Supporting Information

Kinetic Isotope Effect Offers Selectivity in CO₂ Reduction

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Experimental Details

Materials: All reagents used for synthesis were of the highest grade commercially available. The reagents used for electrochemical purpose like tetrabutylammonium perchlorate (TBAP) and ferrocene (Fc) were purchased from Sigma-Aldrich. Acetonitrile (CH₃CN) was purchased from FINAR, Ltd. CH₃CN was dried over CaCl₂ and CaH₂. Ultrahigh purity N2 and CO2 cylinders were purchased from Indian Refrigeration Stores (IRS). Standard mixture gas cylinder having four components 20% H₂, 20% CO, 20% CH₄, purchased from Indian Refrigeration Systems.

Caution! Perchlorate salts are potentially explosive and need to be handled with utmost care. In the present work, the perchlorate salts were used only in small quantities inside an inert atmosphere glove box while following the essential safety protocols, and no issues were encountered.

Instrumental details: All electrochemical experiments were performed using CH instruments (CH 700E electrochemical analyser). Glassy carbon, platinum, and standard double-junction Ag/AgCl reference electrode were purchased from Pine Instruments. During controlled potential electrolysis Agilent GC instrument (model no. 7890B (G3440B), serial no. CN14333203) fitted with a TCD was used to analyse head-space gas mixture. Unit cell determination of single crystals were performed by using a Bruker D8 VENTURE Microfocus diffractometer equipped with PHOTON II Detector, with Mo Kα radiation (λ = 0.71073 Å), controlled by the APEX3 (v2017.3–0) software package. Absorption spectra were recorded in a cuvette of 1 cm path length. Absorption spectra were obtained by a UV-Vis diode array spectrophotometer (Agilent 8453). The FTIR data were measured on a Perkin Elmer Spectrum II instrument. The CaF₂ windows for FTIR spectroscopy were purchased from Sigma-Aldrich. For spectro-electrochemical measurements coupled with IR spectroscopy, the optically transparent thin-layer electrochemical (OTTLE) cell was used which was purchased from the University of Reading.

Preparation of Compounds. All reactions and associated manipulations were carried out either inside an inert atmosphere glovebox or by using standard Schlenk techniques unless specifically mentioned. Solvents were dried following standard procedures. The ligand, Hpy2ald (3-{[Bis(2-pyridinylmethyl)amino]methyl}-2-

hydroxybenzaldehyde), was synthesized following literature report. Ni(ClO₄)₂·6H₂O, NaBPh₄ and Et₃N were obtained from commercial sources and used without further purification. Filtrations were performed through Celite and solvent removal steps were carried out in vacuo inside an inert atmosphere glovebox.

[(Py2ald)₂Ni₂](BPh₄)₂ (1(BPh₄)₂). To a solution of 34.7 mg (0.1 mmol) of HPy2ald in 2 mL of MeOH was added 12.1 mg (0.12 mmol) of Et₃N followed by the addition of 36.6 mg of Ni(ClO₄)₂·6H₂O (0.1 mmol) and the reaction mixture was stirred for 1 hour. 51.3 mg of NaBPh₄ (0.15 mmol) in 2 mL of MeOH was added into the reaction mixture which resulted into the precipitation of a green solid, the reaction mixture was allowed to stir for 3 h followed by filtration. The green solid was collected, dissolved in 5 mL of CH₂Cl₂ and the resulting solution was filtered through Celite. The filtrate was evaporated to dryness and the green solid thus obtained was washed twice with 2 mL of Et₂O and dried under vacuum. The green solid was then dissolved in a mixture of DMF and MeCN and the resulting solution was filtered through Celite. Et₂O was allowed to diffuse into the filtrate at 0°C for overnight to obtain the product as green, needle-shaped, crystals (53.7 mg, 74%). The compound was identified by a singlecrystal X-ray structure determination. Anal. Calcd for C₉₀H₈₀N₆Ni₂O₄B₂·CH₂Cl₂·MeCN·0.5DMF [1(BPh₄)₂·CH₂Cl₂·MeCN·0.5DMF]: C. 70.45; H, 5.54; N, 6.52. Found: C, 70.18; H, 5.20; N, 6.79. Solution magnetic moment (μ_{eff}) = 2.66 BM (The anticipated spin-only magnetic moment for two unpaired electrons is 2.83 BM, as the other two electrons may exhibit spin pairing due to antiferromagnetic coupling). ESI-MS in MeCN: Obsd (calcd) for [(Py2ald)₂Ni₂]²⁺: m/z 404.0980 (404.0982) (Figure S1). Paramagnetic ¹H NMR is shown in Figure S2.

N,N-Bis(2-pyridylmethyl)-N-(2-hydroxybenzyl)amine H(L1) is prepared using published method.

[Ni(L)(H₂O)₂](CIO₄) 2(CIO₄). To a solution of 30.5 mg (0.1 mmol) of H(L1) in 2 mL of MeOH was added 12.1 mg (0.12 mmol) of Et₃N followed by the addition of 36.6 mg of Ni(CIO₄)₂·6H₂O (0.1 mmol) and the reaction mixture was stirred overnight. The resulting solution was filtered through Celite. Et₂O was allowed to diffuse into the filtrate at 0°C for overnight to obtain the product as blue, needle-shaped, crystals (27.9 mg, 56%). The compound was identified by a single-crystal X-ray structure

determination. Anal. Calcd for C₁₉H₂₂N₃NiO₇Cl·H₂O [**2**(ClO₄)·H₂O]: C, 44.18; H, 4.68; N, 8.13. Found: C, 44.53; H, 4.33; N, 8.02. Solution magnetic moment (μ_{eff}) = 2.54 BM (The anticipated spin-only magnetic moment for two unpaired electrons is 2.83 BM). ESI-MS in MeCN: Obsd (calcd) for [Ni(L1)]⁺: m/z 362.0803 (362.0804) (Figure S3). Paramagnetic ¹H NMR is shown in Figure S4.

Cyclic Voltammetry:

All the CV measurements were done using a glassy carbon working electrode, platinum as a counter electrode and non-aqueous Ag/AgCl as the reference electrode for homogeneous electrochemistry. All the experiments were performed in a sealed four neck two compartment electrochemical cell. For the CV data collection, 4 ml 0.5 mM of the catalyst solution in CH₃CN was taken inside a sealed electrochemical cell along with TBAP as the supporting electrolyte. Ferrocene was used as an internal standard and the potentials were corrected with respect to Fc^+/Fc^0 potential. The solution was purged by bubbling N₂ or CO₂ gas before recording the CV as required. Milli-Q water was used as proton source during the electrocatalytic experiments.

Controlled Potential Electrolysis (CPE) and Product Analysis:

10 ml of 0.5 mM catalyst solution in CH₃CN with 5%(V/V) H₂O was purged with CO₂ for 1 hour until the solution gets saturated, the CPE experiments were performed on a CHI 700E potentiostat for 2 hrs using the glassy carbon plate (surface area = 2 cm²) as a working electrode, large Pt wire counter electrode attached with a glass fret containing tetrabutyl-ammonium perchlorate in CH₃CN solution and non-aqueous Ag-AgCl reference electrode, at a constant potential where the peak maxima of the catalysis were observed.

The gaseous products evolved were collected into the burette by vertical displacement of water. The volume of water displaced during the experiment is the amount of gas evolved during the experiment. The gas was collected from the headspace for the analysis using an Agilent GC instrument (model no. 7890B) fitted with thermal conductivity detector (TCD, G3440B). Additionally, these CPE experiments along with the GC analysis were conducted for several times to confirm the reproducibility of the reduced products formation.

Detailed calculation of faradic yield:

For CO₂ saturated solution of Ni-Complex in presence of 5% (V/V) H₂O,

CPE of 0.5 mM 10 mL Ni-Complex at -2.2 V vs Fc^+/Fc^0 in CO₂ saturated acetonitrile solution using H₂O as the proton source (5% (V/V) H₂O) showed the formation of CO and H₂ in GC-TCD chromatogram and HCOOH in Ion chromatography after consumption of 10.2 C charge. The volume of (H₂+CO) measured by water replacement in an inverted burette is 0.65 ml. From the GC-TCD chromatogram, the amount of CO is found to be 42% of the total volume and the rest is H₂. Formate was measured, when the solution, after electrolysis, was extracted with 5 ml water and subsequently analysed by Ion Chromatography.

Amount of HCOOH = $168 \text{ mg/L} = 1.87^{*}10^{-5} \text{ mol}$

FY of HCOOH = (2 × 1.87 × 10⁻⁵ × 96500) / 10.2 = 36%

Total volume of $(CO+H_2)$ in the headspace of inverted burette is = 0.65 ml

Amount of CO = 0.65 * 0.42 / 22400 = 1.2 × 10⁻⁵ mol

FY of CO = (2 × 1.2 × 10⁻⁵ × 96500) / 10.2 = 23%

Amount of $H_2 = 0.65 * 0.58 / 22400 = 1.68 \times 10^{-5}$ mol

FY of $H_2 = (2 \times 1.68 \times 10^{-5} \times 96500) / 10.2 = 32\%$

For CO₂ saturated solution of Ni-Complex in presence of 5% (V/V) D₂O,

CPE of 0.5 mM 10 mL Ni-Complex at -2.2 V vs Fc^+/Fc^0 in CO₂ saturated acetonitrile solution using D₂O as the proton source (5% (V/V) D₂O) showed the formation of CO and D₂ in GC-TCD chromatogram and DCOOD in Ion chromatography after consumption of 8.3 C charge. The volume of (D₂+CO) measured by water replacement in an inverted burette is 0.28 ml. From the GC-TCD chromatogram, the amount of CO is found to be 44% of the total volume and the rest is D₂. Formate was measured, when the solution, after electrolysis, was extracted with 5 ml water and subsequently analysed by Ion Chromatography.

Amount of DCOOD = 240 mg/L = 2.6×10^{-5} mol FY of DCOOD = $(2 \times 2.6 \times 10^{-5} \times 96500) / 8.3 = 63\%$ Total volume of (CO+D₂) in the headspace of inverted burette is = 0.28 ml Amount of CO = $0.28 \times 0.44 / 22400 = 5.5 \times 10^{-6}$ mol FY of CO = $(2 \times 5.5 \times 10^{-6} \times 96500) / 8.3 = 12\%$ Amount of D₂ = $0.28 \times 0.56 / 22400 = 7 \times 10^{-6}$ mol FY of D₂ = $(2 \times 7 \times 10^{-6} \times 96500) / 8.3 = 16\%$ **FTIR-SEC data Collection:** 1 ml 4 mM of catalyst solution was prepared in CH₃CN and purged with N₂/CO₂ . 400 μ I 4 mM of the sample with the addition of 5(V/V) % H₂O was injected into the OTTLE cell. Spectro-electrochemistry was performed using the OTTLE cell connected with the potentiostat (CHI 700E). The sample solution also contained 100 mM TBAP as the supporting electrolyte. A Pt-mesh working electrode, a Pt counter electrode and a Ag-wire was used as the reference electrode. The potential of the reference electrode was calibrated using ferrocene as an internal standard in the same solvent.

FTIR Results:

FTIR of the Hpy2ald The solid-state spectra ligand (3-{[Bis(2pyridinylmethyl)amino]methyl}-2-hydroxybenzaldehyde)³² reveals the presence of two distinct vibrations associated with the C=N bond of the pyridine group and the formyl group attached to the phenyl group. These vibrations are observed at 1654 cm⁻¹ and 1680 cm⁻¹, respectively. Metalation with Ni(ClO₄)₂·H₂O leads to the formation of a dimeric complex bonded through two phenolate bridges. In the solid-state FTIR spectra of the resulting metal complex, both previously mentioned vibrations exhibit a significant redshift, now appearing at 1608 cm⁻¹ for the C=N bond and 1634 cm⁻¹ for the -CHO group (Figure S7A). This shift is indicative of the coordination of both the pyridine and formyl groups to the Ni metal center. To further investigate the stability of the metal complex in acetonitrile solution, which is crucial for subsequent electrochemical studies, FTIR analysis in the solution phase was conducted. Remarkably, the complex displayed precisely the same vibrational frequencies observed in the solid phase (Figure S7B). This observation strongly supports the presence of the dimeric structure in the solution phase. The consistency in vibrational frequencies between the solid and solution phases is crucial evidence, as the monomerization of the complex in solution would lead to an increase in the vibrational frequency of the formyl group. In a monomeric unit, the formyl group would no longer be coordinated to the Ni metal center, resulting in a similar vibration to that observed for the ligand alone. However, this is not the case, as the complex maintains its characteristic vibrational pattern, confirming the persistence of the dimeric structure in the solution phase.

Additional Supporting data:

Reaction Scheme:



Figure S1. Mass spectrum of $[(Py2ald)_2Ni_2](BPh_4)_2(1(BPh_4)_2)$ in MeCN shows the presence of $[(Py2ald)_2Ni_2]^{2+}$ at m/z = 404.0982 (simulated, red line); 404.0980 (obtained, green line).



Figure S2. ¹H NMR (300 MHz, DMSO,δ ppm): δ 51.39, 46.92, 43.30, 38.81, 37.22, 25.57, 23.56, 22.57, 13.19, 12.67, 12.22, 7.15, 6.89, 6.76, 3.40, 2.48, 1.06.



Figure S3. Mass spectrum of **2**(ClO₄) in MeCN shows the presence of [Ni(L1)]⁺at m/z = 362.0804 (simulated, purple line); 362.0803 (obtained, green line).



Figure S4. ¹H NMR (400 MHz, DMSO, δ ppm) δ 43.05, 42.34, 21.65, 12.57, 9.86, 4.33, 2.07, 2.05, 1.22, 1.11, 1.09, 1.07, 1.04, 1.02, 0.83, -5.03, -5.04.

Table S1. X-ray crystallographic data for $[(Py2ald)_2Ni_2](BPh_4)_2$ (1(BPh_4)_2), and $[Ni(L)(H_2O)_2](ClO_4)$ (2(ClO_4)).^a

Compound	1 (BPh ₄) ₂	2 (ClO ₄)
CCDC number	2208720	2310122
temp (K)	145(2)	150(2)
formula	C90H80B2N6Ni2O4	C ₁₉ H ₂₂ CIN ₃ NiO ₇
formula weight	1448.64	498.55
Crystal system	monoclinic	monoclinic
space group	C2/c	P21/c
a, Å	32.431(2)	9.1074(7)
b, Å	24.9205(17)	16.5750(12)
c, Å	24.931(3	14.4535(11)
α, deg	90	90
β, deg	123.2990(10)	107.064(2)

γ, deg	90	90
V, Å ³	16841(3)	2085.8(3)
Z	8	4
ρ _{calcd} , gm/cm ³	1.143	1.588
μ, mm ⁻¹	0.498	1.106
θ range, deg	2.220-25.058	2.643-25.724
completeness to θ , %	99.4	98.7
reflections collected	79376	22085
independent reflections	14855	3916
R(int)	0.0632	0.0462
Restraints ^b	3	0
parameters	943	282
Max., min. transmission	0.7452, 0.6131	0.7453, 0.5370
R1 ^c (wR2) ^d [I>2sigma(I)]	0.0344 (0.0796)	0.0331 (0.0837)
R1 ^c (wR2) ^c	0.0475 (0.0859)	0.0361 (0.0854)
GOF(F2) ^e	1.034	1.062
max, min peaks, e.Å ⁻³	0.333, -0.287	0.584, -0.554

^aMo K α radiation ($\lambda = 0.71073$ Å). ^b1(BPh₄)₂, disordered methyl group of the ligand. ^cR1 = Σ ||Fo|-|Fc||/ Σ |Fo|. ^dwR2 = { Σ [w(Fo2-Fc2)2]/ Σ [w(Fo2)2]}^{1/2}. ^eGOF = { Σ [w(Fo2-Fc2)₂]/(n-p)}^{1/2}, where n is the number of data and p is the number of refined parameters.



Figure S5. Molecular structures of $1(BPh_4)_2$ and $2(CIO_4)$ with 30% probability thermal ellipsoids and partial atom labelling schemes (hydrogen atoms are omitted except for H2O).



Figure S6. FTIR spectra of $1(BPh_4)_2$ in CO saturated acetonitrile while holding the potential at -1.85 V vs Fc⁺/Fc⁰ shows Ni^I-CO (blue spectra); FTIR spectra in CO₂ saturated acetonitrile shows the feature, when holding the potential at -2.2V, showing the formation of Ni^I-CO by CO₂ reduction.



Figure S7: FTIR spectra of ligand HPy₂ald (red trace) and 1(BPh₄)₂ (blue trace) shows the shift of -CHO vibration due to coordination with metal (A); FTIR spectra of 1(BPh₄)₂ in solid phase (blue trace) and in solution phase (MeCN) (green trace) shows the stability of the dimeric form in acetonitrile. (B).



Figure S8. The GC-TCD data of headspace gas after CPE performed under CO₂ saturated acetonitrile solution with 5% (V/V) H₂O for $1(BPh_4)_2$ (red trace); Mixture gas (green trace) along with the blank GCE (grey trace).



Figure S9. Ion-chromatography data after CPE performed under CO₂ saturated acetonitrile solution with 5% (V/V) H₂O for **1**(BPh₄)₂ (red trace); Standard formate (50 ppm) (green trace) along with the blank GCE (grey trace).



Figure S10. Rinse test after electrolysis at -2.2 vs Fc⁺/Fc does not show current similar to **1**(BPh₄)₂, showing no formation of Nickel nano particles.



Figure S11. In acetonitrile solvent, both the dimer (**1**(BPh₄)₂) and monomer (**2**(ClO₄)) exhibit distinct UV characteristics. The dimer displays a prominent peak at 395 nm, indicative of phenolate bridged Ni-centre, whereas the monomer does not exhibit such feature.



Figure S12. UV-vis spectra of $1(BPh_4)_2$) before and after electrolysis for 30 mins at - 2.2 V vs Fc⁺/Fc showing 18% catalyst degradation.