})_3]\) persisting at the electrode surface prior to \([\text{Mn}(\text{bpy})(\text{CO})_3\text{H}]\) formation occurring, indicating that CO\(_2\) is unable to interact with the dimer without a suitable Bronsted acid. In the presence of either TFE or phenol and CO\(_2\), a notable decrease in the surface concentration of \([\text{Mn}(\text{bpy})_2(\text{CO})_3\text{H}]\) occurred, 130 mV positive of the reduction potential of \([\text{Mn}(\text{bpy})_2(\text{CO})_3]\). The extent of decrease in the VSFG signal of \([\text{Mn}(\text{bpy})_2(\text{CO})_3\text{H}]\) was greatest when the lowest pK\(_a\) of phenol and CO\(_2\) were used indicating that CO\(_2\) interaction with the dimer to produce the previously detected mer Mn\(^{11+}\)-CO\(_2\)H also occurs via a protonation-assisted CO\(_2\) binding mechanism. Furthermore, by analysis of the onset of the catalytic current and from knowledge of the electrochemical stability of previously proposed intermediates, a new alternative pathway for CO evolution following mer-Mn\(^{11+}\)-CO\(_2\)H formation via the reduction of a mer-Mn(bpy)(CO)(CO\(_2\)H) intermediate occurs prior to protonation and H\(_2\)O loss (Figure 7b), different from those previously put forward by Deronzier and Grills.

4. CONCLUSIONS AND OUTLOOK

VSFG spectroscopy can follow the Mn electrocatalyst for CO\(_2\) reduction while at the electrode surface, and our results complement the theoretical and other spectroscopic studies in the literature to provide important insights into the remarkable selectivity of this class of catalysts toward CO\(_2\) reduction. The low levels of H\(_2\) production are not due to a lack of H\(^+\) binding when the active \([\text{Mn}(\text{bpy})(\text{CO})_3]\) catalyst is generated as previously postulated, as \([\text{Mn}(\text{bpy})(\text{CO})_3\text{H}]\) forms rapidly at the electrode surface in the absence of CO\(_2\). Instead selectivity toward CO\(_2\) in all catalytic pathways ("dimer pathway" species 2 and 11; "protonation first" species 3, 5, 6, 8, and 9, and "reduction first" species 3, 5, 6, 7, and 9, Figure 1b) arises by
an unusual acid-promoted CO₂ binding mechanism, where acids with a lower pKᵥ actually lead to higher concentrations of CO₂ reduction intermediates. We believe that such an effect has been rarely reported within the large variety of known homogeneous CO₂ reduction catalysts. To date, our studies have focused on one particular class of catalysts and not in aqueous solvent, which may complicate direct comparisons, but we encourage future works to explore if similar proton-assisted CO₂ binding mechanisms are in wider operation among CO₂ reduction catalysts.

Recent techno-economic analyses highlight the need to understand and discover new electrocatalysts that can reduce CO₂ selectively in water, in particular at low pH.²⁷ There are relatively few studies to date on the use of this class of catalysts in water, but from the emerging literature, it does appear that the proton-assisted CO₂ binding mechanisms seen in aprotic solvents may be facilitating the measured high levels of selectivity in aqueous electrolytes as well. While the long-term stability of these Mn catalysts is uncertain, especially under high current densities, initial catalysis studies are promising, and these Mn complexes serve as valuable models for future development of proton/acid tolerant CO₂ reduction catalysts.

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Notes

The authors declare no competing financial interest.

Biographies

Bhavin Siritanaratkul received his D.Phil. in Chemistry from the University of Oxford under the supervision of Fraser A. Armstrong, where he worked on the electrochemistry of enzymes for nicotinamide cofactor regeneration. His prior research experience includes solar water splitting and heterogeneous catalysis for methane conversion. He is currently a postdoctoral researcher with Alex Cowan at the University of Liverpool, working on electrochemical CO₂ reduction.

Catherine Eagle obtained her Masters in Science from Imperial College London (2020) under the supervision of Dr. Rob Davies. Following this, she moved to the University of Liverpool to join Prof. Alex Cowan’s research group as a Ph.D. student to study carbon dioxide utilization by selective reduction of impure and low concentration carbon dioxide streams using molecular catalysts.

Alex Cowan is a Professor of Chemistry at the University of Liverpool where he leads an interdisciplinary team who are developing new catalysts and materials for the production of sustainable fuels and studying their mechanisms. A particular interest of the group is the electrocatalytic reduction of carbon dioxide into useful molecules such as carbon monoxide and the in situ studies of these electrocatalysts.

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