



Cite this: *Chem. Commun.*, 2024, 60, 4826

Received 4th January 2024,
Accepted 2nd April 2024

DOI: 10.1039/d3cc06336d

rsc.li/chemcomm

Kinetic isotope effect offers selectivity in CO₂ reduction†

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A binuclear Ni complex with N,O donors catalyzes CO₂ reduction via its Ni(II) state. The product distribution when H₂O is used as a proton source shows similar yields for CO, HCOOH and H₂. However, when D₂O is used, the product distribution shows a ~65% selectivity for HCOOH. *In situ* FTIR indicates that the reaction involves a Ni–COO* and a Ni–CO intermediate. Differences in H/D KIEs on different protonation pathways determine the selectivity of CO₂ reduction.

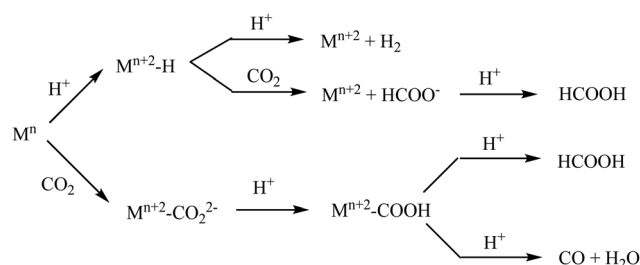
The reduction of CO₂ to chemicals having commercial value has taken centre stage in multi-electron multi-proton catalysis. Apart from the obvious appeal of the chemical conversion of a greenhouse gas to value added chemicals, the inherent challenges in the reaction have attracted the attention of several research groups across the world. Substantial progress has been made in the last few years and several molecular and material catalysts have been developed for this purpose and several of these show considerable reactivity.^{1–14}

Reduction of CO₂ selectively to any of the several possible products poses a challenge. The 2e[−]/2H⁺ reduction of CO₂ can produce either HCOOH or CO and competes with the reduction of protons to form H₂.^{15–20} Several groups have contributed to the current understanding of the mechanism of the reactions involved.^{8,21–26} The reduced metal centre binds either CO₂ or H⁺ to produce M–CO₂ or M–H species (Scheme 1). The M–H species can be further protonated to generate H₂ or it can transfer the H[−] to CO₂ to generate formate. The M–CO₂ species on the other hand generates a M–COOH species upon protonation and then can undergo either a M–C bond cleavage to generate formate or a C–O bond cleavage to generate CO. These species have been observed

chemically as well as by using spectro-electrochemistry and characterized.^{6,20,27}

Selectivity in 2e[−]/2H⁺ reduction has been demonstrated by several groups and it has been proposed that the electronic structure of the M–COOH species plays a vital role in the process.²⁶ When the M–C bond is very covalent, the protonation of the OH-group is favored resulting in C–O bond cleavage and release of CO, while in cases where the M–C bond is not very covalent, the M–C bond cleaves generating HCOOH. The covalency of the M–C bond can be tuned by the choice of the metal as well as the spin states. Using a ligand that has a protonation site has provided relief from the competing HER.^{20,28,29}

In addition to the design of the ligand and the choice of metal controlling the electronic structure of the catalyst, selectivity can also be accessed by kinetic control. For example, at lower concentrations of protons (as well as by using weaker proton sources), the HER is naturally suppressed. In a curious case, the product distribution of 2e[−]/2H⁺ CO₂ reduction by Pd/C was demonstrated to depend on the isotope of the proton source used. *In situ* X-ray characterization verifies the formation of Pd–H species. Substituting H₂O with D₂O reduces the rate of the competing hydrogen evolution reaction (HER) due to lower D⁺ concentration and enhances the carbon dioxide reduction reaction (CO₂RR), leading to a shift from 48% CO in H₂O to 76% CO in D₂O.³⁰ Clearly, the kinetic isotope effect (KIE) involved in the reduction of CO₂ was different from the KIE



Scheme 1 Selectivity for 2e[−]/2H⁺ reduction of CO₂ via the M–COOH pathway.

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† Electronic supplementary information (ESI) available: experimental details, control electrochemical experiments and structural data. CCDC 2208720 and 2310122. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3cc06336d>

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involved in the reduction of H^+ leading to different selectivities in H_2O and D_2O . Similar changes in product distribution were observed during CO_2 reduction by cobalt phthalocyanine immobilized on a coordinating polymer support.³¹ A significant kinetic isotope effect (KIE) was reported for the decomposition of HCOOH to form CO_2 and H_2 by an Ir/Ru complex.³² Another study of isotope-controlled selectivity by quantum tunneling results in different chemical reactivity of cyclopropylmethylcarbene.³³ While isotope effects have been reported in the kinetics of electrochemical CO_2 reduction using molecular catalysts, changes in selectivity have not been reported and whether such changes in selectivity can be obtained in a molecular catalyst under homogeneous conditions are yet to be evaluated.

In this manuscript, we report the synthesis of a novel binuclear Ni catalyst, $[(\text{Py}2\text{ald})_2\text{Ni}_2](\text{BPh}_4)_2$ (**1**(BPh_4)₂), and explores its application in CO_2 reduction by using water as the proton source. The ligand, HPy2ald (3-[[Bis(2-pyridinylmethyl)amino]methyl]-2-hydroxybenzaldehyde), was synthesized following literature report.³⁴ The catalyst shows no selectivity for either CO or HCOOH and exhibits a competing HER in H_2O . However, in D_2O the catalyst exhibits 65% selectivity for HCOOH . *In situ* spectro-electrochemical FTIR provides insight into the mechanism of CO_2 reduction.

Cyclic voltammetry (CV) measurements conducted with 0.5 mM **1**(BPh_4)₂ in N_2 saturated acetonitrile solution unveiled two closely positioned peaks at -1.82 V and -2.05 V vs. Fc^+/Fc^0 , respectively (Fig. 1A and inset). To identify the associated reduction process, CV was conducted using the free ligand HPy2ald under identical conditions. It was observed that the peak at -2.05 V vs. Fc^+/Fc^0 is linked to ligand reduction, potentially involving the reduction of the aldehyde group. Supporting evidence for this transformation is found in corroborating Fourier-transform infrared spectroscopy coupled with spectro-electrochemistry (FTIR-SEC) data. For **1**(BPh_4)₂, when the working electrode is held at -2.05 V vs. Fc^+/Fc^0 , the peak corresponding to the $-\text{CHO}$ group at 1633 cm^{-1} diminishes (Fig. 2A, inset), signifying its reduction, while a new peak in the $2500\text{--}2700\text{ cm}^{-1}$ range emerges, corresponding to the formation of the $-\text{CH}_2\text{OH}$ group (Fig. 2A). More importantly, the

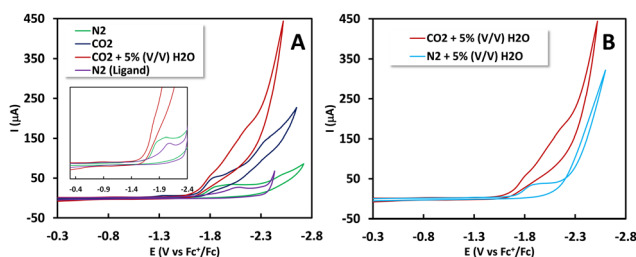


Fig. 1 Cyclic voltammetry of 0.5 mM **1**(BPh_4)₂ (green) and free ligand (purple trace) in N_2 saturated acetonitrile solution, and its catalytic nature in CO_2 saturated acetonitrile in the absence (blue trace) and presence of H_2O (red trace). The inset provides a zoomed-in view of the potential range from -0.4 to -2.4 V in an N_2 atmosphere (A). Comparison of the CV trace of the Ni-complex in CO_2 and N_2 saturated acetonitrile in the presence of 5% (V/V) H_2O shows electrocatalytic CO_2 reduction along with the HER (B). 100 mM tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte.

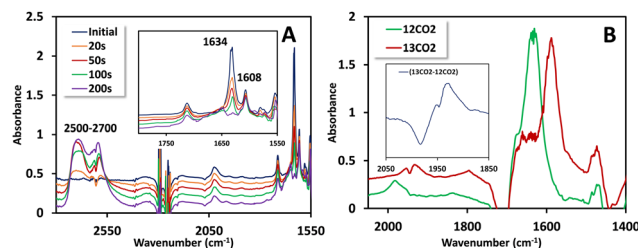


Fig. 2 FTIR-SEC spectra of **1**(BPh_4)₂ (4 mM) in N_2 saturated acetonitrile while keeping the potential at -2.05 V vs. Fc^+/Fc^0 showing conversion of $-\text{CHO}$ to $-\text{CH}_2\text{OH}$. The inset shows the zoomed-in view of the $1550\text{--}1800\text{ cm}^{-1}$ region (A); *in situ* FTIR-SEC spectra (CPE at -2.2 V vs. Fc^+/Fc^0) of the intermediates of **1**(BPh_4)₂ (4 mM) in acetonitrile using $^{12}\text{CO}_2$ (blue trace) and $^{13}\text{CO}_2$ (red trace) as substrates. The inset shows the zoomed-in difference spectra ($^{13}\text{CO}_2\text{--}^{12}\text{CO}_2$) of the $1850\text{--}2050\text{ cm}^{-1}$ region, showing a shift of 44 cm^{-1} (B). 100 mM tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte.

complete reduction of the $-\text{CHO}$ vibration indicates that both $-\text{CHO}$ groups are being reduced. The additional peak at -1.82 V vs. Fc^+/Fc^0 is associated with the $\text{Ni}(\text{II/I})$ reduction. The reduction of Ni^{II} to Ni^{I} was confirmed by FTIR-SEC under one atmosphere CO (Fig. S6, ESI[†]). Ni^{II} does not bind CO, but when FTIR-SEC at -1.85 V vs. Fc^+/Fc^0 was conducted, a clear $\text{Ni}^{\text{I}}\text{--CO}$ vibration at 1980 cm^{-1} was observed. Similar carbonyl species were previously reported in a binuclear cobalt complex bridged by pyrazole.¹¹

In the presence of saturated CO_2 and 5% (V/V) H_2O , a strong reduction current is observed at -2.2 V vs. Fc^+/Fc^0 with a pre-catalytic feature at -1.65 V vs. Fc^+/Fc^0 which indicates CO_2 binding to the reduced Ni^{I} (Fig. 1A). The electrocatalytic current at -2.2 V vs. Fc^+/Fc^0 is not observed in the absence of CO_2 and represents electrocatalytic CO_2 reduction (Fig. 1B). These observations lead to the conclusion that the species responsible for CO_2 binding is $\text{Ni}(\text{I})$ but the electrocatalysis proceeds after further reduction of $\text{Ni}^{\text{III}}\text{--CO}_2^-/\text{Ni}^{\text{III}}\text{--COOH}$ (represented as $\text{Ni}^{\text{III}}\text{--COO}^*$). In the presence of 5% (V/V) H_2O in an N_2 atmosphere, a catalytic current is observed with an onset at -2.3 V vs. Fc^+/Fc^0 , indicating the occurrence of the hydrogen evolution reaction (HER). The absorption spectra of **1**(BPh_4)₂ before and after CPE show an 18% reduction of the bridging phenolate to Ni charge transfer, not present in a monomer (Fig. S11 and S12, ESI[†]) after 30 minutes.

To delve into the reaction mechanism and identify the intermediates involved, FTIR-SEC was carried out in a CO_2 -saturated acetonitrile solution in an OTTE cell. While keeping the working electrode at -2.2 V vs. Fc^+/Fc^0 , the FTIR-SEC results unveiled the presence of two isotope-sensitive vibrations associated with $^{13}\text{CO}_2$ (Fig. 2B). A peak observed at 1633 cm^{-1} , which corresponds to a $\text{Ni}^{\text{I}}\text{--COO}^*$ intermediate, shifted to 1588 cm^{-1} when a heavier isotope of CO_2 ($^{13}\text{CO}_2$) was used. Another peak at 1980 cm^{-1} was also observed, corresponding to the $\text{Ni}^{\text{I}}\text{--CO}$ species previously observed, which is a likely precursor to the carbon monoxide gas detected during the gas analysis. This peak shifted to 1936 cm^{-1} when $^{13}\text{CO}_2$ was used (Fig. 2B, inset). Based on these observations, a plausible mechanism is proposed (Scheme 2). Further evidence for the mechanism is marshalled from kinetic isotope effects discussed later.

Figure 1 consists of four panels (A, B, C, D) illustrating the gas chromatography and calibration for the detection of H_2 , O_2 , N_2 , and CO .

Panel A: Calibration curves showing Charge (C) versus Time (Sec) for $^{12}CO_2-H_2O$ (red line) and $^{12}CO_2-D_2O$ (blue line). The curves are linear, indicating a proportional relationship between charge and time.

Panel B: Gas chromatograms showing Intensity versus Retention time (min) for H_2 , O_2 , N_2 , and CO . The chromatograms show peaks for $^{12}CO_2-H_2O$ (red line) and $^{12}CO_2-D_2O$ (blue line) corresponding to the detected gases.

Panel C: Gas chromatograms showing $\mu S/cm$ versus Retention time (min) for H_2O and D_2O . The chromatograms show peaks for $^{12}CO_2-D_2O$ (blue line) and $^{12}CO_2-H_2O$ (red line) corresponding to the detected water isotopes.

Panel D: Relative concentration of H_2 (red), CO (green), and $HCOOH$ (yellow) for H_2O and D_2O . The concentration is expressed as a percentage (0% to 100%).

The results indicate that H₂ evolution and CO production are inhibited in the presence of D₂O relative to H₂O, while HCOOH production is accelerated. Since these reactions are competitive, the absolute currents being consumed cannot be used to derive a H/D KIE for the individual reactions. However, a relative KIE (KIE* in Scheme 2) (Table 1) can be obtained relative to the HCOOH formation reaction. The reduction of CO₂ to CO exhibits a relative KIE of 3.3, while the H₂ evolution shows a relative KIE of 3.5 relative to any implicit KIE HCOOH may have. Formation of CO requires two protons and it is likely that the second protonation step (protonation of the M-COOH species) is the rds, as suggested by its accumulation during catalysis, resulting in a H/D KIE. The relative KIE observed here is similar to the KIE observed in CO₂ reduction to CO by



Table 1 Relative KIEs calculated for the three processes

Charge consumed	H ₂ O		D ₂ O		Relative KIE (H/D)
	10.2		8.3		
Products	Faradaic yield (%)	Charge (C)	Faradaic yield (%)	Charge (C)	
H ₂	32	3.26	16	1.33	3.5
CO	23	2.35	12	1.00	3.3
HCOOH	36	3.67	63	5.23	1

Co-thiolate complexes where the protonation of the –OH end of a M–COOH species is determined to be the rds.¹⁷ Similarly, the formation of H₂ involves two protonation steps and the second protonation (*i.e.* protonation of M–H) is likely the rds that earns the H/D KIE. A similar KIE was recorded for H₂ evolution by Ni complexes where the protonation of the Ni–H species was the rds.³⁸

The formic acid produced can be formed either *via* Ni–H attack on CO₂ or *via* C-protonation of the Ni–COOH intermediate. The H/D KIE reported for the hydride pathway is substantial (5–10)³⁷ because of the shift of the hydride from the metal to the CO₂ in the TS. The fact that the HCOOH increase in D₂O contradicts this possibility in the case of 1(BPh₄)₂. Rather, the hydrolysis of Ni–COOH *via* C-protonation seems to be the most logical pathway.

In summary, differential H/D KIEs associated with the two competing 2e[−]/2H⁺ CO₂ reduction pathways and that of the HER allow obtaining ~65% selectivity in HCOOH formation. This is the first example where selectivity in CO₂ reduction taking advantage of KIEs could be demonstrated in a molecular system.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

A. D. acknowledges SERB research grant no. CRG/2021/00154 and DST/TMD(EWO)/IC5-2018/03(G). A. M. acknowledges CRG/2022/001931 for funding. S. P., S. A., and S. G. acknowledge the CSIR for senior research fellowship.

Conflicts of interest

There are no conflicts to declare.

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