Durable Solar-Powered Systems with Ni-Catalysts for Conversion of CO2 or CO to CH4

Hunter Shirley, Xiaojun Su, Harshin Sanjanwala, Kallol Talukdar, Jonah W. Jurss,* and Jared H. Delcamp* * 

Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States

Supporting Information

ABSTRACT: Photocatalytic conversion of CO2 to reduced carbon states using sunlight and an earth-abundant catalyst could provide a critically needed source of renewable energy. Very few earth-abundant catalysts have shown CO2 to CH4 reactivity, and significant opportunities exist to improve catalyst durability. Through the strategic design of a novel, redox-active bipyridyl-N-heterocyclic carbene macrocyclic ligand complexed with nickel, CO2 is converted into the energy-rich solar fuel, CH4, photocatalytically with a photosensitizer in the presence of water. Up to 19,000 turnovers of CH4 from CO2 are observed. An exceptional turnover number of 570,000 for CH4 production via a photodriven formal hydrogenation of CO to CH4 was also found. This unique reactivity from a tunable, highly durable macrocyclic framework was studied via a series of photocatalytic and electrocatalytic reactions varying the atmospheric composition, as well as by isotopic labeling experiments and quantum yield calculations to evaluate the effect of ligand structure on product generation.

INTRODUCTION

Solar fuel research has gained substantial attention given the abundance of solar energy that hits the Earth’s surface.1-4 In this context, light-driven CO2 reduction has shown increasing promise toward producing both fuel precursors, such as CO for use in Fischer–Tropsch chemistry, and viable fuels such as methanol and methane.5,6 The conversion of solar energy into chemical energy is appealing because it can provide long-term energy storage in a convenient form that is compatible with existing infrastructure. Catalysts driving this process should ideally be based on inexpensive metals and operate in the presence of water to enable rapid industrial-scale use.5,6 A number of earth-abundant metal complexes have been reported that are capable of catalyzing CO2 reduction to CO or HCO2- through visible light-driven reactions.6-17 Very recently, molecular transition metal catalysts capable of producing methane from carbon dioxide and visible light have emerged; however, reports of this reaction are rare.12,18 Even more rare is the light-driven catalytic reduction of carbon dioxide to methane in the presence of solvent quantities of water.12 In fact, the vast majority of molecular photocatalytic systems for CO2 reduction utilize anhydrous solvents such as acetonitrile or N,N-dimethylformamide.19 In general, improvements to the durability of photocatalytic CO2 reduction systems are greatly needed. Thus, a robust, earth-abundant metal catalyst using sunlight to reduce CO2 to methane in water is critically needed and could provide a key component in solar-to-fuel renewable energy systems.

Tetraaza (N4) macrocycles supporting earth-abundant transition metals have produced some of the highest turnover numbers in CO2 reduction catalysis.20 Additionally, electron-rich N-heterocyclic carbenes (NHCs) have engendered more robust CO2 reduction catalysts in recent examples because they provide strong metal–ligand bonding interactions.16,19,21-27 Combining these two stabilizing features into a single complex is highly desirable, and Jurss and coworkers have recently shown the electrocatalytic reduction of CO2 to CO with two NHC-ligated macrocyclic nickel complexes.23 In this work, the two nickel bipyridyl-NHC macrocyclic complexes (2-Ni and 3-Ni) and a nonmacrocyclic Ni bipyridyl-NHC analogue (1-Ni)23 are evaluated as part of a photocatalytic system with the strongly reducing photosensitizer (PS) Ir(ppy)3 (Figure 1).28 We note that, while...
the Ir(ppy)$_3$ PS does employ a precious metal, it provides a reasonably well-understood photosensitizer to probe the behavior of the earth-abundant nickel catalysts in a model system. Macrocyclic complexes 2-Ni with reduced ligand planarity and 3-Ni with increased ligand planarity are compared to understand the effects of small changes in ligand geometry on catalytic reactivity (Figure S1). 1-Ni is compared with 2-Ni and 3-Ni to probe the effect of macrocyclization on catalysis.

## RESULTS AND DISCUSSION

The photocatalytic reduction of CO$_2$ with 1-Ni, 2-Ni, and 3-Ni was first evaluated under a pure CO$_2$ atmosphere in MeCN with the presence of Ir(ppy)$_3$. Ir(ppy)$_3$ was selected as the PS due to a strong reduction potential ($-2.61$ V vs Fc$/^+$/0) in MeCN. Sacrificial electron donors, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[de]-imidazole (BIH), and triethylamine (TEA), were used, with TEA serving a second role in deprotonating the BIH radical cation generated upon electron transfer to the PS to promote an irreversible electron-transfer event. Initially, 1-Ni, 2-Ni, and 3-Ni were reacted under anhydrous conditions at 2 nM concentration with CO, H$_2$, and CH$_4$ observed (Table 1, entries 1, 4, and 7). Interestingly, 1-Ni gave 108 000 turnovers of CO and 4 000 TON of CH$_4$ (Table 1, entry 1). These CO$_2$ reduction products were accompanied by 278 000 TON of H$_2$. Given that the conditions are anhydrous, the protons for H$_2$ generation likely originate from either BIH or TEA, both of which are acidic after electron transfer. Macrocycle 2-Ni shows a higher selectivity for CO$_2$ reduction products (90% versus 29% carbon-selective (CS) reduction, Table 1, entries 1 and 4) with 310 000 TON of CO versus 33 000 TON of H$_2$. Likewise, 3-Ni gives a similar CS percentage to 2-Ni (82%), albeit at a significantly lower reactivity (76 000 TON of CO, 17 000 TON of H$_2$, Table 1, entry 7). Both macrocyclic structures show high selectivity for CO$_2$ reduction over proton reduction under these conditions with a higher reactivity observed for the less-planar 2-Ni.

A current trend in recent literature has focused on lowering catalyst concentrations in photocatalytic reactions to the micromolar or nanomolar regime (see Tables S2 and S3 for higher-concentration studies). These efforts typically allow for tremendous gains in TON (TON = moles of product/moles of catalyst) values by several orders of magnitude. Low concentration studies are useful for probing the limits of catalyst turnovers and for gaining insight into how a catalyst will perform in an environment where catalytic sites are isolated from one another. For 2-Ni between 0.1 mM to 2 nM, TON values for CO and CH$_4$ were found to increase at approximately an order of magnitude per decade decrease in 2-Ni concentration, ultimately arriving at similar total amounts of product formed (Figure S7). Notably, there are two catalysts in this system (2-Ni and the PS Ir(ppy)$_3$). Introduction of an additional aliquot of Ir(ppy)$_3$ after product evolution had ceased, resulting in resumed catalytic reactivity, which indicates that the active nickel catalyst is exceptionally robust and remains active until the PS decomposes (Figure S15).

In the previous electrocatalytic study, 1-Ni, 2-Ni, and 3-Ni demonstrated increased catalytic activity for CO$_2$ reduction with the addition of 2% H$_2$O in MeCN solutions. As such, the effects of added H$_2$O were explored photocatalytically, where 1-Ni shows significantly reduced reactivity for CO$_2$ reduction in the presence of 2% water (31 000 TON versus 108 000 TON when anhydrous, Table 1, entries 1 and 2). Hydrogen production remained nearly the same for 1-Ni with added water, leading to a worse carbon selectivity (10% CS). Intriguingly, 2-Ni produced 19 000 TON of CH$_4$ with added water and demonstrated the highest CS% observed for a catalyst producing methane (87%, Table 1 entry 5). 3-Ni also shows a significant amount of methane production with added water, although at a lower TON than 2-Ni (Table 1, entry 8). These results suggest that the addition of water uniquely provides a reaction pathway for 2-Ni and 3-Ni to produce CH$_4$. Control experiments are reported in Tables S4–S14, where reaction components were removed systematically, CO$_2$ atmosphere concentrations were lowered, and reaction conditions were varied. In all cases, a Ni catalyst, Ir(ppy)$_3$, a sacrificial electron donor, and CO$_2$ were required for appreciable CO or CH$_4$ formation.

Reductive (eqs 2 and 3) and oxidative (eqs 4 and 5) quenching pathways are both possible. In the presence of BIH, a reductive quenching pathway for Ir(ppy)$_3$ is active (eq 2).
Removal of BIH from the reaction conditions favors an oxidative quenching path for Ir(ppy)$_3^*$ (eq 4).

$$\text{Ir(ppy)$_3^*$ + h} \nu \rightarrow \text{Ir(ppy)$_3^*$}$$  \tag{1}

$$\text{Ir(ppy)$_3^*$ + BIH \rightarrow [Ir(ppy)$_3^*$]}^- + \text{BIH}^+$$  \tag{2}

$$[\text{Ir(ppy)$_3^*$}]^- + \text{Ni cat} \rightarrow \text{Ir(ppy)$_3$} + [\text{Ni cat}]^-$$  \tag{3}

$$\text{Ir(ppy)$_3^*$ + Ni cat} \rightarrow [\text{Ir(ppy)$_3$}]^+ + [\text{Ni cat}]^-$$  \tag{4}

$$[\text{Ir(ppy)$_3^*$}]^+ + \text{TEA} \rightarrow \text{TEA}^- + \text{Ir(ppy)$_3$}$$  \tag{5}

A higher quantum yield may be possible for the reductive pathway under dilute catalyst conditions because BIH remains in high concentration. Additionally, BIH$^+$ can be irreversibly deprotonated to limit the back electron transfer from $[\text{Ir(ppy)$_3$}]^-$ to BIH$^+$. With the oxidative pathway, the quantum yield would be significantly affected by catalyst concentration.

To analyze the efficiency with which each of the active catalysts uses photons, quantum yield determining experiments were conducted at high and low concentrations for each of the three catalysts (Table S15). We note that the observed values (5–15 x 10$^{-13}$) are similar in magnitude to homogeneous bimolecular photosensitized systems and do not vary dramatically with concentration, suggesting a reductive mechanism is operative in this system.

2-Ni is studied in more detail below in the presence of H$_2$O given the rare observation of CH$_4$ production from an earth-abundant catalyst in a photocatalytic system and the high CS%.

Interestingly, while CH$_4$ production was found to rise until catalysis ceased, the amounts of CO and H$_2$ present during photolysis have more dynamic behavior (Figure 2). Initially, CO and H$_2$ are rapidly formed over the first 4 h of monitoring with very little CH$_4$ formation. Between 4 and 24 h, it is evident that as CH$_4$ is produced there is a simultaneous drop in the amounts of CO and H$_2$ that are present. As the reaction continues beyond 24 h, H$_2$ continues to be produced along with CH$_4$. No additional carbon-based reduction products except for formate, methanol, or formaldehyde were observed by $^1$H NMR or gas chromatography (Figures S12 and S13).

This observation reveals that CH$_4$ is produced while H$_2$ and CO are consumed, prompting additional studies to probe if CO is being formally hydrogenated to CH$_4$. By systematically replacing different atmospheres above the photocatalysis reaction mixture, the components needed for efficient CH$_4$ production were examined (Table 2). First, the CO$_2$ atmosphere was replaced with a 1:1 CO$_2$/H$_2$ atmosphere. This change resulted in no additional CH$_4$ production, which suggests that direct production of CH$_4$ from CO$_2$ is not limited by the rate of H$_2$ formation alone in the parent reaction (Table 2, entries 1 and 2). The lack of an overall change in CH$_4$ production suggests that CH$_4$ is being produced from CO. The change in H$_2$ over time is subtle (but reproducible) for the parent reaction (Figure 2). To probe if H$_2$ is necessary for the reduction of CO to CH$_4$, a photocatalytic reaction was run under a pure CO atmosphere (Table 2, entry 3). Again, a similar amount of CH$_4$ was observed, suggesting that the formation (or presence) of H$_2$ is also required before methane production is realized. A 1:1 CO/H$_2$ atmosphere was employed to examine if the amount of CH$_4$ produced depends on both the amount of CO and the amount of H$_2$, and a dramatic increase in CH$_4$ formation was observed at 570 000 TON for this experiment (Table 2, entry 4). The required buildup of both CO and H$_2$ in part explains the differences observed from the previously reported 1 h CO$_2$ reduction electrolyses that did not produce CH$_4$ with these complexes because larger quantities of CO and H$_2$ were accumulated during the substantially longer photolysis reaction times.

The CO/H$_2$ photocatalysis experiment gives a maximum rate observed for a 20 min time period of 500 TON s$^{-1}$. This substantial increase in CH$_4$ evolution shows that H$_2$ is necessary for reactivity when entries 3 and 4 from Table 2 are compared. Because H$_2$ could provide both the protons and electrons necessary for reduction to CH$_4$, a control reaction was performed in which the BIH and TEA were removed from the reaction. This led to no appreciable CH$_4$ formation; however, it is reasonable that BIH or TEA is necessary to access the active reduced catalyst from the initial nickel(II) species ([2-Ni]$^{2+}$). Additionally, running the reaction in the dark with all necessary components present under a 1:1 CO/H$_2$ atmosphere again gave no appreciable CH$_4$.

To confirm that CH$_4$ is being produced from CO and not by decomposition of another reaction component (such as BIH radical cation), carbon-13 labeling studies were performed under dilute conditions (Figure 3). Photoreactions with 2-Ni were run under a $^{13}$CO atmosphere and a $^{12}$CO atmosphere, and the evolved CH$_4$ was analyzed by mass spectrometry. No difference in reactivity in terms of TON was noted for the photoreaction when the TON values of CH$_4$ were compared using $^{13}$CO and $^{12}$CO, and the resulting mass spectra were conclusive for the production of CH$_4$ from CO. The carbon-13 labeled reaction produced an exclusive peak at m/z 17, and the nonlabeled reaction produced a nearly equivalent peak at m/z 16 with a very small peak at m/z 17. The slight peak at 17 is attributed to the natural abundance of the carbon-13 isotope (Figure 3, inset).

![Figure 2. Products observed over time for the photocatalytic reduction of CO$_2$ with 2-Ni at 0.1 mM. Error bars are overlaid on the data points to illustrate the reproducibility of this reaction.](image)

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### Table 2. Photocatalytic Reactions with 2-Ni under Variable Atmospheres$^{a}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Atmosphere</th>
<th>CO (TON$^b$)</th>
<th>H$_2$ (TON$^c$)</th>
<th>CH$_4$ (TON$^d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO$_2$</td>
<td>175000</td>
<td>29000</td>
<td>19000</td>
</tr>
<tr>
<td>2</td>
<td>1:1 CO$_2$/H$_2$</td>
<td>51000</td>
<td>12000</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CO</td>
<td>58000</td>
<td>10000</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1:1 CO/H$_2$</td>
<td>570000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$Reactions performed with 2 nM 2-Ni, 0.1 mM Ir(ppy)$_3$, 10 mM BIH, 5% (v/v) TEA, and 2% (v/v) H$_2$O with a solar-simulated spectrum under 1 atm of pressure at room temperature. $^{b}$TON values are reported at 72 h.
To confirm H2 is reacting with CO to form CH4, a photocatalytic reaction under 1:1 13CO/D2 was conducted, and it produced 13CD4 as the major peak observed with ∼30% relative abundance of 13CH2D2 as identified by mass spectrometry (Figure S16). The observation of 13CH2D2 is presumably due to H2 production pathways being active during catalysis (as is observed under CO2 atmospheres in Table 1), leading to accumulation of H2 in the reaction vessel. Interestingly, only 13CH2D2 and 13CD4 are observed. No appreciable accumulation of isotopically labeled methane with an odd number of hydrogens or deuteriums are observed, which suggests that, mechanistically, both atoms of H2 or D2 are incorporated during CO hydrogenation. Without the observation of specific catalytic intermediates, a catalytic cycle is largely speculative; however, these results confirm that 2-Ni is serving two roles in these photocatalytic reactions to first reduce CO2 to CO, and then to reduce CO to CH4 using H2. Thus, the conversion of CO to CH4 is a formal photodriven hydrogenation of CO to methane using H2 that occurs at 1 atm of pressure and at room temperature, which can be written as eq 6.

\[
CO + 3H_2 \rightarrow CH_4 + H_2O
\]  

This is a unique example of a CO hydrogenation reaction to CH4 powered by visible light at standard temperature and pressure. Thus, catalyst 2-Ni yields a durable system for both the CO2 to CO and CO2 to CH4 photocatalytic reactions, where anhydrous conditions favor fast CO production from CO2 with a high TON of 310 000 (215 TON s⁻¹ maximum rate for a 20 min period) observed.

The interaction of 1-Ni, 2-Ni, and 3-Ni with CO was further investigated by cyclic voltammetry (CV) with and without the presence of 2% H2O (Figure 4). Under CO, no substantial change in current is observed relative to an inert atmosphere in the absence of H2O for any of the catalysts. Interestingly, when water is added, a remarkable increase in current is observed for 2-Ni near −2.5 V vs Fc+/0. No similar increase in current is observed for 1-Ni or 3-Ni, which is consistent with the initial photocatalytic studies that show CH4 production increasing for 2-Ni in the presence of H2O and the atmosphere-dependent photocatalytic studies showing that CH4 is likely being formed from CO as an intermediate. Analogous CV studies under a CO/H2 atmosphere were conducted with 2-Ni showing the largest changes in current (Figures S1−S3). Controlled potential electrolysis at −2.67 V reveals the production of CH4 under a CO/H2 atmosphere calculated at a ∼100% Faradaic efficiency (FE) if all 6e⁻ required to reduce CO to CH4 are supplied by the electrode (see Supporting Information for additional discussion, Figures S5 and S6 and Table S1).

Notably, in the absence of H2, CH4 production was observed only in trace amounts.

Given the multielectron reduction process to reduce CO to CH4 with multiple equivalents of H2, it is not obvious if the catalysts proceed through an active homogeneous or heterogeneous catalyst. To probe the active catalyst state, a series of photocatalytic studies were undertaken, including the following: (1) 1H NMR spectra of the completed reactions showing discrete signals from a metalated complex indicating at least some portion of the catalyst material remains homogeneous (Figures S8 and S9), (2) Hg homogeneity tests showing near identical behavior when Hg and non-Hg reactions are compared (Figures S10 and S11), (3) results of PPh3 and CS2 poisoning tests (Figures S17 and S18), (4) an evaluation of induction period reproducibility (Table S16), (5) a lack of an observable precipitate or film prevalent in the reaction mixture (Figure S19), (6) Maitlis’ filtration test...
(Figure S20), and (7) and the lack of heterogeneous material as determined by a dynamic light scattering experiment (for additional discussion on all of these experiments with references to the early literature on these topics, see the Supporting Information).33–35 While no conclusive evidence of a heterogeneous active catalyst was observed in these photocatalytic studies, the possibility of a heterogeneous active catalyst cannot be ruled out.33–35 Interestingly, during controlled potential electrolysis measurements, several color changes are evident in addition to the buildup of a precipitate after 1 h of electrolysis that is concomitant with a loss in CH₄ production and a decrease in charge accumulation (Figure S5).

CONCLUSION

A series of Ni bipyridyl-NHC complexes have been evaluated in the solar-simulated photocatalytic reduction of CO₂ under various conditions. Macrocyclic 2-Ni gave the highest carbon-selective reduction percentage with CH₄ observed as one of the CO₂ reduction products in the presence of water as a cosolvent. CO and H₂ were both produced rapidly early in the photocatalytic reduction of CO₂ before being consumed as CH₄ is being produced. Importantly, experiments varying atmosphere components reveal that both CO and H₂ are needed for a large gain in CH₄ TON. Cyclic voltammetry studies show that 2-Ni uniquely shows a large current increase under CO in the presence of water and electrocatalytic CH₄ production was achieved with a 1:1 CO/H₂ atmosphere by controlled potential electrolysis. Under dilute photocatalytic reaction conditions with a 1:1 CO/H₂ atmosphere and added water, the durability of 2-Ni-based experiments is exemplary with 570 000 turnovers for CH₄ production. CH₄ was shown to be generated from CO and H₂ via carbon-13 and deuterium-labeling studies, respectively. Further, CH₄ is produced from CO and H₂ via carbon-13 and deuterium-labeling studies, respectively. Carbon-based reduction. These values are extraordinary for an CO production were observed with a high selectivity for formal hydrogenation of CO. Under dilute anhydrous conditions. Macrocyclic labeling studies, respectively. Further, CH₄ is produced from CO and H₂ via carbon-13 and deuterium-labeling studies, respectively. Carbon-based reduction. These values are extraordinary for an CO production were observed with a high selectivity for formal hydrogenation of CO. Under dilute anhydrous conditions. Macrocyclic labeling studies, respectively. Further, CH₄ is produced from CO and H₂ via carbon-13 and deuterium-labeling studies, respectively. Carbon-based reduction. These values are extraordinary for an CO production were observed with a high selectivity for formal hydrogenation of CO.