

5-16-2019

Molecular Nickel-Catalysts for Photocatalytic Reduction of CO₂

Harshin U. Sanjanwala
University of Mississippi

Follow this and additional works at: https://egrove.olemiss.edu/hon_thesis

 Part of the [Pharmacy and Pharmaceutical Sciences Commons](#)

Recommended Citation

Sanjanwala, Harshin U., "Molecular Nickel-Catalysts for Photocatalytic Reduction of CO₂" (2019). *Honors Theses*. 1217.
https://egrove.olemiss.edu/hon_thesis/1217

This Undergraduate Thesis is brought to you for free and open access by the Honors College (Sally McDonnell Barksdale Honors College) at eGrove. It has been accepted for inclusion in Honors Theses by an authorized administrator of eGrove. For more information, please contact egrove@olemiss.edu.

MOLECULAR NICKEL-CATALYSTS FOR PHOTOCATALYTIC REDUCTION OF
CO₂

by
Harshin Umesh Sanjanwala

A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of
the requirements of the Sally McDonnell Barksdale Honors College

Oxford
May 2019

Approved by:

Advisor: Dr. Jared Delcamp

Reader: Dr. Susan Pedigo

Reader: Dr. Jonah Jurss

© 2019
Harshin Umesh Sanjanwala
ALL RIGHTS RESERVED

ACKNOWLEDGEMENTS

I would like to thank Dr. Jared Delcamp for allowing me to join his incredible research group and for his consistent guidance during research. I would like to also give thanks to my outstanding mentor, Hunter Shirley, who has demonstrated a vast amount of patience and encouragement both inside and outside of the lab. I also would like to thank my fellow research friends in the Delcamp Group for creating such a joyful research environment. I would finally like to thank the National Science Foundation (Award Number: 1539035), the University of Mississippi, and the UM Sally McDonnell Barksdale Honors College for their support and funding.

ABSTRACT

HARSHIN UMESH SANJANWALA: Molecular Ni-Catalysts for Photocatalytic Reduction of CO₂
(Under the direction of Dr. Jared Delcamp)

Increased atmospheric CO₂ has been the result of prominent usage of fossil fuels as a fuel source. As fossil fuels are a nonrenewable energy source, scientists are looking towards more renewable energy resources capable of both efficiently producing energy and reducing atmospheric CO₂-emissions. A photocatalyst with an earth-abundant metal capable of chemically reducing CO₂ paired with only water and photon inputs would provide a solution to these pressing issues. Here, studies were performed on three catalysts, each with a nickel metal center. Each catalyst went through a series of photocatalytic tests in various conditions to identify whether a catalyst was capable of producing a viable carbon-based fuel or fuel precursor.

The three catalysts selected were found to have electrochemical activity in previous studies. When each catalyst went through photocatalytic testing, however, one catalyst was capable of producing a large amount of CH₄ with water, a light source, a photosensitizer, and a sacrificial electron donor. This catalyst, labeled as 2-Ni in this manuscript, underwent further studies to determine that the reaction involved in producing methane involved a reaction between CO and H₂ with the 2-Ni catalyst. While all three catalysts showed carbon-based fuel production in varying amounts, the 2-Ni catalyst was capable of producing a relatively impressive TON of CH₄ while also having a high carbon selective reduction percentage.

TABLE OF CONTENTS

I. INTRODUCTION.....	06
II. PHOTOCATALYSIS RESULTS.....	11
1-Ni CATALYST.....	14
2-Ni CATALYST.....	15
3-Ni CATALYST.....	17
III. CONCLUSION.....	18
IV. REFERENCES.....	19
V. SUPPLEMENTAL INFORMATION.....	26

LIST OF FIGURES

Figure 1: Turnover number equation for a catalyst.....	07
Figure 2: Example structure of an N-heterocyclic carbene (NHC).....	08
Figure 3: Structures of 1-Ni, 2-Ni, 3-Ni, and Ir(ppy) ₃	08
Figure 4: Proposed mechanism of the reduction of CO ₂ to CO or CH ₄ photocatalytically.....	09
Figure 5: Structure of BIH.....	11
Figure 6: Formula for carbon selective reduction percentage (CS %).....	13
Figure 7: 2-Ni performing CO ₂ photocatalytic reduction over time.....	15
Figure 8: Hydrogenation of CO to CH ₄	16

I. Introduction.

As the world's energy demand steadily increases, non-renewable energy sources such as fossil fuels, coal, and natural gas become more frequently used.¹ As a result of the increased usage of fossil fuels, there could be an increased amount of atmospheric CO₂. In fact, it is estimated that within the timespan of years 2015 to 2040, there will be a 25% increase in atmospheric CO₂ as the world reaches a peak value of 26.9 billion metric tons of atmospheric CO₂.² Carbon dioxide emissions make up a vast amount of greenhouse gas, and it could result in a number of potential consequences. Some may have even correlated shrinkages in water supplies, increases in droughts and wildfires, reductions in food supply, and rises in sea levels and floods.³

On top of the steadily increasing atmospheric CO₂ amounts, the United States of America (USA) currently is not energy-independent. In other words, the USA is consuming more energy than it is producing, and as of right now, the leading energy import in the USA is fossil fuels.⁴ Furthermore, the USA and China are the biggest emitters of greenhouse gases. One pathway to energy independence could be the chemical reduction of CO₂ through catalytic processes into fuels such as methane, H₂/CO, methanol, carbon monoxide, ethylene, formic acid, and formate.⁵ While organisms such as plants have been reducing CO₂ for millennia, progress towards creating a cost-effective and efficient method of photocatalytic CO₂ reduction with just solar energy and water would be invaluable for both reducing atmospheric CO₂ and creating renewable fuels.⁶ Recently, studies about methane production from CO₂ and visible light have been getting some attention, although this process is still rare.⁷

Photocatalytic conversion of CO₂ to a fuel such as methane is becoming an ideal method for energy production, as the energy for catalysis can be provided from renewable solar energy.⁸ Producing fuels via a renewable energy resource can even provide a significant alternative to other methods of CO₂ reduction that require electricity or use the Fischer-Tropsch process with elevated temperature and pressure.^{9, 10} Furthermore, there is a vast abundance of energy that is capable of being captured from the sun.¹¹ Marc Robert, a leading scientist in CO₂ reduction, suggests that with just an earth-abundant metal, water, and sunlight, it is possible to create an ideal scenario for energy production.^{12, 13}

The C=O bond in CO₂ is strong, with a bonding energy of 750 kJ mol⁻¹. As a result of this sturdy bond, it becomes pivotal to harness an efficient and effective catalyst with a lengthy half-life to be able to consistently break these C=O bonds. Thus, as we are influenced by mother nature's photosynthesis, the future success of these processes depends on the photocatalyst system that is used.¹⁴ In order to create an effective catalyst, various designs from previous studies should be analyzed and evaluated based on turnover numbers (TON).

$$TON = \frac{\text{moles of product}}{\text{moles of catalyst}}$$

Figure 1: Turnover number equation for a catalyst.

In other words, TON is a method of measuring how durable a particular catalyst is. As an introduction to the studied catalysts, it can be noted that tetraaza (N₄) macrocycles can produce some of the highest turnover numbers (TON) for CO₂ reduction.¹⁵ Another durable component to creating a valuable photocatalyst system is the

usage of *N*-heterocyclic carbenes (NHCs) that are often used in organometallic catalysts (Figure 2).

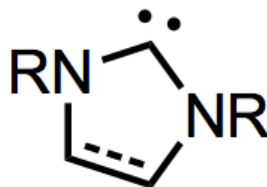


Figure 2: Example structure of an *N*-heterocyclic carbene (NHC).

NHC ligands are capable of coordinating strong bonds with their metal centers and also have strong electron-donating properties.¹⁶⁻²⁴ Many metal centers have been identified to have been able to catalyze CO₂ reduction.²⁵⁻³³ Nickel can be identified as a cost-effective and earth-abundant metal center. Thus, in **Figure 3**, the three complexes that are studied in this manuscript are shown to feature a diaza (N₂) ligand with 2 NHC ligands as replacements for tetraaza (N₄) ligands, and a nickel metal center.

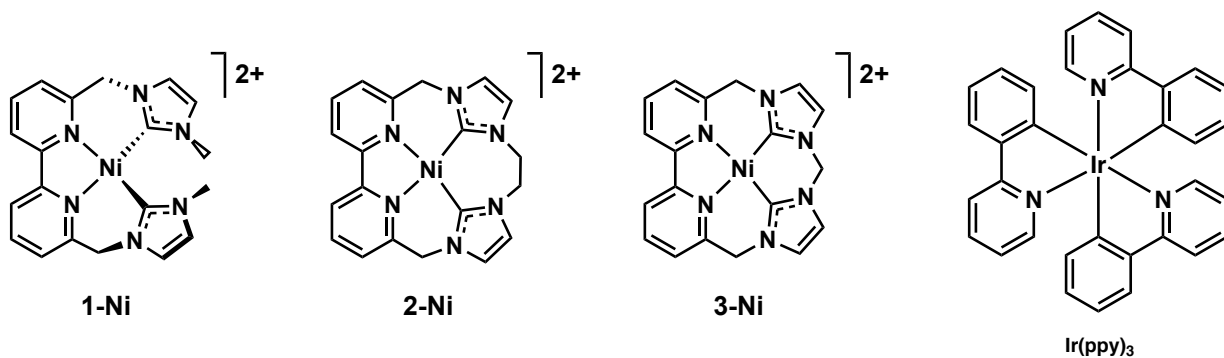


Figure 3: The catalyst structures of 1-Ni, 2-Ni, and 3-Ni. Ir(ppy)₃ serves as the photosensitizer (PS) in Ni-catalyst trials and will be discussed further on.

1-Ni, compared to the other catalysts, does not have an alkyl group fusing the two NHC groups and is therefore not considered a macrocycle. 1-Ni, 2-Ni, and 3-Ni are all in a distorted square planar shape, but 3-Ni is in a slightly more planar position. 1-Ni, 2-Ni, and 3-Ni are already known to be capable of electrocatalytic CO₂ reduction.³⁴ In

these studies, all three catalysts will undergo photocatalytic studies. While the structural differences between each catalyst may initially seem minor, further studies reveal intriguing and varying results amongst each catalyst. **Figure 4** is useful to depict the process of CO₂ reduction.

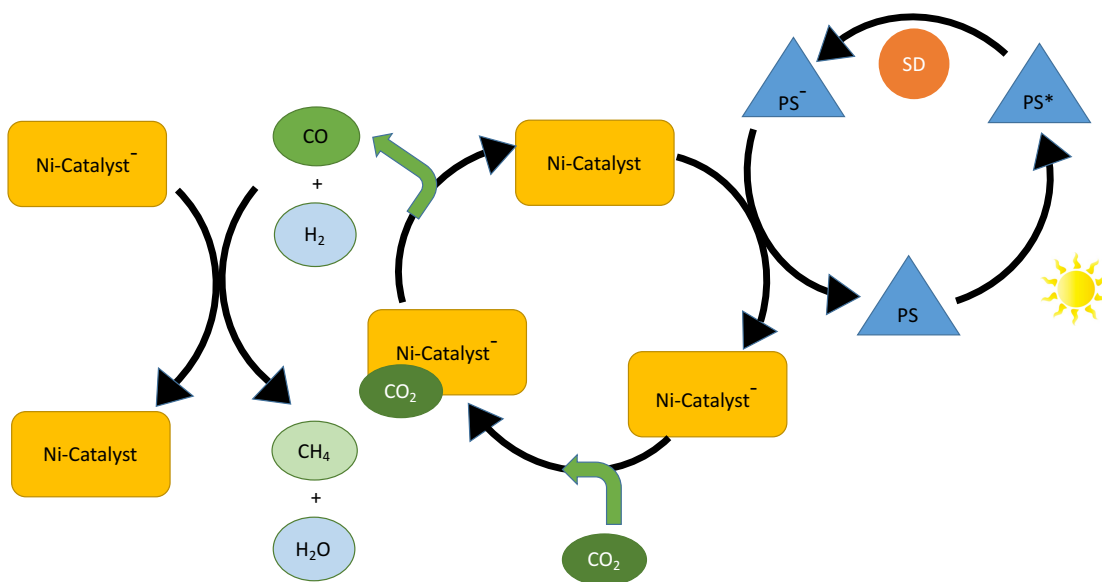


Figure 4: Proposed mechanism for the reduction of CO₂ to CO or CH₄ photocatalytically via a nickel catalyst.

As shown in **Figure 4**, the photosensitizer (PS) absorbs light and provides an electron to the catalytic cycle after an electron transfer from the sacrificial electron donor (SED), thus allowing the Ni-Catalyst to enter a reduced state. In other words, one electron in the photosensitizer enters a higher energy state once a light source reaches the PS. The lower energy level's electron deficiency is replenished by an electron transfer from the sacrificial electron donor. Now that the photosensitizer is in a reduced state, the photosensitizer is able to pass an electron to the Ni-Catalyst, thus reducing it. Once this is complete, the Ni-Catalyst is capable of forming a bond with CO₂, which then splits into

CO. In this proposed mechanism, the other oxygen could have split to form water.

Finally, CO can evolve in another catalytic cycle when H₂ is present to finally become CH₄. The hydrogenation of CO and H₂ into CH₄ and H₂O is shown in **Figure 8** in a chemical equation. H₂ is intrinsically created in this process. The protons for H₂ in the solution could stem from BIH or TEA after they have performed an electron transfer.

II. Photocatalysis Results and Discussion.

For each Nickel catalyst, Ir(ppy)₃ is used as the photosensitizer for initial studies. The purpose of the well-studied Ir(ppy)₃ is to absorb light, receive an electron from BIH or TEA, and provide an electron to the catalytic cycle.³⁵⁻³⁷ 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]-imidazole (BIH) and triethylamine (TEA) are used as the sacrificial electron donors (SDs). As shown in **Figure 4**, SD's contribute to bringing the photosensitizer to a reduced state after light sensitization so that the PS is ready to transfer an electron. TEA is used alongside BIH to allow BIH to become deprotonated after an electron transfer.³⁸ Thus, TEA serves as both an SD as well as a compound to recover BIH after BIH performs an electron transfer to the catalyst. As the BIH has an acidic nature after an electron transfer, two BIH compounds can dimerize to prevent the electron from being passed back to the sacrificial electron donor.

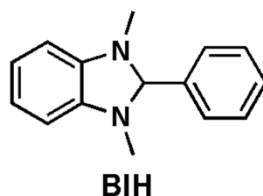


Figure 5: Structure of BIH.

Catalyst concentrations were often lowered to a micromolar or nanomolar concentration. By doing so, the studies were able to more effectively test the individual limits of the respective nickel photocatalysts by eliminating catalyst-catalyst interactions and degradation.³⁹⁻⁴¹

Entry	Catalyst	Additive	CO (TON)	CH ₄ (TON)	CS (%)
1	1-Ni	BIH	108,000	4,000	29%
2	1-Ni	BIH, H ₂ O	31,000	0	10%
3	1-Ni	n/a	130,000	29,000	3%
4	2-Ni	BIH	310,000	0	90%
5	2-Ni	BIH, H ₂ O	175,000	<u>19,000</u>	<u>87%</u>
6	2-Ni	n/a	9,000	0	20%
7	3-Ni	BIH	76,000	0	82%
8	3-Ni	BIH, H ₂ O	8,000	5,000	28%
9	3-Ni	n/a	5,000	1,000	29%

Table 1: Photocatalytic results from CO₂ reduction with Ni-1, Ni-2, and Ni-3. All components are within an MeCN solution and include 5% TEA. The additive “H₂O” is 2% H₂O and “BIH” is 10 mM BIH. The stop time is chosen based on a cease in product formation. Reactions were undergone in a solar simulated spectrum. Further details on reaction setup are shown in the Supplemental Information section. The underlined value indicates a rare scientific observation.

The goal of these catalysts is to produce CH₄ and have a high amount of carbon-based fuel products. All reactions in **Table 1** contain TEA as a sacrificial electron donor, so BIH serves as an additional sacrificial electron donor. The most worthwhile observation on **Table 1** is entry 5 with a CH₄ TON of 19,000 when 2-Ni is present in

water and BIH. Furthermore, the carbon selective (CS) reduction percentage of entry 5 is 87%. Carbon selective (CS) reduction percentage can be described in **Figure 6**.

$$CS (\%) = \frac{CO\ TON + Methane\ TON}{Total\ Product\ TON} \times 100$$

Figure 6: The carbon selective (CS) reduction percentage as a formula. CS (%) is essentially the percentage of carbon-based TON over the total product TON.

Thus, the percentage of carbon-based TON for carbon-based fuels CO and CH₄ over the total TON within the entry was 87% for entry 5. These results lead into further experiments that are explained in the 2-Ni section. Photocatalysts are rarely able to produce CH₄ at such a rate and have a high CS percentage, so 2-Ni is a promising catalyst in the study and will be discussed more in-depth later.

1-Ni Catalyst:

1-Ni is a non-macrocyclic compound that lacks an alkyl group between NHC groups. According to **Table 1**, 1-Ni was able to produce CO TON of 108,000 and CH₄ TON of 4,000 photocatalytically. A previous study indicated that the 1-Ni complex did not produce any CH₄ TON under electrochemical conditions, which could mean that differing conditions of catalysis can lead to varying outcomes.³⁴ In entry 3 of **Table 1**, 1-Ni is shown to have held an impressive TON count for CH₄, however the CS percentage was only 3%. In other words, 1-Ni in the absence of BIH and H₂O did not favor carbon-based fuel products well enough to be studied further. It is also worth mentioning that under 2% H₂O conditions, 1-Ni's CO TON was drastically reduced. In fact, the CS percentage was reduced from 29% in anhydrous conditions to 10% when water was added. In summary, 1-Ni is a capable catalyst with significant turnover numbers for CO, however the CS percentage is not notable when compared to 2-Ni and 3-Ni.

2-Ni Catalyst:

The most extensively studied catalyst in this manuscript is the 2-Ni catalyst. As previously mentioned, 2-Ni was proven to have produced CH₄ TON of 19,0000 while also having a CS percentage of 87%. For these reasons, 2-Ni underwent further tests.

2-Ni and 3-Ni are both macrocyclic complexes with similar CS percentages. However, 2-Ni was found to have a significantly increased TON in both CO and CH₄ compared to 3-Ni. For further inquiring of 2-Ni, the TON numbers of CO, H₂, and CH₄ were compared over an extended period of time.

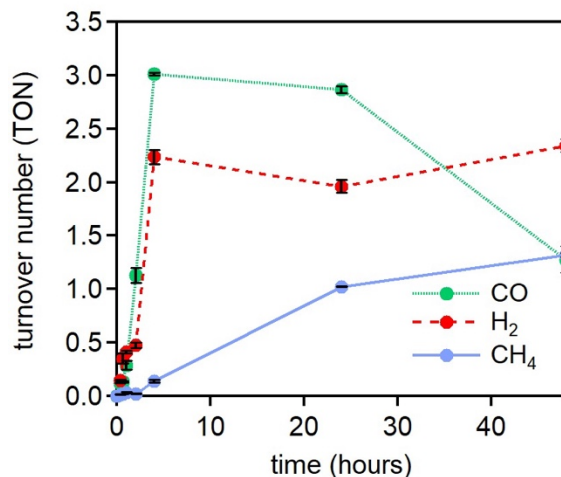


Figure 7: 2-Ni performing CO₂ photocatalytic reduction in a concentration of 0.01 mM. TON of CO, H₂, and CH₄ concentrations over an extended period of time. Data table used from submitted manuscript.

CO and H₂ TON are initially high. However, when CO and H₂ begin to decrease, CH₄ production conversely increases. This trend is a pivotal aspect to understanding the conditions required for methane production. In essence, **Figure 7** suggests that CH₄ production requires CO and H₂ within the 2-Ni catalytic conversion process to produce methane. To find out other required products, further testing ensued. In order to confirm

if the presence of CO and H₂ are necessary, the atmospheres above the reaction test tubes were altered and tested.

Atmosphere	CH ₄ TON
CO ₂	19,000
1:1 CO ₂ :H ₂	12,000
CO	10,000
1:1 CO:H ₂	<u>570,000</u>

Table 3: Photocatalytic reaction with 2 nM 2-Ni, 0.1 mM Ir(ppy)₃, 10 mM BIH, 5% (v/v) TEA, 2% (v/v) H₂O. Exposed to a solar simulated spectrum. Recorded values are peak TON values. Underlined value indicates noteworthy observation.

Based on **Table 3**, atmospheres containing CO₂, 1:1 CO₂:H₂, and CO resulted in standard amounts of methane production. However, when the atmosphere is 1:1 CO:H₂, the methane TON reached a tremendous value of 570,000. As suggested by **Figure 7**, CO and H₂ are most likely linked to producing CH₄ in an equation. Furthermore, control trials were taken when BIH, TEA, or the light source was removed. The results led to a severe reduction in CH₄ production. These control trials conclude that BIH, TEA, and a light source are also required to activate the 2-Ni catalyst in order to catalytically create CH₄. In the end, a seemingly small difference of one carbon was able to dramatically improve the results of this catalyst. Following carbon-13 labeling studies, it can be assumed that the reaction is as follows:



Figure 8: The hydrogenation of CO to CH₄.

3-Ni Catalyst:

3-Ni, although very similar in structure to 2-Ni, was not as capable of producing large amounts of CO or CH₄ according to **Table 2**. The CS percentage for 3-Ni was able to reach 82% when no water was added, and some methane was produced when water was added to reach 5,000 CH₄ TON. The overall TON numbers were simply a reduced version of 2-Ni, but the fact that methane TON did reach 5,000 indicates a similar mechanism between 3-Ni and 2-Ni. These reasons could be explained by the increased ligand planarity of 3-Ni as compared to 2-Ni, but it is not exactly certain. Similar to 1-Ni and 2-Ni, 3-Ni underwent various control trials that dictated the importance of solar stimulated illumination, BIH (SD), Ir(ppy)₃ (PS), and MeCN in the reaction.

III. Conclusion.

In an attempt to advance the field of photocatalytic CO₂ conversion to carbon-based fuels, various nickel-based catalysts with a diaza NHC ligand that were previously synthesized were tested under varying conditions for photocatalytic activity. The three compounds, 1-Ni, 2-Ni, and 3-Ni, were all reported to have produced CO and CH₄ TON. However, further studies indicated that the 2-Ni complex with H₂O was able to reach 19,000 CH₄ TON and have an exceptional CS percentage of 87%. Following this trail, further conclusions were made about trends in the reactants. A test was taken over a period of time, where the amount of CH₄ was found to increase as both CO and H₂ decreased. Furthermore, a 1:1 CO:H₂ atmospheric trial with 2-Ni led to a phenomenal CH₄ TON of 570,000. Thus, it can be inferred that 2-Ni is able to produce CH₄ as long as CO, H₂, and other factors are present or produced within the reaction. The catalyst, confirmed through ¹H NMR, Hg homogeneity tests, and PPh₃ and CS₂ tests help to identify the catalyst as a homogenous catalyst instead of a heterogeneous catalyst.^{CC, DD, EE}

In conclusion, each nickel catalyst demonstrated photocatalytic activity. However, because of the seemingly small differences within each catalyst, varying results were concluded from the test results. 2-Ni in particular has shown exciting potential as an industrial catalyst, and the catalyst may be used in further studies and development in the efforts of becoming a widely-used catalyst for CO₂ reduction to methane.⁴⁵

References.

1. IEA Key World Energy Statistics. (n.d.). Retrieved from <https://www.iea.org/statistics/kwes/supply/>
2. Outlook for Future Emissions. (n.d.). Retrieved from https://www.eia.gov/energyexplained/index.php?page=environment_outlook_for_emissions
3. Cairoli, S. (2017, November 21). Consequences of Carbon Emissions for Humans. Retrieved from <https://education.seattlepi.com/consequences-carbon-emissions-humans-4138.html>
4. U.S. Energy Information Administration - EIA - Independent Statistics and Analysis. (n.d.). Retrieved from <https://www.eia.gov/totalenergy/data/browser/index.php?tbl=T01.01#/?f=M&start=200001>
5. Hammer, N. I.; Sutton, S.; Delcamp, J. H.; Graham, J. D. Photocatalytic Water Splitting and Carbon Dioxide Reduction. *Handbook of Climate Change Mitigation and Adaptation*; Chen, W. Y., Suzuki, T., Lackner, M., Eds.; Springer: 2017; DOI: 10.1007/978-3-319-14409-2_46.
6. Navarrete, A., Centi, G., Bogaerts, A., Martín, Á, York, A., & Stefanidis, G. D. (2017). Harvesting Renewable Energy for Carbon Dioxide Catalysis. *Energy Technology*, 5(6), 796-811. doi:10.1002/ente.201600609
7. Rao, H.; Schmidt, L. C.; Bonin, J.; Robert, M. Visible-Light-Driven Methane Formation from CO₂ with a Molecular Iron Catalyst. *Nature* 2017, 548, 74–77.

8. Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: From CO₂ to Chemicals, Materials, and Fuels. Technological Use of CO₂. *Chem. Rev.* 2014, 114, 1709–1742.
9. Fischer–Tropsch process. (2019, February 16). Retrieved from https://en.wikipedia.org/wiki/Fischer–Tropsch_process
10. Brown, S. Catalysis in the Refining of Fischer–Tropsch Syncrude. *Platinum Met. Rev.* 2011, 55, 263–267.
11. Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation. *Chem. Rev.* 2013, 113, 6621–6658.
12. Robert, M. (2016). Running the Clock: CO₂ Catalysis in the Age of Anthropocene. *ACS Energy Letters*, 1(1), 281-282.
doi:10.1021/acseenergylett.6b00159
13. Rao, H.; Bonin, J.; Robert, M. Toward Visible-Light Photochemical CO₂-to-CH₄ Conversion in Aqueous Solutions Using Sensitized Molecular Catalysis. *J. Phys. Chem. C* 2018, 122, 13834–13839.
14. Wu, J., Huang, Y., Ye, W., & Li, Y. (2017). CO₂ Reduction: From the Electrochemical to Photochemical Approach. *Advanced Science*, 4(11), 1700194.
doi:10.1002/advs.201700194

15. Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation. *Chem. Rev.* 2013, 113, 6621–6658.
16. N-Heterocyclic Carbene (NHC) Ligands [Cross-coupling Reaction using Transition Metal Catalysts]. (n.d.). Retrieved from https://www.tcichemicals.com/eshop/en/af/category_index/12645;jsessionid=917AF21EE293D4010973A635A2646285
17. Thoi, V. S.; Kornienko, N.; Margarit, C. G.; Yang, P.; Chang, C. J. Visible-Light Photoredox Catalysis: Selective Reduction of Carbon Dioxide to Carbon Monoxide by a Nickel N-Heterocyclic Carbene/Isoquinoline Complex. *J. Am. Chem. Soc.* 2013, 135, 14413–14424.
18. Carpenter, C. A.; Brogdon, P.; McNamara, L. E.; Tschumper, G. S.; Hammer, N. I.; Delcamp, J. H. A Robust Pyridyl-NHC-Ligated Rhenium Photocatalyst for CO₂ Reduction in the Presence of Water and Oxygen. *Inorganics* 2018, 6, 22.
19. Boudreaux, C. M.; Liyanage, N. P.; Shirley, H.; Siek, S.; Gerlach, D. L.; Qu, F.; Delcamp, J. H.; Papish, E. T. Ruthenium(II) Complexes of Pyridinol and N-Heterocyclic Carbene Derived Pincers as Robust Catalysts for Selective Carbon Dioxide Reduction. *Chem. Commun.* 2017, 53, 11217–11220.
20. Huckaba, A. J.; Sharpe, E. A.; Delcamp, J. H. Photocatalytic Reduction of CO₂ with Re-Pyridyl-NHCs. *Inorg. Chem.* 2016, 55, 682–690.

21. Jin, T.; He, D.; Li, W.; Stanton, C. J.; Pantovich, S. A.; Majetich, G. F.; Schaefer, H. F.; Agarwal, J.; Wang, D.; Li, G. CO₂ Reduction with Re(I)-NHC Compounds: Driving Selective Catalysis with a Silicon Nanowire Photoelectrode. *Chem. Commun.* 2016, 52, 14258–14261.
22. Stanton, C. J., 3rd; Vandezande, J. E.; Majetich, G. F.; Schaefer, H. F., 3rd; Agarwal, J. Mn-NHC Electrocatalysts: Increasing π Acidity Lowers the Reduction Potential and Increases the Turnover Frequency for CO₂ Reduction. *Inorg. Chem.* 2016, 55, 9509–9512.
23. Stanton, C. J., 3rd; Machan, C. W.; Vandezande, J. E.; Jin, T.; Majetich, G. F.; Schaefer, H. F., 3rd; Kubiak, C. P.; Li, G.; Agarwal, J. Re(I) NHC Complexes for Electrocatalytic Conversion of CO₂. *Inorg. Chem.* 2016, 55, 3136–3144.
24. Agarwal, J.; Shaw, T. W.; Stanton, C. J., 3rd; Majetich, G. F.; Bocarsly, A. B.; Schaefer, H. F., 3rd NHC-Containing Manganese(I) Electrocatalysts for the Two-Electron Reduction of CO₂. *Angew. Chem., Int. Ed.* 2014, 53, 5152–5155.
25. Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO₂ Reduction. *ACS Catal.* 2017, 7, 70–88.
26. Takeda, H.; Ohashi, K.; Sekine, A.; Ishitani, O. Photocatalytic CO₂ Reduction Using Cu(I) Photosensitizers with a Fe(II) Catalyst. *J. Am. Chem. Soc.* 2016, 138, 4354–4357.
27. Shimoda, T.; Morishima, T.; Kodama, K.; Hirose, T.; Polyansky, D. E.; Manbeck, G. F.; Muckerman, J. T.; Fujita, E. Photocatalytic CO₂ Reduction by Trigonal-Bipyramidal Cobalt(II) Polypyridyl Complexes: The Nature of Cobalt(I) and

- Cobalt(0) Complexes Upon Their Reactions with CO₂, CO, or Proton. *Inorg. Chem.* 2018, 57, 5486–5498.
28. Guo, Z.; Cheng, S.; Cometto, C.; Anxolabehere-Mallart, E.; Ng, S. M.; Ko, C. C.; Liu, G.; Chen, L.; Robert, M.; Lau, T. C. Highly Efficient and Selective Photocatalytic CO₂ Reduction by Iron and Cobalt Quaterpyridine Complexes. *J. Am. Chem. Soc.* 2016, 138, 9413–9416.
29. Guo, Z.; Yu, F.; Yang, Y.; Leung, C.-F.; Ng, S.-M.; Ko, C.-C.; Cometto, C.; Lau, T.-C.; Robert, M. Photocatalytic Conversion of CO₂ to CO by a Copper(II) Quaterpyridine Complex. *ChemSusChem* 2017, 10, 4009–4013.
30. Rao, H.; Bonin, J.; Robert, M. Non-Sensitized Selective Photochemical Reduction of CO₂ to CO under Visible Light with an Iron Molecular Catalyst. *Chem. Commun.* 2017, 53, 2830–2833.
31. Rosas-Hernandez, A.; Alsabeh, P. G.; Barsch, E.; Junge, H.; Ludwig, R.; Beller, M. Highly Active and Selective Photochemical Reduction of CO₂ to CO Using Molecular-Defined Cyclopentadienone Iron Complexes. *Chem. Commun.* 2016, 52, 8393–8396.
32. Hong, D.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Kojima, T. Visible-Light-Driven Photocatalytic CO₂ Reduction by a Ni(II) Journal of the American Chemical Society Article DOI: 10.1021/jacs.9b00937 *J. Am. Chem. Soc.* 2019, 141, 6617–6622 6621 Complex Bearing a Bioinspired Tetradentate Ligand for Selective CO Production. *J. Am. Chem. Soc.* 2017, 139, 6538–6541.

33. Rao, H.; Lim, C. H.; Bonin, J.; Miyake, G. M.; Robert, M. Visible-Light-Driven Conversion of CO₂ to CH₄ with an Organic Sensitizer and an Iron Porphyrin Catalyst. *J. Am. Chem. Soc.* 2018, 140, 17830–17834.
34. Su, X., Mccardle, K. M., Panetier, J. A., & Jurss, J. W. (2018). Electrocatalytic CO₂ reduction with nickel complexes supported by tunable bipyridyl-*N*-heterocyclic carbene donors: Understanding redox-active macrocycles. *Chemical Communications*, 54(27), 3351-3354. doi:10.1039/c8cc00266e
35. Kuramochi, Y., & Ishitani, O. (2016). Iridium(III) 1-Phenylisoquinoline Complexes as a Photosensitizer for Photocatalytic CO₂ Reduction: A Mixed System with a Re(I) Catalyst and a Supramolecular Photocatalyst. *Inorganic Chemistry*, 55(11), 5702-5709. doi:10.1021/acs.inorgchem.6b00777
36. Koike, T.; Akita, M. Visible-Light Radical Reaction Designed by Ru- and Ir-Based Photoredox Catalysis. *Inorg. Chem. Front.* 2014, 1, 562–576.
37. Rodrigues, R. R.; Boudreaux, C. M.; Papish, E. T.; Delcamp, J. H. Photocatalytic Reduction of CO₂ to CO and Formate: Do Reaction Conditions or Ruthenium Catalysts Control Product Selectivity? *ACS Appl. Energy Mater.* 2019, 2, 37–46.
38. Burks, D. B.; Davis, S.; Lamb, R. W.; Liu, X.; Rodrigues, R. R.; Liyanage, N. P.; Sun, Y.; Webster, C. E.; Delcamp, J. H.; Papish, E. T. Nickel(II) Pincer Complexes Demonstrate That the Remote Substituent Controls Catalytic Carbon Dioxide Reduction. *Chem. Commun.* 2018, 54, 3819–3822.
39. Ha, E. G.; Chang, J. A.; Byun, S. M.; Pac, C.; Jang, D. M.; Park, J.; Kang, S. O. High-Turnover Visible-Light Photoreduction of CO₂ by a Re(I) Complex Stabilized on Dye-Sensitized TiO₂. *Chem. Commun.* 2014, 50, 4462–4464.

40. Won, D. I.; Lee, J. S.; Ji, J. M.; Jung, W. J.; Son, H. J.; Pac, C.; Kang, S. O. Highly Robust Hybrid Photocatalyst for Carbon Dioxide Reduction: Tuning and Optimization of Catalytic Activities of Dye/ TiO₂/Re(I) Organic-Inorganic Ternary Systems. *J. Am. Chem. Soc.* 2015, 137, 13679–13690.
41. Bonin, J.; Robert, M.; Routier, M. Selective and Efficient Photocatalytic CO₂ Reduction to CO Using Visible Light and an Iron-Based Homogeneous Catalyst. *J. Am. Chem. Soc.* 2014, 136, 16768–16771.
42. Widegren, J. A.; Finke, R. G. A Review of the Problem of Distinguishing True Homogeneous Catalysis from Soluble or Other Metal-Particle Heterogeneous Catalysis under Reducing Conditions. *J. Mol. Catal. A: Chem.* 2003, 198, 317–341.
43. Crabtree, R. H. Resolving Heterogeneity Problems and Impurity Artifacts in Operationally Homogeneous Transition Metal Catalysts. *Chem. Rev.* 2012, 112, 1536–1554.
44. Artero, V.; Fontecave, M. Solar Fuels Generation and Molecular Systems: Is It Homogeneous or Heterogeneous Catalysis. *Chem. Soc. Rev.* 2013, 42, 2338–2356.
45. Shirley, H., Su, X., Sanjanwala, H., Talukdar, K., Jurss, J., & Delcamp, J. H. (2019, March 29). Durable Solar-Powered Systems with Ni-Catalysts for Conversion of CO₂ or CO to CH₄. *J. Am. Chem. Soc.*, Article ASAP. DOI: 10.1021/jacs.9b00937

Supplemental Information:

Photocatalyst Testing.

Catalysts were made into a stock solution with MeCN and then placed into a scintillation tube. If a nano or micromolar concentration was used, then serial dilution with volumetric flasks should occur. Ir(ppy)₃ was also made into a stock solution with MeCN and then placed into a scintillation tube. The catalyst (0.2 μmol), BIH (5 mg), TEA (0.1 mL), and Ir(ppy)₃ (0.2 μmol or 0.1 mg) were then injected into a glass tube surrounded by aluminum foil to prevent light exposure. MeCN served as the solvent for the reaction and was added to the reactants to reach a total of 3 mL. Additional MeCN was added, and then the glass tube was sealed with a septum. The sealed test tube was then set into a CO₂ atmosphere as the mixture bubbled down to 2 mL. Afterwards, the reaction was set up in a solar simulated environment. The reaction setup can be shown in an image in **Figure S1**.

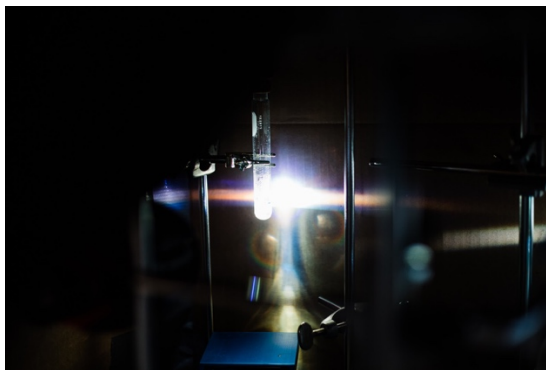


Figure S1: Reaction setup containing all required components for the reduction of CO₂ to CO and H₂.

While this reaction was occurring, samples were taken to a custom Agilent 7890B gas chromatography (GC) with an Agilent PorapakQ column and a methanizer at 20 minutes, 40 minutes, 1 hour, 2 hour, 4 hour, and 24 hours. Conditions such as gas, presence of BIH, presence of Ir(ppy)₃, and molar concentration of catalyst were altered depending on the trial. All results in this manuscript are the average of two repeated experiments.

Additional Trials.

Condition	CO (TON)	H₂ (TON)	CH₄ (TON)	CS (%)
Standard	175,000	29,000	19,000	87%
No H ₂ O	310,000	33,000	0	90%
No BIH	9,000	36,000	0	20%
No TEA	165,000	8,000	0	95%
Argon instead of CO ₂	0	0	0	-
No Ir(ppy) ₃	0	0	0	-
Darkness instead of Solar Simulated Spectrum	0	0	0	-
No 2-Ni	0	0	0	-

Figure S2: The table displays TON values under various altered conditions in order to prove the relevance of certain components. Standard conditions were as follows: 2 nM 2-Ni Catalyst with 0.1 mM Ir(ppy)₃, MeCN solvent, 10 mM BIH, 2% H₂O, 5% TEA, CO₂, and a solar simulated environment.

Catalyst	Condition	CO (TON)	H ₂ (TON)	CH ₄ (TON)
1-Ni	Standard	31,000	320,000	0
1-Ni	No H ₂ O	108,000	278,000	4,000
2-Ni	Standard	175,000	29,000	19,000
2-Ni	No H ₂ O	310,000	33,000	0
3-Ni	Standard	8,000	34,000	5,000
3-Ni	No H ₂ O	76,000	17,000	0

Figure S3: The table shows the effect that H₂O presence has in different catalysts. Ni catalysts at 2 nM concentration. 0.1 mM Ir(ppy)₃, MeCN solvent, 10 mM BIH, 2% H₂O, 5% TEA, CO₂, and a solar simulated environment. Recorded at 72 hours.

Amount of BIH	CO (TON)	H ₂ (TON)	CH ₄ (TON)
10 mM	175,000	29,000	19,000
5 mM	144,000	68,000	11,000
1 mM	69,000	161,000	12,000
0.5 mM	36,000	82,000	11,000
0.1 mM	19,000	198,000	6,000

Figure S4: The table helps to identify the preferred amount of BIH for reduction of CO₂. 2 nM 2-Ni catalyst under variable BIH conditions. 0.1 mM Ir(ppy)₃, MeCN solvent, varying amounts of BIH, 2% H₂O, 5% TEA, CO₂, and a solar simulated environment.