TRANSITION METAL PHOSPHIDES FOR HIGH ENERGY EFFICIENCY
ELECTROCATALYTIC CO$_2$ REDUCTION: INVESTIGATING MECHANISMS AND
STRUCTURE-ACTIVITY RELATIONSHIP

By
KARIN UTE DOEHL CALVINHO

A dissertation submitted to the
School of Graduate Studies
Rutgers, The State University of New Jersey
In partial fulfillment of the requirements
For the degree of
Doctor of Philosophy
Graduate Program in Chemistry and Chemical Biology

Written under the direction of
G. Charles Dismukes

And approved by

_____________________________________
_____________________________________
_____________________________________
_____________________________________

New Brunswick, New Jersey

October 2020
ABSTRACT OF THE DISSERTATION


BY KARIN UTE DOEHL CALVINHO

Dissertation Director:

G. Charles Dismukes

Electrochemical reduction of carbon dioxide, powered by renewable electricity, enables the sustainable production of chemicals, polymers, and fuels, potentially displacing fossil carbon sources and mitigating the effects of global warming. However, the activation of CO₂ is a kinetic bottleneck for this process. Low energy efficiencies and poor product selectivities prevent the commercial development of this technology. As such, we sought to develop viable catalysts for the CO₂ reduction reaction (CO₂RR) that 1) operate at high energy efficiency; 2) are capable of catalyzing C-C coupling for producing high-value chemicals; 3) are synthesized from earth-abundant materials, and 4) are robust and stable for extended lifetimes. Inspired by nature’s formate and carbon monoxide dehydrogenases, we investigated the CO₂RR activity of seven different transition metal phosphides. Furthermore, we applied experimental and theoretical tools to unravel reaction mechanisms and extract design principles that can guide the development of next-generation catalytic materials.

In Chapter 1, we report the application of five nickel phosphides for CO₂RR, at ambient conditions in neutral electrolyte. The most selective nickel phosphides operate at exceedingly low overpotential (~10 mV), yield no hydrogen by-product, and form non-
volatile C$_3$ and C$_4$ products. Both products, methylglyoxal and furandiol, can be used as precursors for polymers. We propose a reaction mechanism that is initiated by hydride transfer to CO$_2$, generating formate, which is further reduced to formaldehyde. Formaldehyde proceeds through a self-condensation mechanism, akin to the formose reaction, to yield methylglyoxal, and the aromatic compound 2,3-furandiol. The mechanism is supported by reduction of reaction intermediates that yield the same product ratios as the reduction of CO$_2$. Nickel phosphide catalysts are affordable, abundant, highly active, and could represent a breakthrough in the sequestration of CO$_2$ into fuels and chemical feedstocks for use in the polymer industry.

In Chapter 2, copper phosphide (Cu$_3$P) is investigated for CO$_2$ reduction. Hydrogen is the major product detected, with less than 2% faradaic efficiency for formate. A detailed structural analysis of the Cu$_3$P [001] facet identifies isolated Cu(I) sites as likely active sites for both H$_2$ and formate production. This study shows that Cu(I) alone is insufficient to promote highly active CO$_2$RR to C$_2^+$, and that stronger bidentate formate binding is necessary for CO$_2$RR to outcompete H$_2$ production.

In Chapter 3, this thesis addresses the reactivity of Fe$_2$P, iso-structural to Ni$_2$P. Metallic iron has two fewer electrons than nickel in its d-orbitals, thereby binding the phosphorus ad-layer more strongly than Ni$_2$P. Accordingly, binding of surface hydrides (P-H*) on Fe$_2$P is weaker than on Ni$_2$P, and therefore, they are predicted to be more reactive. Consequently, Fe$_2$P catalyzes to CO$_2$ reduction with a maximum of 53%. The major product is ethylene glycol (FE of 22% at -0.05 V), but formic acid (C$_1$), methylglyoxal (C$_3$), and 2,3-furandiol (C$_4$) are also present. Phosphorus, hydroxide, hydride, CO$_2$, and formate binding to Fe$_2$P are investigated by Grand Canonical DFT (GC-DFT), accounting
for the effects of the applied potential and solvent on electrocatalysis. Results reveal that weakly bound Fe$_3$P-H surface hydrides on the P-reconstructed surface are the precursors to both CO$_2$RR and HER. The surface hydrides become more hydridic as the bias increases, favoring high turnover of low barrier hydride transfer reactions, such as those that produce ethylene glycol, over C$_3$ and C$_4$ products, explaining the higher selectivity towards shorter chain products.

Finally, in Chapter 4, the biased Ni$_2$P surface is computationally modeled using GC-DFT and experimentally characterized using operando Raman spectroscopy. GC-DFT calculations confirm an earlier report of stable surface reconstruction that enriches phosphorus at the Ni$_3$ hollow sites and predict the adsorption of two hydrides onto P* coupled to its displacement to a μ$_2$-bridging site (Ni-P*-Ni) with tetrahedral coordination. Operando Raman spectroscopy provides support for these predictions, showing the dynamic behavior of the surface under applied bias at neutral, acidic, and basic pH. The assignment of experimental vibrational modes is validated with DFT phonon calculations. The deeper understanding of the surface which this study provides will inform mechanistic predictions and the rational design of catalysts, which are critical to improving the catalytic performance of the hydrogen evolution reaction and CO$_2$ reduction.
Dedication

For Luiz Ribeiro, my partner, my love, and my best friend.
Acknowledgments

This document is a compilation the following publications:


Charles Dismukes has an unwavering vision of how Chemistry can inform changes that can transform energy storage and production of useful carbon-containing compounds into a sustainable endeavor in Earth and space. Nature both guides his work and serves as a beautiful reminder of our duty to protect her. His vision, which I will carry forward, has inspired me to come to Rutgers, and his commitment to excellence has ensured I was always challenged to go beyond. His support on personally challenging times enabled me to carry on. For all of that and much more, I am very grateful for having him as an advisor.

Anders Laursen single-handedly got me started on CO$_2$ reduction, and taught me to navigate electrochemistry, synthesis, catalysis, surface science, and analytical chemistry. He also was by my side for troubleshooting every issue, polishing hypotheses, discussing ideas, extracting meaning out of data, and genuinely being a fantastic mentor. No one
talks about all the piping, glassblowing, the leaks, and cylinder changes that are a part of this work. He was there for it too. Thank you for all the support, insights, knowledge, time, and partnership. You deserve much of the credit for the work in this thesis.

My committee members have given invaluable input that contributed tremendously to my formation as a scientist. Eric Garfunkel has welcomed me to Rutgers, opened doors to many collaborations, and offered his insight into the surface physics of these compounds. Martha Greenblatt and her group members taught me a great deal about solid state chemistry and how to approach the understanding of crystalline structures. I would not be able to navigate the field of heterogeneous catalysis without their guidance.

The most senior lab members in our group have also immensely contributed to my formation. From the very beginning, Paul Smith and Graeme Gardner were incredibly patient mentors, who taught me the jargon, how to do peer reviews, how to keep up with literature, what was important in the field – and a lot about oxygen evolution too. I can also thank Paul for getting me started on trivia nights. Spencer Porter mastered science diplomacy and taught by example how to manage projects with many moving parts. He showed me how to explore and cherish each place and introduced me to the best Bahn mi sandwiches in Edison. Then, Joshua Flynn joined the lab for exploring solid-state chemistry – and make our trivia team stronger. Later, Mahak Dhiman has very swiftly brought amazing synthesis skills to the team and taught me a lot about how to make nanomaterials.

My peers have been a tremendous source of friendship, support, and knowledge. Shinjae Hwang has an incredible talent for surface science and taught me all I know about interfaces. His calm and ordered approach to research has often brought balance to my
(sometimes creative) chaos. For the many wonderful conversations at the end of the day, thank you. Krishani Teeluck has been great lab mate, friend, and is for sure the mightiest of all. Thank you for sharing your stories, your mom’s banana bread, for giving me plants and teaching me how not to kill them. Apostolos Zournas has a very contagious, joyful approach to science and helped me pinpoint problems when I needed it most. I will be forever thankful. Hengfei has taken on more and more of the group’s responsibilities, and his commitment is unrivaled. Yifei Li has been the latest addition to the group, and it has been such a joy to see her grow and take charge in continuing the research on CO$_2$ reduction. I am excited to see where she is going to take it. To Ken Kostenbacher, thank you for all the conversations about how to make sugars from CO$_2$. Your enthusiasm is infectious.

I also owe much gratitude to the students who trusted me to be their mentor and worked diligently to execute much of the experiments reported here. I was very lucky to work with incredibly talented and brilliant students. Timothy Goetjen, Kyra Yap, and Anika Jalil, you have each brought your whole selves to this experience and have learned some things from me but taught me much more. You all became trusted friends, and I am thrilled to see you have embraced careers in research and are excelling at it.

One of the most amazing aspects of graduate school has been the opportunity to work with incredibly talented scientists across the country. Some colleagues say they want to collaborate, and some go above and beyond. Rob Wexler, Tian Qiu, Arvin Kakekhani, Sayan Banerjee, and Andrew Rappe have put an incredible amount of effort in sharing their discoveries and crafting research proposals together with us, and I am thankful for it. Aziz Alherz has made the ultimate commitment to understand the chemistry of
transition metal phosphides at operating conditions. He worked without hesitation throughout the Great Pandemic of 2020 to make this thesis possible and was a great source of support throughout all of it. Charles Musgrave has been incredibly generous, sharing advice, his unmatched intellectual insights, and prioritizing this work. Thank you for supporting, guiding, and enabling this work.

Collaborators at Rutgers have greatly enriched and supported this work too. To Gene Hall, thank you for sharing your expertise and helping me with uncountable experiments. To Nagarajan Murali, thank you for teaching me a lot about NMR. Tom Emge, thank you for all the help with crystallography. To Gennady Ananyev, thank you for always coming up with a way of getting old electronics to work and engineering experiments. To Bill Schneider, thank you for helping design and build all sorts of widgets, and for always getting me out of (mechanical) trouble.

I am indebted to the people who keep the Chemistry Department running smoothly. Thank you specially to Joe Hebert, Lydia Haynes, Ann Doeffinger, Anu Kadam, Srilekha Vangala, Nicol O’Mealley, and Shaneika Nelson, in particular.

To the New York Catalysis Society, thank you for making me feel part of a community of talented scientists that can envision a way of making any reaction faster. To the friends from BRASCON and Abroaders, thank you for bringing me back to my roots and showing that science can be done superbly in a Brazilian way – resourceful, informal, creative, upbeat, and gregarious.

Without financial support from BASF, DOE, and TechAdvance, this work would not be possible. To BASF, thank you for creating opportunities for Rutgers students to get in touch with so many scientists who are dedicated to catalyst development. Seeing
chemists that have an impact in so many lives truly inspired me to go beyond publishing research. To TechAdvance, thank you for funding our project and turning my attention to the possibility of being an entrepreneur.

To my family, thank you for always loving me.

To Luiz Ribeiro, thank you for taking me on the greatest adventure of my life when you married me. Thank you for moving across the country to support my decision of going to grad school on the East Coast and for taking the hard side of the commute. But more importantly, thank you for loving me unconditionally.

Finally, I would not have enjoyed this journey so much if it were not for the wonderful friends I met here. In Brazil, we say that friends are “the family that we get to choose”. This has never been truer. Valdir Barth, Vitorino Castro, Érik de Amorim, Silvio Dantas, Alison Acevedo, Eduardo Troian, Julia Puffal, Bernardo Rivas, Lisia Dias, Victor Pupim, and Pedro Lopes were there for the trips, the weekends, the board games, the holiday dinners, the parties, the birthdays, and for support when things got tough. To the friends that have managed to be a present even when geography made it hard: Buca Seiffert, Lucas Paiva, Camila Yuri, Ricardo Mellegari, Joelza Vernick, Philippe Cirino, Victoria Chan, Roberto Tovar, Aurorae Tran, Fernanda Rios, Livia Palmerton, Carleara Weiss, Jessica Akemi, Paulo Regis, Patricia Basile, Ugo Nunes, and Magno Formiga. Thank you.
# Table of Contents

Abstract .......................................................................................................................... ii  
Dedication ....................................................................................................................... v  
Acknowledgments .......................................................................................................... vi  
Table of Contents .......................................................................................................... xi  
List of Tables .................................................................................................................... xiv  
List of Figures .................................................................................................................. xv  
Chapter 1: Selective CO$_2$ reduction to C3 and C4 oxhydrocarbons on nickel phosphides at overpotentials as low as 10 mV ............................................................. 1  

1:1 Introduction .............................................................................................................. 2  
1:2 Results and Discussion ............................................................................................ 4  
  Catalyst crystallinity and purity.................................................................................. 4  
  Electrolysis Setup ....................................................................................................... 5  
  CO$_2$ reduction products ............................................................................................ 7  
  Current vs. Potential ................................................................................................... 8  
  Selectivity vs. Potential ............................................................................................. 10  
  Energy Efficiency ....................................................................................................... 13  
  Surface changes following catalysis .......................................................................... 14  
  Reaction mechanism on nickel phosphides ............................................................. 16  
1:3 Conclusions .............................................................................................................. 21  
1:4 Experimental .......................................................................................................... 22  
  Catalyst Synthesis ..................................................................................................... 22  
  Powder X-Ray diffraction ......................................................................................... 23  
  Electrochemistry ........................................................................................................ 23  
  Gas Chromatography ................................................................................................. 25  
  High-Performance Liquid Chromatography (UV/RID) ........................................... 25  
  Acknowledgements .................................................................................................... 26  
1:5 References ............................................................................................................... 27  

Chapter 2: CO$_2$ electro-reduction on Cu$_3$P: Selective design of a formate pathway on Cu(I) and structural activity insights into H$_2$ selectivity ........................................... 31
Abstract ................................................................................................................................. 31
2.1 Introduction ...................................................................................................................... 31
2.2 Results and Discussion.................................................................................................... 34
  Catalyst Preparation............................................................................................................ 34
  Catalyst Bulk Characterization Pre- and Post-Catalysis .................................................. 35
  Electrochemical Activity .................................................................................................... 36
  Literature comparison ........................................................................................................ 39
  Surface Post-Catalysis Characterization ......................................................................... 40
  Atomic Surface Structure .................................................................................................. 43
  Active Site and Reaction Mechanism ................................................................................ 44
2.3 Conclusions .................................................................................................................... 48
2.4 Experimental Section ...................................................................................................... 50
  Catalyst Synthesis ............................................................................................................ 50
  Catalyst Characterization .................................................................................................. 51
  Electrochemistry ................................................................................................................ 52
  Product Detection/Quantification ....................................................................................... 52
2.5 Acknowledgements .......................................................................................................... 53
2.6 References ....................................................................................................................... 54

Chapter 3: Electrocatalytic CO₂ Reduction on Isostructural Fe₂P vs. Ni₂P: Shifting Carbon Product Selectivity to Ethylene Glycol on Iron Phosphide ........................................ 61
Abstract ................................................................................................................................ 61
3.1 Introduction ...................................................................................................................... 62
3.2 Results and Discussion .................................................................................................... 65
  Catalyst purity and active surface ..................................................................................... 65
  Electrochemistry ................................................................................................................. 68
  CO₂ Reduction Reaction Products .................................................................................. 70
  The Effect of Applied Bias on CO₂RR vs HER selectivity .............................................. 72
  Nature of bonding of adsorbates to the surface ............................................................... 75
  Origin of the C₂ product selectivity .................................................................................. 80
3.3 Conclusions ..................................................................................................................... 80
3.4 Methods .......................................................................................................................... 82
Chapter 4: A Theoretical and Experimental Study of the Ni$_2$P Surface Under

Electrochemical Conditions .......................................................................................................................... 95

Abstract ...................................................................................................................................................... 95

4.1 Introduction .......................................................................................................................................... 96

4.2 Results ................................................................................................................................................ 99

  Surface Reconstruction of Ni$_2$P (0001) ...................................................................................... 99

  Experimental validation ...................................................................................................................... 104

4.3 Conclusions ....................................................................................................................................... 109

4.4 Methods ............................................................................................................................................ 111

4.5 References ....................................................................................................................................... 115

Appendices ............................................................................................................................................... 118

Appendix A: Chapter One Supplemental Materials ............................................................... 119

Appendix B: Chapter Two Supplemental Materials ............................................................. 158

Appendix C: Chapter Three Supplemental Materials ............................................................ 175

Appendix D: Chapter Four Supplemental Materials ............................................................. 202
List of Tables

Table 1.1. Standard electrochemical potentials at pH 7.0.................................................. 8
Table 1.2. Turnover frequency at the potential with maximum CO$_2$RR selectivity, based on electrochemical surface area ................................................................. 13
Table 1.3. Energy efficiency of the CO$_2$RR at the potential with maximum selectivity, considering a perfect oxygen evolution anode......................................................... 14
Table 4.1. Raman spectra assignment based on DFT-calculated vibrational frequencies and reference experimental data................................................................. 105
List of Figures

Figure 1.1. Scheme of the sandwich-type electrochemical cell used ........................................ 4
Figure 1.2. Ni$_2$P voltammetry and chronoamperometry .......................................................... 9
Figure 1.3. Partial current densities ......................................................................................... 11
Figure 1.4. Faradaic efficiency for CO$_2$RR as a function of potential and catalyst composition .......................................................................................................................... 12
Figure 1.5. XPS spectra of Ni$_2$P catalyst before and after CO$_2$RR ....................................... 15
Figure 1.6. Standard Gibbs free energy changes of possible carbon-carbon bond forming reactions at 298 K and pH7 .................................................................................................................. 19
Figure 1.7. The proposed reaction mechanism ......................................................................... 21
Figure 2.1. PXRD pattern of as synthesized Cu$_3$P NS/Cu ....................................................... 33
Figure 2.2. Linear sweep voltammetry ..................................................................................... 37
Figure 2.3. LMM Auger spectra ............................................................................................... 40
Figure 2.4. A: Top-view Cu$_3$P[00I]-Cu$_3$P$_3$ surface termination ........................................ 45
Figure 3.1. Computed adsorption energies vs applied electrical bias ...................................... 66
Figure 3.2. Fe$_2$P surface top view highlighting the Fe$_3$ hollow site and P adsorbed .......... 67
Figure 3.3. iR-corrected linear sweep voltammetry, chronoamperometry, faradaic efficiency, and steady-state current density ........................................................................................................... 69
Figure 3.4. Proposed mechanism for formation of CO$_2$RR products .................................. 73
Figure 3.5. Computed adsorption energies vs. applied electrical bias .................................... 74
Figure 3.6. Energy gap between orbitals near the Fermi level ............................................... 77
Figure 4.1. Illustration of the extent of the Ni$_2$P surface reconstruction ............................. 101
Figure 4.2. Computed adsorption energies as a function of bias ............................................. 102
Figure 4.3. Geometries of Hs/OHs adsorbed on P ................................................................. 103
Figure 4.4. Raman spectra of Ni$_2$P film on nickel foil with no electrolyte ........................... 104
Figure 4.5. Raman spectra of Ni$_2$P under applied potential over time ............................... 107
Figure 4.6. Raman spectra of Ni$_2$P under applied potential over time ............................... 108
Chapter 1: Selective CO$_2$ reduction to C$_3$ and C$_4$ oxhydrocarbons on nickel phosphides at overpotentials as low as 10 mV


†These authors contributed equally.

This work has been previously published with all rights retained
Citation: Energy Environ. Sci., 2018, 11, 2550-2559
https://doi.org/10.1039/C8EE00936H

Abstract

We introduce five nickel phosphide compounds as electro-catalysts for the reduction of carbon dioxide in aqueous solution, that achieve unprecedented selectivity to C$_3$ and C$_4$ products (the first such report). Three products: formic acid (C$_1$), methylglyoxal (C$_3$) and 2,3-furandiol (C$_4$), are observed at potentials as low as +50 mV vs. RHE, and at the highest half-reaction energy efficiencies reported to date for any > C1 product (99%). The maximum selectivity for 2,3-furandiol is 71% (Faradaic efficiency) at 0.00 V vs. RHE on Ni$_2$P, which is equivalent to an overpotential of 10 mV, with the balance forming methylglyoxal, the proposed reaction intermediate. P content in the series correlates closely with both the total C products and product selectivity, establishing definitive structure-function relationships. We propose a reaction mechanism for the formation of multi-carbon products, involving hydride transfer as the potential-determining step to oxygen-bound intermediates. This unlocks a new and more energy-efficient reduction route that has only been previously observed in nickel-based enzymes. This performance contrasts with simple metallic catalysts that have poor
selectivity between multi-carbon products, and which require high overpotentials (>700 mV) to achieve comparable reaction rates.

1:1 Introduction

The electrochemical reduction of carbon dioxide (CO\textsubscript{2} Reduction Reaction, CO\textsubscript{2}RR) using water as hydrogen source has the potential to enable sustainable production of fuels, chemicals and polymers from renewable energy sources. While active and selective catalysts for CO\textsubscript{2} reduction to CO\textsuperscript{1–7} and HCOOH\textsuperscript{3,8–10} have been developed over the past few years, the generation of high-value multi-carbon products is not yet sufficiently efficient. Copper and alloys thereof are the only catalysts proven to generate C\textsubscript{2} and C\textsubscript{3} alkanes, alcohols, ketones and aldehydes at significant rates.\textsuperscript{11,12,21–24,13–20} However, copper-based catalysts are still limited by three problems: 1) poor selectivity of the reaction produces a wide range of carbon products, 2) high overpotentials waste energy to heat, and 3) significant H\textsubscript{2} co-production competes with the desired organic compounds.

Nørskov and co-workers have proposed a mechanism for the conversion of CO\textsubscript{2} to CH\textsubscript{4} on copper, based on density functional theory (DFT)\textsuperscript{25}, that involves initial reduction to adsorbed CO (*CO), which blocks surface H-adsorption sites and suppresses the significant competing hydrogen evolution reaction (HER). Their proposed potential-determining step (PDS) occurs when HCO* binds parallel to the Cu surface to create bonding interactions to both C and O atoms. The calculated PDS requires an applied potential of -0.74 V vs. RHE, which corresponds to the experimental onset of methane and ethylene production observed by Hori \textit{et al.}\textsuperscript{11} Since the PDS involves the binding of HCO*, the theoretical overpotential for methane formation should scale with the CO
binding energy for different metal surfaces. This descriptor is near the optimal value for copper, rationalizing its ranking as the best pure transition metal catalyst for reducing CO₂ beyond 2-electron reduction products. Binary materials that favor binding the HCO* intermediate through both the carbon and oxygen atoms should break the scaling relationships obeyed by simple metals and could potentially improve catalytic activity. Both nickel and phosphorous allow for increased stabilization of oxygen-bound intermediates, potentially decreasing the overpotential for reaction. Additionally, they form multiple binary compounds that can absorb hydrogen atoms which have different hydride bond strength (hydricity). Moreover, the two principal enzymes that convert CO₂ to CO and subsequently couple C-C bonds, both utilize nickel in the active site. Both enzyme’s utilize sulfide+cyanide ligands to nickel, possibly to tune hydricity. Here, we approximate this ligand set using phosphorous which provides an iso-electronic replacement for the S+CN⁻ ligands. Nickel phosphides have been reported as highly active HER catalysts. Using them for CO₂RR is contrary to the belief that effective catalysts should have poor HER activity, yet still efficiently transfer adsorbed hydrogen atoms to a *CO intermediate. In contrast, other theoretical predictions by Rossmeisl et al. claim that having hydrogen binding energy near thermo-neutral is critical for predicting the ability of pure metals to generate products beyond CO, and is equally as important as the *CO binding energy. This represents a shift in dogma for CO₂RR research and underscores the importance of reversible hydrogen binding for both HER and CO₂RR activities.
Based on these various insights, we synthesized a family of five nickel phosphide compounds: \( \text{Ni}_3\text{P} \), \( \text{Ni}_2\text{P} \), \( \text{Ni}_{12}\text{P}_5 \), \( \text{Ni}_5\text{P}_4 \), and \( \text{NiP}_2 \), and evaluated their performance as electrocatalysts for CO\(_2\)RR. Our results demonstrate that product selectivity greatly improves with increasing P content in this series. This is the first report of the formation of methylglyoxal (C3) and 2,3-furandiol (C4) products, with potential applications in the polymer industry. The best nickel phosphide catalyst achieves essentially complete discrimination over the HER, and an energy efficiency of 99% with the lowest overpotential reported thus far for any \( \geq \text{C1} \) products.

1:2 Results and Discussion

Catalyst crystallinity and purity

Compositional purity, crystal phase and crystal facet exposure are critical variables when comparing catalyst performance. Five different nickel phosphide compounds
(Ni$_3$P, Ni$_2$P, Ni$_{12}$P$_5$, Ni$_3$P$_4$, and NiP$_2$) were synthesized by solid state reaction at 700°C, in vacuum-sealed quartz tubes, using high purity elemental precursors. Comparison of the unique powder X-Ray diffraction patterns to the nickel phosphide reference patterns (Figure S1-S5), verified that each was a single, pure phase, lacking contamination from secondary phases or amorphous material below the 2% detection limit. The nickel phosphides were intentionally synthesized at high temperature to achieve thermodynamic equilibrium among facets (i.e., polycrystallinity). Polycrystallinity was confirmed by SEM analysis, showing particles with roughly spherical morphology, lacking distinct faceting, and with sizes ranging from 1-20 µm in diameter (Figure S6).

**Electrolysis Setup**

The performance of polycrystalline electrocatalysts has, to date, been limited by the ability to consistently reproduce stable catalyst/electrode interfaces from powdered catalysts supported on conductors. Our group has developed a successful protocol for preparing electrodes from nickel phosphides by mixing them with a binder and pressing them into rigid pellets$^{27,28}$. Due to the metallic nature of nickel phosphides,$^{27,28}$ no addition of conductive carbon was required. To obtain electrodes with a 2 cm diameter, the different polycrystalline powders were mixed with 1% (w/w) neutral Nafion™ (Sigma Aldrich 5 wt. % solution in lower aliphatic alcohols and water, neutralized with 4 mg NaOH pellets/mL of solution). After grinding with a mortar and pestle until the solvent had evaporated, the mixture was transferred to an aluminum die containing an aluminum mesh for mechanical support (McMaster-Carr, 20x20 mesh size, 0.016” wire diameter), then pressed at 7 ton/cm$^2$. The resulting pellets were porous and had a mean thickness of 575 µm (see ESI Figure S7). The aluminum die was used directly as the
working electrode support in a sandwich-type cell, depicted in Figure 1. During the reaction, only the catalyst pellet was exposed to the electrolyte, and the back of the aluminum support was connected to the potentiostat. Aluminum was chosen for the support as it has been previously shown to have low activity for CO$_2$RR and HER.$^{34}$ The use of relatively large and porous electrodes can lead to substantial iR-drop and significant errors in potential determination.$^{35}$ Resistive losses from the electrolyte were minimized by the use of a 0.5M KHCO$_3$ buffer, resulting in a stable solution resistance of 6–8 ohms. Potentiostatic electrochemical impedance spectroscopy (PEIS) was performed before each experiment to measure the uncompensated resistance, which was used for positive feedback iR compensation (Figure S7). The solution resistance during the reactions consistently changed by less than 0.5 ohm (< 2 mV). All potentials were measured against a commercial Hg/Hg$_2$SO$_4$ reference electrode, and converted to the thermodynamically relevant reversible hydrogen electrode (RHE) scale.

Avoiding gaseous CO$_2$ depletion is a concern for CO$_2$RR.$^{36,37}$ To minimize mass transport limitations, in addition to the carbonate buffer, CO$_2$ gas was fed through the bottom of the cell via a glass frit (4–8 µm pores), generating bubbles of 50 to 150 µm (measured by optical imaging). Such small bubble sizes are sufficient to ensure CO$_2$ saturation at operating currents lower than 10 mA/cm$^2$, as shown in a prior study by Lobaccaro et al.$^{37}$

Gas-phase products were detected by an online gas chromatograph, using both thermal conductivity and flame ionization detectors, arranged in series. The working electrode had a large surface area (3.14 cm$^2$) to electrolyte volume (6 mL) ratio (S/V = 0.52 cm$^{-1}$) to maximize the concentration of liquid phase products in the electrolyte, in accordance
with recent literature recommendations.\textsuperscript{37,38} This allowed for direct product quantification by HPLC, that was further corroborated by NMR and LCMS analyses for unambiguous product assignments and yields (refer to ESI Figures S12 and S13).

**CO$_2$ reduction products**

Table 1 lists the reduction potentials (E\textsuperscript{0*}) and the number of electrons required to reduce CO$_2$ to various products, including the three products observed in this work (formate, methylglyoxal, and 2,3-furandiol). E\textsuperscript{0*} at pH 7.0 vs. RHE was calculated from tabulated\textsuperscript{39,40} thermodynamic data when available, and otherwise estimated by Mavrovouniotis’ method of individual group contributions\textsuperscript{41} (details in ESI Table S8). While formate is widely reported as a CO$_2$ reduction product,\textsuperscript{3,8–10} this is the first report of the formation of methylglyoxal and 2,3-furandiol under electrochemical conditions. The E\textsuperscript{0*} values reveal the latter products are thermodynamically easier to form than CO, formate and H$_2$, suggesting a possible approach for selectivity. To test the origin of the carbon products, isotopic labeling with $^{13}$CO$_2$ as carbon source was conducted (refer to figure S14 in ESI). This confirmed that dissolved CO$_2$ was indeed the sole source of carbon for C\textsubscript{1}, C\textsubscript{3} and C\textsubscript{4} products. Control experiments using Ar-purged KHCO$_3$ electrolyte reduced the CO$_2$RR currents to 20% of their previous value, confirming that dissolved CO$_2$, rather than ionized forms of (bi)carbonate, is the main substrate for CO$_2$RR on nickel phosphides.
Table 1.1. Standard electrochemical potentials at pH 7.0

<table>
<thead>
<tr>
<th>Product</th>
<th>Half-Reaction</th>
<th>$E^0$ (V vs RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$2 (e^- + H^+ ) \rightleftharpoons H_2$</td>
<td>0.00</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>$CO_2 + 2 (e^- + H^+) \rightleftharpoons HCOOH$</td>
<td>-0.02</td>
</tr>
<tr>
<td>CO</td>
<td>$CO_2 + 2 (e^- + H^+) \rightleftharpoons CO$</td>
<td>-0.10</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>$CO_2 + 8 (e^- + H^+) \rightleftharpoons H_3C_COOH$</td>
<td>+0.23</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>$3 CO_2 + 12 (e^- + H^+) \rightleftharpoons C_3H_4O_2 + 4H_2O$</td>
<td>+0.02</td>
</tr>
<tr>
<td>2,3-furandiol</td>
<td>$4 CO_2 + 14 (e^- + H^+) \rightleftharpoons C_4H_6O_3 + 5H_2O$</td>
<td>+0.01</td>
</tr>
</tbody>
</table>

**Current vs. Potential**

Figure 2 (A) presents voltammograms for Ni$_2$P, obtained using Ar saturated 0.5 M sodium phosphate buffer (grey), and CO$_2$ saturated 0.5 M KHCO$_3$ (blue), both at (pH 7.5). Under an argon atmosphere, the reductive current due to hydrogen evolution sharply increases with increasing overpotential. In contrast, under CO$_2$ saturation, the current is suppressed at all negative potentials, indicating that CO$_2$RR intermediates bind to some or all of the same sites that would otherwise be active for HER. Most notably, at positive potentials, the observed current increases in the presence of CO$_2$, indicating that CO$_2$RR dominates. Four of the nickel phosphides express this behavior, with the exception of NiP$_2$, which reaches open circuit potential (OCP) below 0 vs RHE (see ESI Figure S9).
Figure 1.2. Ni$_2$P voltammetry and chronoamperometry

(A) iR-corrected linear sweep voltammetry of Ni$_2$P at 0.5 mV/s. In grey, argon-purged 0.5 M phosphate buffer, pH 7.5. This current corresponds solely to the HER; in blue, CO$_2$-saturated 0.5 M KHCO$_3$, where the current is due to CO$_2$ reduction and HER. Binding of CO$_2$RR intermediates partially suppresses HER. Furthermore, the current for CO$_2$RR is seen to be larger than those attributed to HER in the phosphate buffer at low overpotentials (see inset).

(B) Representative chronoamperometry measurements at different potentials for Ni$_2$P. Due to the high porosity of the catalyst, there is an initial charging period (as previously reported in acid and base), after which the current stabilizes. Voltammetry and chronoamperometry for all stoichiometries can be found in the ESI Figure S9.

The stability of the catalyst current density was assessed by chronoamperometry, and is presented in Figure 2(B) for Ni$_2$P (and for the remaining stoichiometries in the ESI Figure S10).

The total current decreases in the first half hour of the experiment at all negative potentials (break-in period), due to the reduction of the surface phosphoxides, as well as the build-up of a pH gradient within the porous electrocatalyst, in agreement with our previous HER study using nickel phosphides. After the initial break-in period, the current stabilizes, and no significant loss of CO$_2$ current activity is observed." (page 3, under "Current vs. Potential). The total charge passed in the break-in period amounts to less than 1% of the total charge that contributes to products. To measure corrosion resistance, dissolved nickel in the solution was quantified by ICP-OES. Less than
0.023% of the nickel in the catalyst was dissolved after 2.5 hours of electrolysis (see ESI - Table S7), equivalent to trace amounts lost during reduction of the oxidized surface.

**Selectivity vs. Potential**

Figure 3 plots the Faradaic efficiency of each product as a function of potential and catalyst composition. Reduction of CO$_2$ to 2,3-furandiol and methylglyoxal is predominant from 0.05 V to -0.10 V vs. RHE on the more phosphorus-rich nickel phosphides (Ni$_{12}$P$_5$, Ni$_2$P, Ni$_5$P$_4$, and NiP$_2$), with Ni$_2$P giving the highest Faradaic yield at the lowest overpotential. In contrast, the low-phosphorous Ni$_3$P resulted in significantly less CO$_2$RR relative to HER and poorer selectivity, with more formic acid production than the other catalysts. The maximum selectivity of 84% for methylglyoxal was obtained on NiP$_2$ at -0.10 V. The reaction on NiP$_2$ was not performed at potentials more positive than -0.05 V vs RHE because the catalyst reached OCP near 0V, thus reducing the current and product formation below the detection limit. For 2,3-furandiol, the maximum faradaic efficiency of 71% was observed at 0 V vs RHE on Ni$_2$P.

Although formic acid is produced at all potentials, its Faradaic efficiency never exceeds 5% for any of the catalysts. At more reductive potentials (<-0.2 V vs. RHE), the reaction selectivity shifts to HER. This behavior is in stark contrast with what is observed on copper catalysts$^{38}$, where, at high overpotentials, hydrogen evolution is suppressed, and CO$_2$RR favored. This, along with the low overpotentials at which C-C coupling occurs, indicates that the mechanism of CO$_2$RR on nickel phosphides is radically different from those previously reported for simple metal catalysts.
Figure 1.3. Partial current densities obtained by the product of faradaic efficiency and current density at 3 hours of chronoamperometry. The total CO$_2$RR current is the sum of the partial current densities for 2,3-furandiol, methylglyoxal, and formic acid. Currents are normalized to the geometric surface area of the electrode. Lines are inserted only to guide the eye.

Another important figure of merit is the CO$_2$RR current density that can be achieved, depicted in Figure 4. In general, all catalysts except Ni$_3$P show distinct profiles with peaks indicative of discrete potentials that drive CO$_2$ reduction more efficiently, albeit at different peak potentials. The maximum CO$_2$RR specific current density from NiP$_2$ is -470 µA/cm$^2$ at -0.05V and a second substantial peak (-380 µA/cm$^2$) is evident at -0.3 V, suggestive of the population of two different electronic states. The former CO$_2$RR specific current density is twice that of polycrystalline copper for C$_3$ products at -1.1 V vs. RHE.$^{38}$ Only a single peak occurs on Ni$_2$P (-330 µA/cm$^2$) at -0.40 V vs. RHE, with currents that are tenfold lower at more positive potentials. For comparison, Ni$_5$P$_4$, which is notably the most active HER catalyst among the studied phases$^{27,42}$, exhibits smaller
CO\textsubscript{2}RR currents across a broader range of potentials with peaks at -0.4 V (-200 µA/cm\textsuperscript{2}) and +0.05 V (-80 µA/cm\textsuperscript{2}). The latter peak is the highest CO\textsubscript{2}RR activity among all the catalysts at this potential.

Figure 1.4. Faradaic efficiency for CO\textsubscript{2}RR as a function of potential and catalyst composition. The remaining faradaic efficiency is for H\textsubscript{2} (omitted for clarity). Electrolysis conducted in 0.5 M KHCO\textsubscript{3} (CO\textsubscript{2} saturated, pH 7.5). The three most phosphorus-rich stoichiometries, NiP\textsubscript{2}, Ni\textsubscript{5}P\textsubscript{4} and Ni\textsubscript{12}P\textsubscript{5} show selectivity for 2,3-furandiol and methylglyoxal at potentials between 0.05 V and -0.10 V.

Turnover frequencies (TOF) were determined by normalizing current density to electrochemical surface area and are listed in Table 2. TOF reveals the remarkable activity of NiP\textsubscript{2} and Ni\textsubscript{12}P\textsubscript{5} for methylglyoxal (MG) production, while for Ni\textsubscript{2}P and Ni\textsubscript{12}P\textsubscript{5} the TOF for 2,3-furandiol (FD) production. The TOFs for MG and FD products on Ni\textsubscript{2}P and NiP\textsubscript{2}, respectively, are the most selective and, additionally, produce no H\textsubscript{2} at their peak potentials. By contrast, Ni\textsubscript{12}P\textsubscript{5} has lower CO\textsubscript{2}RR selectivity between these
products and favors HER activity. Ni$_3$P produces mainly H$_2$ at all potentials and has low selectivity for CO$_2$RR, although its TOF for formate is the highest among the nickel phosphides. The TOFs for MG and FD on Ni$_3$P are of the same magnitude as the two main products, methane and ethylene, on polycrystalline copper, (~$10^{-4}$ s$^{-1}$ at -0.7 V vs RHE) but at substantially larger overpotentials.$^{38}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential (V vs RHE)</th>
<th>Turnover frequency ($10^{-6}$ mol of product/surface atom $\cdot$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HCOO$^-$</td>
</tr>
<tr>
<td>Ni$_3$P</td>
<td>-0.10</td>
<td>219</td>
</tr>
<tr>
<td>Ni$_{12}$P$_5$</td>
<td>0.00</td>
<td>16.4</td>
</tr>
<tr>
<td>Ni$_2$P</td>
<td>0.00</td>
<td>14.0</td>
</tr>
<tr>
<td>Ni$_3$P$_4$</td>
<td>+0.05</td>
<td>14.5</td>
</tr>
<tr>
<td>NiP$_2$</td>
<td>-0.10</td>
<td>2.16</td>
</tr>
</tbody>
</table>

**Energy Efficiency**

Energy efficiency ($\varepsilon_e$) is a practical metric useful when comparing CO$_2$ reduction catalysts for energy storage applications, and is defined as the ratio of the thermoneutral potential (free energy) for each product to the applied electrical energy, Eq [1]$^{43}$

$$\varepsilon_e=\Sigma(E^{0}_{x}xFE/E_{cell})$$

[1]

Table 3 gives the energy efficiency for CO$_2$RR, assuming a perfect oxygen evolution catalyst at the anode. The values range from 8% for Ni$_3$P to the maximum 99% for Ni$_2$P. For comparison, the energy efficiency is only 23% on polycrystalline copper.$^{38}$
Table 1.3. Energy efficiency of the CO$_2$RR at the potential with maximum selectivity, considering a perfect oxygen evolution anode

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential (V vs RHE)</th>
<th>CO$_2$RR Energy Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$P</td>
<td>-0.10</td>
<td>8</td>
</tr>
<tr>
<td>Ni$_2$P$_x$</td>
<td>0.00</td>
<td>65</td>
</tr>
<tr>
<td>Ni$_2$P</td>
<td>0.00</td>
<td>99</td>
</tr>
<tr>
<td>Ni$_2$P$_x$</td>
<td>0.05</td>
<td>83</td>
</tr>
<tr>
<td>NiP$_2$</td>
<td>-0.10</td>
<td>92</td>
</tr>
</tbody>
</table>

Surface changes following catalysis

The surface stability of all catalysts was further evaluated by X-ray photoelectron spectroscopy (XPS) before and after reaction. Figure 5 the experimental and fitted XPS spectra for the Ni$_2$P catalyst (additional XPS results are shown in ESI Figures S20-S24). XPS spectra are internally referenced to carbon (red peak) at a binding energy of 284.8 eV (see Figure 5), and an additional peak (blue) from partially oxidized carbon (adventitious), which appears at the binding energy characteristic of aldehydes and terminal hydroxides$^{44}$. Post-catalysis, the carbon peaks increase in intensity, along with the appearance of carbonate species (K 2p doublets from K$_2$CO$_3$ are also observed, see ESI). Both carbonate and potassium binding energy shifts are also in agreement with the presence of hydrated and anhydrous K$_2$CO$_3$ (electrolyte) post-catalysis.$^{44,45}$ In the post-reaction of Ni$_2$P, the blue C1s peak is shifted to a binding energy that could be attributed to aromatic carbons bound to hydroxide, such as those in 2,3-furandiol (reference for 1,2-dihydroxybenzene is shown).$^{44}$ This assignment is tentative as the peak could also be attributed to adventitious carbon that was not observed in the pristine catalyst.
The Ni 2p XPS spectra of Ni$_2$P (Figure 5B and E) show the characteristic $2p_{3/2}$ and $2p_{1/2}$ doublets, each with corresponding satellite peaks. The Gaussian modelling shows that three distinct chemical species are present. The species are ascribed to Ni$^{5+}$ from Ni$_2$P and Ni$^{2+}$ nickel hydroxide and/or oxide mixture (Ni(OH)$_2$/NiO), as well as Ni$^{2+}$ from Ni$_3$(PO$_4$)$_2$.\textsuperscript{44,46} This is in agreement with previous studies suggesting that nickel phosphides surface-oxidize to form a partially hydrated surface phosphate on top of the pristine nickel phosphide.\textsuperscript{27,29} The surface phosphate layer thickness will be less than 1 nm, estimated by the probe depth of XPS in Ni(s). It should be noted that the relative content (estimated by peak height) of Ni$^{5+}$ relative to Ni$^{2+}$ from the combined Ni(OH)$_2$/NiO and Ni$_3$(PO$_4$)$_2$ decreases upon catalytic turnover. When the catalyst is air-exposed post-catalysis, the surface re-oxidizes. The relative change indicates that the surface nickel oxide/phosphate thickness increases when oxidation occurs in the
electrolyte, compared to oxidation in air post-synthesis. The latter conditions favor the formation of a hydroxylated surface phosphate.

The P 2p XPS spectra of Ni$_2$P shows two sets of doublets in the 2p$_{3/2}$ and 2p$_{1/2}$ regions, which are ascribed to P$^{\delta-}$ and PO$_4^{3-}$. The ratio of P$^{\delta-}$/PO$_4^{3-}$ is seen to increase after catalytic turnover, indicating that the surface phosphate has a higher degree of hydration post catalysis due to exposure to the electrolyte. The atomic ratio of P$^{\delta-}$/Ni$^{\delta+}$ is ~1.9 both before and after catalytic turnover, respectively, and indicates that the catalyst composition does not change significantly in its reduced form (See ESI for complete XPS analysis results).

After reaction, bulk changes were also evaluated by powder X-Ray diffraction (ESI Figure S1-5). For Ni$_3$P, Ni$_{12}$P$_5$, Ni$_2$P and Ni$_5$P$_4$, no detectable crystalline impurity was formed after catalysis (< 2%). However, NiP$_2$, the most active catalyst, originally a pure monoclinic phase, partially converts (9%) to the cubic NiP$_2$ phase. Additionally, four minor peaks appear that could not be assigned based on XRD.

**Reaction mechanism on nickel phosphides**

Because all three reduction products are oxygenates, the C–C coupling step presumably occurs before the two carbon-oxygen bonds in CO$_2$ are broken. Additionally, the predominant formation of C-C coupling products implies that key reaction intermediates are bound to the catalyst by oxygen atom(s) rather than by the carbon atom, in contrast to the proposed mechanisms on catalysts that form formate as major product.$^{47}$

Because the formation of all three products takes place at near-equilibrium potential, it is helpful to consider both thermodynamic and kinetic constraints on the possible reaction
pathways to C-C coupling products. We consider the 2-electron reduction of CO\textsubscript{2} to formate first.

On formate-forming metals, where larger overpotentials are common, it is hypothesized that CO\textsubscript{2} binds through the oxygen atoms to the catalyst surface, upon the transfer of a single electron in a bent configuration followed by a proton-coupled electron transfer (PCET) to yield formate.\textsuperscript{48} However, the equilibrium potential for the single electron transfer to form the radical anion is -1.45 V vs. RHE in aqueous media\textsuperscript{49}, which is prohibitive for product formation in this study. More recently, it has been suggested that on metals such as tin, the first step of CO\textsubscript{2} reduction to formate is PCET\textsuperscript{50}, as opposed to the single electron transfer suggested above. However, transition metals that are believed to operate through this mechanism still require strongly reducing potentials (-0.7 to -1.0 V vs. RHE).

Only a few catalysts are able to reduce CO\textsubscript{2} to HCOO\textsuperscript{-} at near thermoneutral potential: the formate dehydrogenase enzyme\textsuperscript{51}, thought to operate through hydride transfer (CO\textsubscript{2} + H\textsuperscript{-} → HCOO\textsuperscript{-})\textsuperscript{52} and palladium-based materials,\textsuperscript{8,10} which are also known to form active hydrides. DFT calculations of the hydrogen evolution reaction on Ni\textsubscript{2}P, Ni\textsubscript{3}P, and Ni\textsubscript{5}P\textsubscript{4} indicate the presence of multiple types of hydride sites comprised of both Ni and P atoms at relevant potentials for HER and CO\textsubscript{2}RR.\textsuperscript{28,53–55} Notably, P sites are considered the most active for HER. These factors, together with the low potential at which the reaction operates, points to a hydride transfer mechanism for the initial step. This pathway is particularly favorable because the two-electron mechanism avoids the formation of high-energy radicals, both anionic CO\textsubscript{2}\textsuperscript{-} and electro-neutral COOH. We next examine possible C-C coupling reactions that could generate methylglyoxal and
2,3-furandiol. Figure 6 highlights the standard Gibbs free energy ($\Delta G^0$) of a few possible reactions, calculated from tabulated values of $\Delta G^0$ of formation$^{39-41}$ (see ESI section 17). Standard free energy changes may guide the prediction of a suitable pathway even though the values may differ for non-standard conditions. The $\Delta G^0$ for C-C coupling reactions becomes increasingly unfavorable in the sequence: reductive carboxylation of alcohols (-50 kJ/mol for methanol) < self-condensation of aldehydes (-25 kJ/mol for formaldehyde) < reductive CO coupling (+70 kJ/mol) < the reduction of $\beta$-ketocarboxylic acids to ketoaldehyde (+100 kJ/mol) < the carboxylation of carboxylic acids (+210 kJ/mol for acetic acid). Reductive coupling of CO units, while shown to be important for the formation of ethylene on copper at strongly reducing potentials$^{48}$, is unlikely on nickel phosphides at low applied overpotentials, as the catalyst is highly oxophilic and selectively generates formate, not carbon monoxide. It should be noted that while the reductive carboxylation of methanol is highly exergonic, alcohols are kinetically very unreactive.$^{56}$ Therefore, the most energetically favored pathway for carbon-carbon coupling, under mild conditions in a bicarbonate buffer, is aldehyde self-condensation.
The literature on formaldehyde self-condensation to form trioses and tetroses suggests that the reaction is catalyzed by Lewis acids in the presence of water. Binding of the carbonyl group of formaldehyde to a Lewis acid significantly lowers the barrier for proton abstraction from the C-H bond of formaldehyde, allowing C-C bond formation and producing glycolaldehyde. Nickel phosphides have Lewis acid character due to the partial positive charge on the nickel atoms, as shown in the XPS measurements (see Figure 5B and E), and could catalyze this aldehyde condensation. CO$_2$ itself can also catalyze this condensation via carbonylation of nucleophilic oxides and phosphides. One significant finding is that acetate is not formed, despite being thermodynamically favored (Table 1). This supports the aldehyde condensation pathway proposed, since forming C$_3$ products is both kinetically and thermodynamically favored.
Based on these steps, we propose that CO$_2$ reduction on nickel phosphides proceeds through the mechanism depicted Figure 7. In step 1, CO$_2$ inserts into a surface hydride bond to generate an adsorbed formate species, $^*$HCOO$^-$. This is believed to be the potential-determining step (PDS) because the Tafel slopes for all three observed products are roughly the same (see ESI Figure S19). We note that all three products are preceded by hydride exchange reactions with the surface, in steps 1, 2 and 10, and thus, the PDS for each product may be similar although chemically distinct steps. In step 2, formate is protonated and attacked by a second hydride, forming formaldehyde (H$_2$CO*) upon elimination of hydroxide. Although formaldehyde is not detected, it is highly reactive and presumably surface-bound to nucleophillic phosphide, whereupon two successive, energetically favored, aldehyde self-condensation reactions occur to generate glyceraldehyde. Step 6, the keto-enol tautomerization of an unactivated methyl group, is predicted to have the highest energy barrier, and thus accounts for the accumulation of the methylglyoxal precursor. This step is followed by another energetically favorable self-condensation of aldehyde with formaldehyde on the catalyst. The cyclization in step 8 forms a more stable five-membered ring by intramolecular condensation of an alcohol and an aldehyde. The hydride abstraction in step 10, the terminal product-forming reaction, is driven by the stability of the aromatic furan ring. There is precedent in literature for the hydride abstraction by nickel phosphides, as this is believed to be the mechanism for the thermally activated hydrodeoxygenation reaction that they are known to catalyze.$^{58}$ The proposed mechanism was validated by reduction of selected intermediates (formate, formaldehyde, methylglyoxal) as individual starting reagents in the absence of CO$_2$. In all cases, the resulting product distribution matched the expected
end products in precisely the same stoichiometries observed when starting from CO₂ (refer to ESI Table S10).

Figure 1.7. The proposed reaction mechanism that accounts for the three detected products highlighted in blue, for the electrocatalyzed reduction of CO₂ on nickel phosphides in concentrated dissolved bicarbonate electrolyte. The proposed surface-bound intermediates are highlighted in yellow. All intermediates are hypothesized to bind to the catalyst via oxygen

The foregoing mechanism may account for the observed preference for P-rich nickel phosphides in forming C₃ and C₄ products, as these contain more of the nucleophilic P sites for binding both CO₂ and reactive hydride formation, the kind that exhibit nearly thermoneutral binding energy.⁵⁴,⁵⁵ Such sites are favored to undergo CO₂ addition in the initial PDS, step 1. Surface reconstruction may contribute to the formation of additional P adatoms.⁵⁴,⁵⁵ In particular, the theoretically predicted reconstruction of Ni₂P [0001] produces a P-rich termination that is calculated to be highly nucleophilic.

1.3 Conclusions

This study demonstrates for the first time the use of transition metal phosphides for CO₂ reduction. Transition metal phosphides are the first class of materials, other than enzymes, that are able to convert CO₂ to C₃ and C₄ products in aqueous media at a near-thermoneutral potential with high selectivity, making them the best available electrocatalysts for forming >C₂ products. Copper is the only other non-biological
catalyst that is able to produce multicarbon products with more than 1% Faradaic efficiency. Five different nickel phosphide compounds examined here exceed this value, with NiP$_2$ the largest at 100%. When the kinetically facile HER reaction is discriminated against by using low overpotentials, the lowest energy C$_n$ products appear. A strong structure-selectivity relationship favoring higher MW C$_n$ products emerges among the five nickel phosphide catalysts as P content increases (NiP$_2$ most selective and Ni$_3$P least selective). Likewise, a strong structure-activity relationship between the integrated current producing C$_n$ products and P content emerges. Each catalyst exhibits a different current-potential profile to form C$_n$ products with distinct peaks. This is indicative of the population of discrete electronic states that form the key intermediates which produce these products. These relationships differ dramatically from pure metallic electrodes, notably copper. This study proposes a reaction pathway for the energy-efficient synthesis of multi-carbon chemicals from CO$_2$, via formate and formaldehyde intermediates, without the carbon monoxide intermediate formed when using pure metallic electrodes. Future work will focus on expansion of the mechanistic understanding of this reaction, as well as electrode engineering and catalyst development to improve current densities to industrially relevant values.

1.4 Experimental

Catalyst Synthesis

Nickel metal powder (Sigma Aldrich, 99.99%, <150 µm) was mixed with stoichiometric amounts, plus 1.5% molar excess, of red phosphorus (Alfa Aesar, 98.9%, 100 mesh). The powders were ground with an agate mortar and pestle for 10 min, transferred to a quartz tube, then flushed with argon and evacuated to less than 100 mTorr three times.
The evacuated quartz tubes contained batches of ~5 grams of sample, which were sealed and heated at a rate of 0.5 °C/min stepwise (350 °C, 450°C, and 550°C) to 700°C. The temperature was maintained for 6 hours at each intermediate step, and 24 h at the final temperature (to avoid hotspot formation due to the exothermic reaction). The powders were then analyzed by PXRD and, if not phase-pure, excess phosphorus or nickel was added and the procedure repeated as many times as necessary. The synthesized Ni₃P contained excess metallic nickel, which was removed by stirring with 10% HCl under nitrogen for 12 hours, and by washing with copious amounts of water. The acid wash was repeated as many times as necessary for complete removal of Ni, verified by PXRD.

**Powder X-Ray diffraction**

Powder X-Ray diffraction was conducted at room temperature on a Philips Xpert system, spinning at 100 rpm, in a Bragg-Brentano geometry, Cu K-alpha 0.15418 nm, calibrated daily with a Si standard. The step size used for the diffraction patterns was 0.02°, and the scan speed was 0.013°/s. The sample holder was 3 mm deep and ½” in diameter.

**Electrochemistry**

Each CO₂RR faradaic efficiency value reflects the average of at least 3 replicates. The standard deviation between HPLC measurements was smaller than 2%. The cell used was a custom-made glass-reinforced nylon-6,6 electrochemical cell, with silicon O-rings and PEEK fittings (IDEX HS). The working electrode was separated from the counter electrode by a Nafion 115 membrane (Fuel Cell Store). Platinum black deposited on Pt foil (Alfa Aesar, 99.9%) was utilized as the counter electrode. The Hach Hg/Hg₂SO₄
reference electrode was calibrated daily against a pristine Accumet SCE electrode. This
SCE was periodically calibrated against a freshly flame-annealed Pt electrode in 0.5 M
H₂SO₄ under 1 atm H₂ to calibrate to the RHE scale. The working electrode was
prepared by mixing 1.400 g of the catalyst with 1 (w/w) % neutralized Nafion
suspension and was then pressed at 22 ton onto an aluminum die. The die, containing the
pressed catalyst pellet was employed directly as the working electrode and current
collector, with only the nickel phosphide exposed to the electrolyte. Aluminum was
selected as a support because it is inert for CO₂RR\textsuperscript{34}. CO₂ (Air Gas, instrument grade,
with a Supelco hydrocarbon trap) was supplied through the bottom of the cell to both the
working and counter electrodes at a flow rate of 5 sccm (certified MKS P4B mass flow
controllers). The headspace of the working electrode compartment was sampled every
30 minutes for gas chromatography.

Electrochemical measurements were performed with a Gamry 5000E potentiostat.
Before each electrolysis, the electrolyte (0.5 M KHCO₃, Chelex treated) was pre-
saturated with CO₂ for at least an hour. Then, a chromatograph was taken to ensure that
no air was present in the headspace. An electrochemical impedance spectrum at the open
circuit from 1 Hz to 1MHz was taken to find out the uncompensated resistance (typically
between 6 and 11 ohm). Chronoamperometry was then performed for 3 hours with
positive feedback IR compensation. Between experiments, the electrochemical cell was
rinsed with Millipore water and the working electrode catalyst pellet was lightly
polished with a fine-grit silicon carbide polishing pad (BASi) before being re-used for
multiple experiments at all potentials. In doing this, the longevity of the electrodes was
confirmed, with no significant difference in product distribution observed as the
electrodes were re-used. Additional replicas were made using fresh electrodes at all potentials to ensure that the product distribution was not affected across the investigated potential region.

**Gas Chromatography**

Detection and quantification of possible headspace products (Hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene) was performed by an auto-sampling online HP 5890 Series II GC, with a 500 µL sample loop. The GC was fitted with a 6’ packed HayeSep D, and a 6’ packed MoleSieve 13X column, with thermal conductivity and flame ionization detectors connected in series. Samples were taken before reaction to check for air presence, and then every 30 minutes thereafter. Calibration curves were constructed from certified gas standards (Gasco) by CO₂ dilution using mass flow controllers (MFCs). The hydrogen calibration was done with *in situ* generated gas through electrolysis of water on platinum, under argon (supplied by an MFC), and diluted post-reaction with CO₂.

**High-Performance Liquid Chromatography (UV/RID)**

Liquid products were identified and quantified on a Perkin-Elmer Flexar HPLC equipped with an auto-sampler, refractive index (RID) and UV-VIS detector. An HPX 87H Aminex column (BioRad) was used, with injection volumes of 20 µL. The runtime was 60 minutes at a flow rate of 0.3 mL/min and 35°C. Calibration (R²>0.999) was conducted with standards of concentrations between 0.1 mM-50 mM. The standards were: formaldehyde, glycerol, ethylene glycol, methanol, and ethanol, in 0.5 M KHCO₃, detected using the RID. Acetic acid, formic acid, citric acid, oxalate, malic acid, and succinic acid standards were prepared at concentrations of 0.01 mM - 5 mM and
detected by UV at 210 nm. Product assignment was confirmed by $^1$H NMR and LC-MS, as described in detail in the ESI.

**Acknowledgements**

This work was supported by Rutgers TechAdvance through grant 205718. K.U.D.C. thanks the BASF Catalysis Division for a generous fellowship. A.B.L. gratefully acknowledges funding from Rutgers, NSF-CBET/EERE grant #CBET-1433492 and DOE-EERE-FCTO grant #EE0008083. K.M.K.Y., T.A.G. and A.L. acknowledge support from the Aresty Undergraduate Research Institute. T.A.G. thanks the Rutgers Energy Institute for Summer support. G.C D. thanks support received from the Pray Family Fund.
1.5 References


Chapter 2: CO₂ electro-reduction on Cu₃P: Selective design of a formate pathway on Cu(I) and structural activity insights into H₂ selectivity

Anders B. Laursen†, Karin U. D. Calvinho†, Timothy A. Goetjen, Kyra M. K. Yap, Shinjae Hwang, Hongbin Yang, Eric Garfinkel, and G. Charles Dismukes

†These authors contributed equally.

Abstract: Here, we report the first investigation of Cu₃P nanosheet with a predominantly [001] facet orientation as a CO₂ reduction reaction (CO₂RR) catalyst. This catalyst show undiminished activity after 16 hours of catalysis due to the retention of crystalline structure and surface chemical speciation and no detectable corrosion. CO₂RR in 0.1 M KHCO₃ finds formate as the sole carbon product, in contrast to the range of products on Cu metal, CuO, and Cu₂O. This unusual selectivity occurs at the expense of turnover rate. The high reactivity of surface hydrogen species makes H₂ the major product. A detailed structural analysis of the Cu₃P [001] facet and predicted surface termination, identifies isolated surface CuP₃ sites (formally Cu(I)) as likely active sites for hydride formation for both H₂ and formate production; explaining the product distribution. These results contradict assertions that Cu(I) alone is sufficient to promote highly active CO₂RR to C₂⁺; show that labile Cu-H (hydride) bond formation is needed to produce formate at low overpotentials, and predict that stronger bidentate formate binding is necessary for CO₂RR to outcompete H₂ production.

2.1 Introduction

The electrochemical carbon dioxide reduction reaction (CO₂RR) produces fuels or chemicals from water and CO₂ and is powered by electricity that can be sourced from
renewables (solar, wind, etc.). Hence, this reaction is a sustainable process for recycling CO₂ captured from point sources or air and can play a central role in addressing climate change. An added advantage of CO₂RR is that excess electricity from intermittent renewable sources may be stored as chemicals for later reinjection into the grid.

Since Hori’s foundational work in the 1980’s[1–4] the development of new CO₂RR catalysts has received considerable attention. Catalysts with high activity and selectivity have been uncovered for generating carbon monoxide (CO)[5–13] and formate (HCOO⁻),[14–22] but high overpotentials are still required for formaldehyde (CH₂O),[23–25] methane (CH₄),[26–30] and methanol (CH₃OH)[31–36] production. In recent years, major improvements have been made in increasing selectivity and lowering overpotentials for C₂⁺ products such as ethanol (C₂H₅OH),[37–42] ethylene(C₂H₄),[43–51] isopropanol (C₃H₇OH),[45,52,53] methylglyoxal (C₃H₄O₂),[54] 2,3-furandiol (C₄H₄O₃),[54] and hydrocarbons.[55] Nanostructured Cu is the most common electrocatalyst for ethanol and ethylene production, where the mechanism is believed to proceed via a coupling of adsorbed *CO intermediates.[56–58] Oxide-derived copper catalysts have thus far shown the most promise for selectively making C₂ products, with Faradaic efficiencies up to 70%.[42,59–66] The C₂ activity has been attributed to residual Cu(I) species in the Cu metal formed upon reduction.[61] However, the major drawback of these copper-based catalysts is the high overpotential requirement, with corresponding low cathodic energy efficiency (45%).[50]

Distinct from copper, the formation of C₃ and C₄ products on nickel phosphides has shown significant advantages in terms of Faradaic efficiency (72% for 2,3-furandiol), overpotential (10 mV), and cathodic energy efficiency (> 90%), while current densities
have lagged behind (<0.5 mA/cm²). Mechanistically, the C₃-C₄ products form through hydride transfer to CO₂, successively generating *formate then *formaldehyde (similar to the pathway in natural enzymes⁶⁷–⁶⁹), which polymerizes via enol condensation and dehydrates to methylglyoxal.⁵⁴,⁷⁰ Surface activation of *methylglyoxal generates an enol that can add CO₂ forming 2,3-furandiol.⁵⁴
Herein, we report the catalytic activity of copper(I) phosphide, Cu₃P, for the electrochemical reduction of CO₂ to formic acid. The copper-phosphorous phase diagram indicates that pure copper forms a single binary compound Cu₃P at increasing P content and temperatures below 700°C.⁷¹ Such simple phase behavior enables assessment of the oxidation state preference for CO₂RR.
Similar to nickel phosphides, Cu₃P can be expected to form surface hydrides in aqueous solution during reductive polarization. However, unlike CuP₃, six binary nickel phosphide compounds form at 700°C, and each can form multiple structurally and energetically distinct hydrides. These hydrides may potentially react with water (or protons) to form H₂, or with CO₂ to form either formic acid or CO and water or undergo further CO₂RR. What controls the branching between these pathways and turnover frequency (TOF) is the subject of extensive current research. Concepts so far considered in controlling reactivity have been hydricity, oxidation state, crystal structure, and morphology of these surface species. Here we introduce CuP₃ as a member of the transition metal phosphide that provides new insights into this family of electrocatalysts.

2.2 Results and Discussion

Catalyst Preparation

The synthesized catalyst on Cu foil (Cu₃P NS/Cu) was masked to ensure only the front foil surface was exposed. A flourosilicone polymer gasket and HDPE mask were fabricated to protect the electrical back-contact area and accurately select the exposed geometric electrode area.

The activity of Cu₃P NS/Cu was benchmarked to Cu foil, prepared as described in literature, and Cu₂O thin film on Cu foil (Cu₂O/Cu), formed by thermal oxidation of Cu foils modified from ref, annealed at 500°C for 6 hr in air. Cu₃P was etched in 30% NH₄OH prior to catalytic evaluation to remove the surface oxide formed due to air-exposure after electrode synthesis. It was observed that, in the absence of this treatment, the combined HER and CO₂RR Faradaic efficiencies did not
reach 100% even after 16-hour reactions at the highest reductive potentials (-0.5 V vs RHE) (see Figure S1). No additional gas or liquid products could be detected. The less than stoichiometric Faradaic yield indicates that some charge is directed to Cu-phosphor-oxide reduction. The re-reduction of the surface oxide back to Cu$_3$P is similar to what is observed for the reduction of Cu$_2$O to Cu under the relatively small applied overpotentials investigated here.\textsuperscript{[40]}

**Catalyst Bulk Characterization Pre- and Post-Catalysis**

PXRD was used to determine the crystalline structure of Cu$_3$P NS/Cu, see Figure 1A. Pristine Cu$_2$O/Cu was shown to be a mixture of Cu$_2$O, CuO, Cu$_8$O, and Cu by PXRD (see Figure S2-S4), and electropolished Cu foil shows only the presence of metallic Cu with some anisotropy in the grain-size, as is common in rolled metal foils. SEM analysis was used to investigate the morphology of the three investigated catalysts (see SI for details on post-catalysis prep). The morphology of pristine Cu$_3$P NS/Cu was observed to consist of nanosheets, with nanometer sized sheets extending vertically up from the substrate with random orientation in the xy-plane (see Figure C). Individual sheets were mainly 0.2 - 0.5 μm in thickness and 1-8 μm in width, with some smaller hexagonal sheets observed (100-500 nm and < 30 nm in thickness, see additionally Figure S5-S6. From the cross-section analysis in Figure C, the film thickness is seen to be 10-30 μm and continuously porous throughout. The latter provides electrolyte penetration through the entire catalyst film. SEM images of the benchmark Cu$_2$O/Cu porous film show very small pores, hardly resolved by the SEM in the cross-section view (Figure C) < 1 μm and corroborated in literature.\textsuperscript{[78]} The electropolished Cu-foil is smooth within the resolution of the SEM. Some Cu-grain-boundaries may be resolved as slight differences
in contact in the back-scatter detector. All three samples show that the morphology is retained after electrolysis. For the Cu$_3$P NS/Cu, one sample replicate showed a coarse particular deposit on the Cu$_3$P NS structure (data not shown) in certain regions; however, this was accompanied by a relatively higher carbonate signal in XPS. This indicates that the deposit is carbonate and simply due to incomplete sample rinsing. The HRTEM HAADF image in Figure 1D shows the hexagonal nanosheet structure with two sheets next to each other (see also low magnification HAADF STEM in Figure S5. STEM EELS mapping of this site shows the Cu and P sheets with a thin phosphor-oxide layer, 3.4 ± 0.9 nm, seen as a higher oxygen concentration (deep blue color). HAADF STEM images show this layer is disordered, see Figure S6. Figure E shows the HR-STEM HAADF image of a Cu$_3$P nanosheet along the [001] zone axis with atomic resolution, the crystal structure overlay verifies that the Cu$_3$P[001] facet is the major surface facet exposed to the electrolyte. This establishes that the facet exposure differs from that reported previously by Han et al, likely due to the different synthesis methods.$^{[79]}$

**Electrochemical Activity**

Fig. 1A compares the linear sweep voltammetry (LSV) of the Cu$_3$P NS/Cu in CO$_2$-saturated 0.1M KHCO$_3$ electrolyte (pH 6.8) to Ar-saturated 0.1 M phosphate buffer (pH 6.8). The cathodic current is suppressed at potentials negative of -0.7 V vs RHE in the presence of CO$_2$, while positive of this potential, the current is the same within experimental uncertainty. We note that the open-circuit potential for the Cu3P NS/Cu catalyst immediately after electrocatalysis (electroreduction) is about -0.1 V vs RHE. The open-circuit potential indicates the limiting potential for the electrocatalyst to
remain in its reduced state, since at any potential more positive of this value electro-oxidation of the catalyst (or formed products) would occur. This effectively limits the active region for CO$_2$RR to -0.1 – -0.5 V vs RHE.

Figure 2.2. Linear sweep voltammetry (scan rate: 10 mV/s) of Cu$_3$P in 0.1 M KHCO$_3$(aq) under CO$_2$ and phosphate buffer under Ar. B: Total hydride turnover-frequency (TOF) per site vs potential. C: Formic acid Faradaic efficiency on Cu$_3$P NS/Cu, Cu$_2$O/Cu, and Cu at potentials between -0.1 to -0.5 V vs RHE. D: Formic Acid TOF per site vs potential.

The Faradaic Efficiency (FE) for the observed formic acid (FA) product is shown in Figure 2C for Cu$_3$P NS/Cu, Cu$_2$O/Cu, and Cu. It is seen that the FE of Cu$_3$P NS/Cu is nearly constant with minor increase throughout the potential range (FE = 1.1 % ± 0.6 %); whereas FE increases with applied potential for the two benchmark materials. Furthermore, Cu$_3$P NS/Cu only makes FA in the entire potential region. As shown in Figure S1 in the ESI, the residual current density is used to form hydrogen, H$_2$. This high preference for making H$_2$ over CO$_2$ reduction agrees with the LSV trace showing
suppression of current in the presence of CO$_2$. This behavior contrasts with the strong preference for CO$_2$ reduction on selected compounds of nickel phosphide catalysts.$^{[54]}$ The turnover frequency (TOF) for the two-electron transfer (equivalent to a hydride transfer) to either hydrogen or formic acid production was calculated for Cu$_3$P NS/Cu and the two benchmark Cu-catalysts using their electrochemical surface areas (see SI for details). It should be noted that this method relies on the specific capacitance for each transition metal phosphide/oxide/metal which is unknown and so a common literature approximation is used here to allow direct comparison to other studies.$^{[80-82]}$ The TOF has the advantage of normalizing to the true surface area when comparing nanoporous Cu$_2$O/Cu or Cu$_3$P NS/Cu to flat Cu catalysts. Since the hydrogen species on nickel phosphides are best described as a hydride (H$^-$) species (partial negative charge on H),$^{[82,83]}$ we adopt a similar description for Cu$_3$P NS/Cu. This description posits that a surface hydride may either react with CO$_2$ to form FA (formate + H$^+$), or with water (or protons depending on pH) to form H$_2$. Hence, hydride TOF is a good descriptor for universal activity for both HER and CO$_2$RR. Fig. 1B shows that the hydrogen TOF for Cu$_3$P NS/Cu is higher at all potentials than the Cu-based references. However, as stated above, the FE to CO$_2$RR is low and specific for FA, hence, the formic acid TOF is shown in Fig. 1D. From this, it may be seen that at all potentials the low FE (seen in Fig. 1C) for Cu$_3$P NS/Cu is actually caused by a very high TOF for HER masking a good TOF for FA production; in fact the Cu$_3$P NS/Cu is on par with the FA TOF on both benchmark catalysts across all potentials. Comparing the two benchmark catalysts, it is seen that at low overpotentials Cu$_2$O produces a higher TOF to FA over the Cu-benchmark catalysts, but at more negative potentials, the Cu foil catalyst produces more
FA than Cu₂O/Cu. This is in agreement with an earlier onset of CO₂RR on Cu₂O compared to on Cu observed in literature.[78,84] Cu₃P NS/Cu thus serves as a more selective catalyst for FA production across a wider potential range than any single one of the benchmark catalysts, though its low FE is still unsuitable for application in the CO₂RR reaction.

**Literature comparison**

Since very few CO₂RR studies report the TOF, we may only compare the FE at optimized potentials. Here we consider “optimal” as the highest FE at the lowest possible overpotential, ensuring the highest energy efficiency of the reaction. While this is not the only requirement for a viable process, it is an important first criteria. Firstly, we note that the thermodynamic limiting potential for FA synthesis is reported as non-linearly dependent on pH, with a change from Nernstian behavior below the FA pKa ~ 4, while above this pH it is -0.035V vs RHE.[58] Hence, the maximal FE to FA on Cu₃P NS/Cu we observe is 0.9% at -0.1 vs RHE (η = 65 mV) or ~1.8% at potentials between -0.4 and -0.5 V vs RHE (η > 365 mV). For comparison, CuO₂/CuO/CuS has shown the largest FA selectivity for a Cu-based catalyst at 84% FE at -0.7 V vs RHE.[85] (η = 665 mV) in 0.5 M KHCO₃. The authors did not investigate the FE vs potential dependence for the CuO₂/CuO/CuS catalyst, thus precluding comparison at the same overpotential. Other state-of-the-art FA catalysts are nanostructured SnO₂[21] or Pd-Pt alloy on carbon,[22] with a FE of 8% at -0.36 V vs RHE (η = 325 mV) and 88% at -0.4 V vs RHE (η = 365 mV), respectively. Thus, Cu₃P NS/Cu is not the most selective FA catalyst but does exhibit activity at the lowest applied potentials for non-platinum group metal catalysts.
Surface Post-Catalysis Characterization

The chemical surface species of Cu₃P NS/Cu, Cu₂O/Cu, and Cu were analyzed by XPS. Cu 2p XPS spectra show insufficient binding energy shifts between Cu (932.50–933.10 eV) and Cu₂O (932.20–932.80 eV) to unequivocally assign them, and only a minor shift for CuO (932.90–934.60 eV).[86]

![Graph showing LMM Auger spectra](image)

Figure 2.3. LMM Auger spectra (A) Cu₃P NS/Cu, (B) Cu₂O/Cu, and (C) Cu before and after catalysis. (D) and (E) shows the P 2p binding region of Cu₃P NS/Cu pristine and post-catalysis, respectively.
Instead, the Cu Auger LMM lines have been used to determine the surface speciation. We analyze both Auger peak position and shape. Figure C shows the spectrum of pristine Cu (post-sputtering) with the characteristic kinetic energy peak position for metallic Cu and three well-defined satellites, two at lower and one at higher kinetic energy. After extended electrocatalytic reaction, the kinetic energy of the Auger peak decreases to a point between that of Cu and CuO; in addition, the peak shape broadens. The spectra can best be interpreted as the superposition of two oxidation states of Cu, likely Cu and CuO. This interpretation is in agreement with the (less conclusive) XPS spectra (see ESI) based on the chemical binding energies (and satellites). Figure B shows the Auger spectrum of pristine Cu$_2$O/Cu showing a broad intense satellite at kinetic energies from 916–909 eV, and a peak position of 917.8 eV. Comparing this to the NIST database,\cite{86} this is indicative of a CuO species dominating the surface, in agreement with the analysis of the XPS binding energy (see ESI). The absence of strong satellite peaks at high kinetic energy indicates that the reduced surface specie is not Cu but Cu$_2$O. In summary, the pristine Cu$_2$O/Cu catalyst is best assigned as a surface Cu$^{2+}$ oxide on a Cu$^{1+}$ oxide with the Cu substrate below the detection depth by XPS and Auger. We denote this surface as CuO/Cu$_2$O/Cu. Analysis of the PXRD pattern of this catalyst indicates an interfacial sub-oxide (Cu$_6$O) existing between the Cu$_2$O and the Cu-foil which is also below the detection depth of XPS and Auger spectroscopy. Auger spectra of CuO/Cu$_2$O/Cu taken after extensive reaction changes, and only indicates the presence of Cu$_2$O, with a peak position of 915.7 eV and a small satellite feature at 913-908 eV (and a very weak satellite peak position around 920 eV). This is in agreement with the XPS assignment showing only one chemical Cu-species (see ESI). Pristine
Cu3P NS/Cu) shows an Auger LMM peak position of 917.4 eV, a satellite peak at 919.9 eV and at 915.5 eV (see Figure C), and no evidence for CuO in XPS. The agreement between the single chemical Cu-species identified by Auger spectroscopy before and after catalysis shows that this is the same surface species, and that it is distinct from that of Cu2O, as described above. The sharpness of the Auger LMM peak is suggestive of a metallic state, whereas the Cu-2p region in XPS shows 2p satellites less pronounced than for Cu-metal (see ESI). Together, this suggests a Cu-species with an oxidation state between Cu0 and Cu1+. This is consistent with greater P→Cu charge transfer in Cu3P than in Cu2O, as expected based on elementary concepts in bonding (electronegativities and orbital overlaps).

Finally, we examined the P 2p3/2 and 2p1/2 doublet region which we attribute (based on peak positions) to the transition metal phosphide and surface oxide (see Figures D&E). We observed no significant difference between the spectra before and after catalysis. Both samples show a P 2p3/2-peak at low binding energy (P2p3/2 = 129.4 eV and 129.1 eV, before and after catalysis respectively), from the transition metal phosphide. The slight reduction in binding energy after catalysis indicates an overall slight reduction of the surface P-species post-catalysis, indicative of improved P→Cu charge transfer. Additionally, both samples also show a doublet at high binding energy with a P2p3/2 peak position at 133.1 and 132.9 eV, respectively. By comparison the P2p3/2 peak position for reference compounds in the NIST database shows binding energies of Ni3(PO4)2 = 133.3 eV, Na2HPO3 = 132.9 eV, and NaH2PO2 = 132.6-132.9 eV[86]. On this basis, we assign the surface speciation upon air-exposure to the formation of
phosphorous oxide (likely a hypophosphite/phosphate), analogous to the behavior of nickel phosphides.\textsuperscript{[82,83]}

**Atomic Surface Structure**

Cu\textsubscript{3}P is a high melting temperature (900°C), diamagnetic, non-conducting, inert solid (it does not react with water or air). Its standard enthalpy of formation relative to red P is $\Delta H_f^0 = -39.7 \pm 2.1 \text{ kJ mol}^{-1}$.\textsuperscript{[87]} It crystalizes in the hexagonal space group, P\textsubscript{6}3\textsubscript{cm}, No. 185, which can be viewed as Cu\textsubscript{6}P prisms with Cu atoms outside the faces of the prism.\textsuperscript{[88]} Hence, P is coordinated to 11 Cu atoms, an unusually high number.\textsuperscript{[88]}

Cu\textsubscript{3}P[00\text{I}] is known to be the preferred cleavage plane of bulk crystals in the absence of structure directing ligands.\textsuperscript{[89]} Literature studies predict that [002] and [1\text{I}0]-facets are the most stable non-reconstructed facets based on highest atomic packing density at the surface using the Bravais-Friedel-Donnay-Harker (BFDH) crystal morphology algorithm.\textsuperscript{[90]} Based on our HRTEM results, we show that during synthesis TOP acts as a structure directing agent selecting the Cu\textsubscript{3}P[00\text{I}] surface. The Cu\textsubscript{3}P[00\text{I}] facet may produce three different bulk terminations (prior to any surface reconstruction): Cu\textsubscript{4}, Cu\textsubscript{3}P\textsubscript{3}, and Cu\textsubscript{6} (see SI Figure S11). For Cu\textsubscript{3}P[00\text{I}], the most phosphorous rich termination is the Cu\textsubscript{3}P[00\text{I}]-Cu\textsubscript{3}P\textsubscript{3} (see Figure 1B and SI Figure S12). P rich terminations has been generally shown to be the more stable termination based on DFT calculations of the related Ni\textsubscript{x}P\textsubscript{y} compounds.\textsuperscript{[82,91,92]} The Cu\textsubscript{3}P\textsubscript{3} termination of the Cu\textsubscript{3}P[00\text{I}] facet and is also the most atomically dense, suggesting a high degree of saturated bonds, another sign of a low surface energy (higher stability).

The higher stability of P rich termination of both copper and nickel phosphides can be understood in terms of the bonding types described above: P enrichment relative to the
bulk composition means more M-P (M = Ni/Cu) neighbors per unit area, hence a lower surface energy. In the following we use this prediction, that Cu$_3$P$_3$ is the exposed termination of Cu$_3$P[001] during CO$_2$RR.

**Active Site and Reaction Mechanism**

The CO$_2$RR mechanism has been extensively studied on Cu metal and other mono-metallic surfaces.\[^{56-58,93,94}\] However, much less is understood about the reaction on binary surfaces such as transition metal oxides and, in particular, transition metal phosphides. More is known about the CO$_2$RR mechanism on the nickel phosphides.\[^{54}\] CO$_2$RR on metallic Cu surfaces is postulated to proceed through *CO intermediates that combine on the surface to form the monoanion of ethene-1,2-dione, *O*CCO$^-$, where * indicates a surface bound atom.\[^{58}\] This postulate comes from indirect evidence that OCCO$^-$ is known to be an isolable (stable) ion.\[^{95,96}\] Such bidentate binding would require two adjacent surface atomic sites. A similar mechanism was recently proposed on a transition metal phosphide, FeP[2II] nanoarray catalyst which produced only methanol or ethanol in addition to H$_2$.\[^{36}\] For this compound DFT studies indicated the Fe-Fe site distances are within a C-C coupling distance of two CO units. However, the authors’ calculations showed a $\sim$0.8 eV barrier to ethanol formation. This barrier is not in agreement with the experimental observation of the product formation at -0.2 V vs RHE; casting doubt on the *a priori* assumption of a *CO mediated mechanism. Figure A depicts the Cu$_3$P[001]- Cu$_3$P$_3$ surface, where it can be seen that the (bulk) Cu-Cu distance of 4.11 Å is much greater than the 1.54 Å C-C bond distance of ethylene glycol, for instance (an approximate model for the OCCO$^-$ intermediate on Cu), thus precluding a Cu-centered *CO +*CO coupling reaction on this surface. Since no CO product is
observed on Cu$_3$P NS/Cu, the CO$_2$RR mechanism appears to be very different from that on metallic Cu.

DFT calculations have suggested that all H-species bound on nickel phosphides are hydridic in nature (partial negative charge on H), making this latter mechanism feasible.\cite{82,83}

Figure 2.4. A: Top-view Cu$_3$P[001]-Cu$_3$P$_3$ surface termination showing nearest Cu-Cu bond distance and Cu-P distance. Two types of trigonal CuP$_3$ sites: dark blue Cu is above surface P and light blue Cu is below surface P; B: Side view of the Cu$_3$P[001]-Cu$_3$P$_3$ surface termination. C: Atomic orbital diagram of the trigonal pyramidal [CuP$_3$] units surface sites and the tetrahedral [CuP$_4$] units of the active site with monodentate ligand binding at the [CuP$_3$] unit. D: Reaction mechanism of Cu$_3$P[001]-Cu$_3$P$_3$ and schematic active sites for formate.

Figure B shows a side-view of the Cu$_3$P[001]-Cu$_3$P$_3$ termination. The surface may be described as alternating rows of Cu and P atoms (with sub-surface layer Cu-P-tetrahedra), which together form CuP$_3$ trigonal pyramidal clusters (alternating triangles of CuP$_3$ (in blue in Figure 4B)). Within the CuP$_3$ triangles, the Cu is distorted slightly
out of the P-plane, alternating between sitting above and below the surface plane. The Cu-P distance is measured to be ~2.37 Å in the crystal structure. The Cu-Cu distance between Cu-P triangles distorted in the same direction out of the P-plane is 6.959 Å, while it is 4.111 Å between Cu atoms within alternately distorted sites.

Figure D shows a proposed mechanism on a CuP₃ trigonal pyramidal site present on the Cu₃P[00ι]-Cu₃P₃ termination. This mechanism postulates a hydridic species (H⁻) on the Cu₃P surface analogous to the related NiₓP-compounds[82], and that predicted on Cu₃P [Ι0].[90] There are three high symmetry surface sites on Cu₃P[00ι]-Cu₃P₃; two CuP₃ trigonal pyramidal (dark and light blue, Figure (A)) and one tetrahedral subsurface site (magenta and dark purple, Figures (A) and (B)). The latter sub-surface site is coordinatively saturated and therefore less likely to participate directly in the reaction mechanism. We also note that the surface P atoms are coordinated to 7 Cu atoms; being coordinatively saturated they are unlikely to participate in the catalytic substrate binding. Since both the CuP₃ triangles populating this surface are coordinatively unsaturated (Cu is 3-coordinate and either slightly above surface (dark blue) or slightly below surface (light blue) the binding of substrate protons (to form hydrides) or CO₂ can easily proceed through a simple displacement from trigonal pyramidal to tetrahedral. Hydride formation is expected to be quite facile for the Cu sites that lie above the surface. Figure C shows a qualitative atomic orbital diagram for the Cu(I) ion (4s¹3d⁰ electronic configuration) in the tetrahedral (subsurface) and trigonal pyramidal sites. It can be seen that the subsurface site has a lower electron energy in the ground state compared to the trigonal pyramidal CuP₃ which has higher energy filled d-orbitals. By analogy, it is evident that mono-dentate binding of hydride, formate, or CO₂ to form tetrahedral active
site geometry in lower energy configurations; thus, favoring the mono dentate binding motif at CuP$_3$.

The mechanism starts with a 2-electron reduction and substrate binding ($\text{H}^+$) to the trigonal pyramidal Cu(I) resulting in distortion to a tetrahedral geometry concurrent with hydride formation (H$^-$). This reaction is driven by the change of electronic configuration to 4s$^0$3d$^{10}$, which is energetically favored in tetrahedral geometries, and by hybridization of H(1s) and Cu(3p$_x$) orbitals to form the hydride bond (here denoted as H(1s$^2$) for simplicity). Importantly, this orbital assignment can also account for the observed absence of a reaction rate dependence on applied potential, since these orbitals are isolated by energy and symmetry from other states near the Fermi level. In the next reaction step (see Figure 4D), hydride formation at CuP$_3$ is the precursor for oxidative insertion of CO$_2$ into the Cu-H bond, resulting in the formation of a monodentate *formate species (analogous to the proposed mechanism on Ni$_3$P).$^{[54]}$ In the final step, the *formate intermediate is released by protonation while the Cu(I) moves to its original trigonal pyramidal location, together with a return of the electronic configuration to 4s$^1$3d$^9$, leaving the surface open for subsequent catalytic turnover.

In contrast to Cu$_3$P, the Ni$_2$P surface offers a slightly shorter distance Ni$_3$P-trigonal site and one fewer electron per Ni which would readily allow stronger binding of bidentate formate. The proposed mono-dentate binding of formate to CuP$_3$ results in weaker binding and lower population than on Ni$_2$P, thus explaining why hydride formation out-competes hydrogen production.

Finally, we note that there are literature reports of Cu$_3$P[110] facet synthesis, which also forms three terminations (see ESI). Literature DFT calculations predict that the
Cu₃P[1̅0]-Cu₅P₂ termination is the most stable surface termination but undergoes a slight reconstruction to a more P-rich termination (see above). This termination exposes a distorted Cu₃ trigonal surface motif, which consists of two corner-sharing tetrahedral units and one corner-sharing trigonal planar CuPₓ-unit (see SI Figure S15 with the vertex P missing. This multi-Cu site has clear similarities to the Ni₂P[00̅1]-Ni₂P₃ surface[92] — which consists of three corner sharing tetrahedra with the vertex P missing at low applied potentials[72] — the most active for CO₂RR of the nickel phosphide compounds.[54] This Cu₃P[1̅0]-Cu₅P₂ surface would allow for C-C coupling, since the Cu-Cu distances are only 2.57-2.71 Å. This surface has also been predicted by DFT calculations to have an H-binding energy of -12 and -36 meV on the two nonequivalent Cu₃ triangles formed by surface reconstruction.[90] Due to the near thermoneutral H bonding, these sites are expected to be highly labile and consequently, could be more active for CO₂RR than the Cu₃P[00̅1]-Cu₅P₃ facet and Ni₂P[00̅1]-Ni₂P₃ (with H-binding energies of ~ -0.5 eV). Unfortunately, we note that the reported Cu₃P[1̅0] was grown on a Ni foam and contains significant amounts of Ni, and when we attempted to apply the reported synthesis conditions to a Ni-free environment (using a Cu foam support), the resulting catalyst showed no preferential faceting. If an appropriate synthesis could be developed, the investigation of Cu₃P[1̅0] nanosheets could confirm the importance of M₃ triangle sites as the active site for CO₂RR resulting in Cₙ>1 products.

2.3 Conclusions

Among the several polymorphs of CuₓP, each with slightly differing structures, we have produced a single-phase catalyst (P63cm space group) supported on metallic copper, which is well suited to electrochemical applications and mechanistic studies. Unlike
most Cu, CuOₓ, or copper oxide-derived CO₂RR electrocatalysts which have low carbon selectivity to C₁ and C₂ products, the Cu₃P NS/Cu catalyst exclusively forms formate at very low overpotentials. Energetic considerations imply the CO₂RR mechanism occurs via surface hydrides (not via one-electron pathways). Surface hydrides formed in the aqueous electrolytes strongly favor HER over CO₂RR, similar to Ni₃P but in contrast to other NiₓPₓ compounds.⁵⁴,⁸²,⁸³ We have proposed a mechanism that explains this selectivity by considering the Cu₃P[001] facet with Cu₃P₃-termination (predicted to be the most stable surface). We have given an electronic and structural argument explaining why the CuP₃ trigonal pyramidal sites form hydrides that favor oxidative CO₂ insertion to formate with higher selectivity compared to both the Cu₂O and Cu benchmarks, which are known to yield C₁ and C₂ products at high overpotentials. Literature reports have correlated the latter activity to the Cu⁺ sites retained on the surface under reductive conditions. Here, we have shown that the Cu⁺ site alone is insufficient to achieve high CO₂RR activity, and that a multi-copper site is essential to produce C₂ or larger products.

Cu₃P NS/Cu exhibits a fairly negative open circuit potential of ~100mV vs RHE, which is more negative than what is observed on e.g. Ni₃P, Ni₁₂P₃, Ni₂P, and Ni₅P₄,⁵⁴ and which we argue is one manifestation of the different electronic structure that causes Cu₃P to be more prone to oxidation than the nickel based phosphides.

The presented data from Cu₃P NS/Cu allows us to deduce the following list of attributes needed to design a particularly active CO₂RR catalyst:

Cu(I) alone is insufficient for an active CO₂RR site; formation of a labile Cu-H (hydride) bond is the precursor to formate production.
An active site that allows bidentate bonding of the *formate intermediate is needed to out-compete HER (as in Ni$_2$P).

To form C$_2$ and larger products, an additional requirement is a second hydridic site (P-H) within bonding distance (<4.1Å) that enables reduction of *formate to *formaldehyde, which is a precursor to C-C coupling.$^{[54]}$

Coordinative stability of the Cu(I) species during catalytic turnover as occurs for Cu$_3$P provides long term operational current stability for >16 hours.

The synthesis of Cu$_3$P with the [110] facet exposure is also suggested by this investigation to yield a more stable CO$_2$RR catalyst.

2.4 Experimental Section

Catalyst Synthesis

Due to low conductivity, a bulk powder of Cu$_3$P could not serve as a electrocatalyst at any relevant current density. Instead, to ensure an intrinsic Cu$_3$P activity was determined, a phase-pure Cu$_3$P nanostructured film was synthesized on a mechanically polished Cu foil substrate. The resulting uniformly Cu$_3$P-coated Cu foil electrode was termed Cu$_3$P NS/Cu. Briefly, catalyst synthesis (see SI for details): Cu foils are mechanically polished, sonicated three times in 1 M HCl, water, and acetone; and air-dried. The reaction vessel was evacuated of O$_2$, re-filled with N$_2$ prior to 45 min reaction of the cleaned foils in tri-octylphosphine/tri-octylphosphine oxide (TOP/TOPO) solution under a N$_2$ flow at 310°C, maintained by immersion in a pre-heated sand bath (ensuring rapid heating to reaction temperature). After air quenching, the foil was sonicated in an acetone/ethanol mixture to remove excess loose Cu$_3$P product, yielding
the final catalyst used in subsequent analyses. It is important to note that the catalyst was stored in a desiccator to avoid excess surface oxidation by moist air.

**Catalyst Characterization**

Powder X-ray diffraction (PXRD): PXRD was conducted on a PANalytical X’Pert Pro system. Patterns were interpreted using the X’Pert HighScore Software referenced to the International Center for Diffraction Data, ICDD. See SI for details.

X-ray Photoemission Spectroscopy (XPS): A Thermo K-Alpha spectrometer was used with a flood gun for charge compensation. Spectra were calibrated against carbon (284.8 eV). For the Cu foil sample, a 3.5 mm diameter spot (much larger than the imaged area) was cleaned to remove the native oxide with Ar sputtering at 1 keV until only metallic Cu 2p peaks were detected.

Scanning Transmission Electron Microscopy and Electron Energy Loss Spectroscopy (STEM & EELS): High angle annular dark field (HAADF) imaging and EELS mapping were performed using a Nion UltraSTEM 100, operating at 60 kV. Probe convergence and HAADF collection angle used was 30 mrad and >80 mrad, respectively. Cu₃P nanosheets were removed from substrate and dispersed in acetone before placement on a lacey carbon TEM grid.

Scanning Electron Microscopy: A benchtop Phenom instrument at 10 keV acceleration was utilized to image samples. Samples were mounted on Al-stubs using carbon tape and cross-section samples precut using scissors. Cross-section regions were chosen where minimal compressive damage was observed.
Electrochemistry

The reaction was performed in a custom glass-fiber reinforced nylon-6,6 electrochemical cell, as described previously.[54] A Nafion 115 membrane separated a Platinum black/Pt foil anode from the Hg/Hg2SO4 reference electrode and the working electrode (WE) foil. An aluminum tape strip was contacted to the back of the WE and was masked off using a fluorosilicone gasket.

Purified CO2 was supplied to both the working and counter compartments at 5 sccm. The WE headspace was sampled every 60 minutes by gas chromatography (GC), and the liquid solution analyzed by liquid chromatography after each potential change. The 0.1 M KHCO3 electrolyte was Chelex treated to capture contaminants.[97] Electrochemical impedance spectroscopy was utilized to determine the uncompensated solution resistance, typically 80 Ω. The WE surface oxide was removed with concentrated ammonium hydroxide for 30 s before re-using electrodes at all potentials; no significant product distribution difference was seen between fresh or used electrodes, indicating no potential “memory” affecting results. See SI for details.

Product Detection/Quantification

Gas-Chromatography (GC): Product detection and quantification of possible headspace products (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene) was performed by in-line auto-sampling on a HP 5890 Series II GC with serial connected thermal conductivity and flame ionization detectors. See SI for details.

High-performance liquid chromatography (HPLC): Liquid products were quantified on a Perkin-Elmer Flexar HPLC equipped with an auto-sampler, refractive index and UV-vis detectors. Using an HPX 87H Aminex column, flow rate of 0.3 mL min⁻¹ at 65°C,
standards were calibrated between 0.05 and 10 mM. Product assignment was confirmed by $^1$H-NMR. Each measurement reflects the average of at least 3 replicates, with standard deviations <2%.

2.5 Acknowledgements

This work was supported by Rutgers TechAdvance through grant 205718. K.U.D.C. thanks the BASF Catalysis Division for a generous fellowship. Authors gratefully acknowledge funding from the NSF-CBET/EERE grant #CBET-1433492 and the continuation DOE-EERE-FCTO grant #EE0008083. T.A.G. acknowledges support from the Aresty Undergraduate Research Institute and thanks the Rutgers Energy Institute for Summer support. G.C.D. thanks the Pray Family Foundation for their support.
2.6 References


[89] Steel Data, “Copper Phosphide - Cu3P,” can be found under http://www.steeldata.info/etch/demo/help/compounds/41.html, **n.d.**


Chapter 3: Electrocatalytic CO₂ Reduction on Isostructural Fe₂P vs. Ni₂P: Shifting Carbon Product Selectivity to Ethylene Glycol on Iron Phosphide

Karin U. D. Calvintosh, Abdulaziz Alherz†, Kyra M. K. Yap†, Anders B. Laursen, Shinjae Hwang, Zachary J. L. Bare, Charles B. Musgrave, G. Charles Dismukes

†These authors contributed equally.

Abstract

The electro-catalyzed conversion of carbon dioxide and water to organic chemicals and fuels is a renewable process with the potential to replace petroleum feedstocks while lowering atmospheric CO₂. Chief among these are monomer precursors to renewable plastics such as ethylene glycol. We introduce iron phosphide (Fe₂P) as a new, earth-abundant catalyst for the electrochemical reduction of CO₂ (CO₂RR) to ethylene glycol with a maximum Faradaic efficiency (FE) of 22% at -0.05 V, and to other carbon products: formic acid (C₁), methylglyoxal (C₃), and 2,3-furandiol (C₄) at 0 V vs. RHE, reaching 53% total carbon FE. Comparatively, the isostructural Ni₂P favors the production of 2,3-furandiol, with no formation of ethylene glycol.

To explain this selectivity shift, we investigate the influence of replacing nickel by iron in the crystal structure through a Grand Canonical DFT (GC-DFT) model to realistically incorporate the effects of the applied potential and solvent on electrocatalysis. Both theoretical and experimental results reveal that weakly bound Fe₃P-H surface hydrides on the P-enriched (reconstructed) surface are the precursors to both CO₂RR and HER. The surface hydrides become more hydridic as the bias increases, favoring high turnover of low barrier hydride transfer reactions, such as those that produce ethylene glycol, over C₃ and C₄ products, explaining the higher selectivity towards shorter chain products. Finally, density of states maps reveal that adsorbed formate bonding is
stabilized on the surface as the potential is stepped from 0V to -0.1 V, but at -0.2 V, as
the orbitals re-hybridize, anti-bonding states get closer to the Fermi level and formate
adsorption is destabilized, providing a rationale for the experimentally observed peak
CO$_2$RR current at -0.1V.

3.1 Introduction

The electrochemical reduction of waste carbon dioxide (CO$_2$RR) is a promising
renewable technology for generating valuable carbon-based products, including
monomers for polyethylene and polyethylene terephthalate (PET).$^{1,2}$ Commercializing
this technology would aid in the replacement of petrochemicals and tackle global
warming. In recent years, there have been many developments in electrocatalysis leading
to high activity and selectivity for the conversion of CO$_2$ to CO$_3$$^{13-12}$ or HCOOH.$^{13-21}$
Conversely, very few catalysts have been developed that can produce high-value, multi-
carbon products with notable efficiency. Most state-of-the-art catalysts that facilitate C-
C coupling are copper-based, and produce a mixture of two or more of C$_2$H$_4$, C$_2$H$_6$,
C$_2$H$_5$OH and/or n-propanol.$^{22-34}$ However, these catalysts suffer from: 1) low selectivity
and tunability to a single product, 2) high required overpotentials, and 3) limited
stability.

Transition metal phosphides (TMPs) are a family of CO$_2$RR catalysts that have recently
emerged. Although TMPs were predicted to predominantly catalyze HER at the expense
of CO$_2$RR activity$^{35}$, our group has shown that nickel phosphides are exceptional
CO$_2$RR catalysts inspired by natural CO$_2$RR enzymes.$^{36}$ In particular, Ni$_2$P and NiP$_2$
readily discriminate against H$_2$ formation to produce CO$_2$RR oxyhydrocarbons with FE
of 71% at 0 V vs. RHE on Ni$_2$P for C$_4$ formation and 84% at -0.10 V vs. RHE on NiP$_2$
for $C_3$ formation. This discrimination has been attributed to different chemical mechanisms, with nickel phosphides catalyzing hydride insertion (*H) into C to produce adsorbed formate bound through its oxygen atom(s) (HCOO*), in contrast to Cu-based catalysts which are proposed to operate via proton-coupled electron transfer to generate products bound through carbon (*CO). Density functional theory (DFT) studies produced key evidence that shows that HER on nickel phosphides (e.g. on Ni$_2$P and Ni$_3$P) proceeds through a hydride catalytic site that binds weakly to a reconstructed P adatom layer (*PH) at near thermoneutral binding energies ($\Delta G_{H,\text{bind}} \sim 0$).

We predict that di-iron phosphide, Fe$_2$P (iso-structural with di-nickel phosphide, Ni$_2$P) stabilizes formation of the P* layer. Because metallic iron atoms have two fewer electrons than nickel, and an ionization potential closer to P than that of nickel, DFT predicts that more electron density transfers from P to Fe in Fe$_2$P than from P to Ni in Ni$_2$P. Accordingly, we expect weaker binding energies of surface hydrides (P-H*) on Fe$_2$P than on Ni$_2$P, and therefore, lower hydride populations and shorter residence times on the catalyst surface. Thus, both thermodynamic and kinetic factors should favor faster HER over slower CO$_2$RR. We examine this hypothesis experimentally and theoretically through DFT calculations.

Another iron phosphide phase (FeP) has been previously reported to selectively catalyze electrochemical CO$_2$RR towards methanol and ethanol at -0.2 V vs RHE. Sun and coworkers predict that the reduction mechanism undergoes a proton-mediated CO$_2$RR mechanism involving a CO intermediate. Yet, while plausible, this pathway is predicted to have a barrier as high as 2.3 eV, inconsistent with the potentials applied experimentally.
Although this report is not the first observation of electrochemical ethylene glycol production from CO₂ (preceded by Au⁴³, Ru⁴⁴, and Cu²,⁴⁵ based catalysts at high overpotentials, -0.58 V vs. RHE⁴³), it is the first such observation of catalysis by a transition metal phosphide and achieves a major improvement by lowering the overpotential to 0.0 V vs. RHE.

Finally, state-of-the-art Grand Canonical Electronic Density Functional Theory (GC-DFT) calculations are employed to explore the effects of applied potentials on electrocatalytic activity. This method models the free flow of electrons to and from the electrode to maintain the applied bias by self-consistently solving for the number of electrons that minimizes the grand free energy at a specified chemical potential corresponding to the applied bias. This in turn predicts surface electronic densities as a function of applied potential, which reveal unanticipated trends in computed adsorption energies that traditional DFT approaches fail to predict.

We report catalyst activity with CO₂ and hydrides as a function of bias via thermodynamics calculations of adsorption energies. The Fe₂P surface structure is predicted to reconstruct via the formation of a phosphorus adatom layer on Fe₃ hollow sites, analogous to Ni₂P. P* is shown to bind significantly more strongly on Fe₂P than on Ni₂P which weakens bonding of both surface hydride and hydroxide ligands, with consequences on the Faradaic efficiency (FE) of both CO₂RR and HER products. More stable reconstructions in the form of strong P-Fe₃ bonds – relative to P-Ni₃ – consequently result in weaker Fe₃P-H bonds that lead to a lower surface hydride population and shorter surface lifetimes. As a result, the high energy Fe₃P-H surface hydrides will likely favor HER and short-chain CO₂RR products such as ethylene
glycol, which tend to exhibit smaller hydride transfer barriers. C₃ and C₄ products with supposedly high barriers cannot be produced as efficiently as increasing the applied potential only biases the reaction more towards HER. Based on the insights gained from our GC-DFT results, we postulate that the hydride bond strength is an important descriptor for CO₂ reduction to formate. Our results indicate that the surface hydride bond changes irregularly with bias, and this irregularity correlates to some extent with experimental observations.

3.2 Results and Discussion

Catalyst purity and active surface

Phase-pure, polycrystalline iron phosphide (Fe₂P) was synthesized by solid state reaction at 800°C for 24 h. The high temperature and long reaction time were used to ensure thermodynamic facet equilibrium. Figure S1 shows the powder X-ray diffraction pattern (PXRD) of the as-synthesized Fe₂P powder match of all observed peaks to the ICDD reference pattern confirms that the catalyst was phase-pure within the detection limit.

Multiple experimental and theoretical studies have shown that the Ni₂P [0001]₃⁷,₄₆,₄₇ – and therefore by extension iso-structural Fe₂P [0001] – are the most stable and active exposed surfaces. Both Ni₂P and Fe₂P [0001] surfaces have repeating layers with M₃P and M₃P₂ stoichiometries, thus averaging to a total stoichiometry of M₂P (See Figure S2). Using the CANDLE solvent model, the DFT analysis of the Fe₂P [0001] surface facet indicated that the Fe₃P₂-terminated surface has a lower surface energy and is a more stable termination than the Fe₃P termination by approximately 5.3 meV/Å².
Figure 1 shows the adsorption energy of H*, OH* and P* to the Fe₃ hollow site on the Fe₃P₂ terminated surface (shown in Figure 2). Relative to H* and OH*, P* has highly favorable adsorption energy onto the Fe₃ hollow site across the investigated range of applied potentials of +0.2 V to -0.20 V vs. RHE at a pH of 7.5.

![Graph showing adsorption energies](image)

Figure 3.1. Computed adsorption energies vs applied electrical bias
Computed adsorption energies (eV) vs. applied electrical bias (V vs. RHE, pH = 7.5) using GC-DFT. Two unique adsorption sites are examined: the Fe₃ hollow and the reconstructed P site (Pr). Strong adsorption of P on the Fe₃ site shows that the surface is thermodynamically more stable when P-reconstructed (P*) than not. Adsorption energies of H* and OH* vs. applied bias show that population of states centered around -0.1 V vs. RHE decreases adsorbate affinity on Fe₃ hollow, while the reverse trend occurs for H* and OH* adsorbates on the reconstructed P@Fe₃ site, where their affinities increase.
Figure 3.2. Fe₃P surface top view highlighting the Fe₃ hollow site and P adsorbed
Fe₂P (0001) surface top view highlighting the Fe₃ hollow site and P adsorbed on the B) native surface, C) phosphorus-reconstructed surface, with D) H and E) OH adsorbed on the P adatom of the reconstructed surface

Our calculations indicate that P* adsorption is favored at 100% site coverage; thus, it is likely that the entire Fe₂P [0001] facet reconstructs to form the fully covered P* surface (see ESI, Figure S3). The predicted Fermi level for the fully reconstructed P*/Fe₃P₂/Fe₂P [0001] surface indicates that the point of zero charge is 0.46 V vs. RHE, in agreement with the measured open circuit potential of 0.45 V. P* adsorption at a [distorted Fe₃ or Fe₃P hollow] site on this facet of the reconstructed surface is less favorable by ~0.2 eV than adsorption at the Fe₃ hollow site and requires more extensive reorganization of adjacent Fe atoms, as shown in Figure S3. These larger atomic displacements required to form this less symmetric reconstructed surface indicate a larger barrier and likely slower kinetics vs the symmetric P-Fe₃ hollow reconstruction. Hence, both thermodynamic and kinetic barriers indicate the symmetric P-Fe₃ hollow reconstruction forms more easily and is the likely catalytic surface. Similarly, Rappe et al found that P* reconstruction is energetically favorable on analogous Ni₃ hollow sites of Ni₂P and likely serves as the catalytic site for HER³⁸,⁴⁸.

Relative to Ni₂P, the surface reconstruction on Fe₂P is significantly more favorable by ~1.1 eV/site (Figure S4). The much stronger P* affinity on reconstructed Fe₂P is
expected based on the fewer electrons of Fe\(^0\) ([Ar]3d\(^6\) 4s\(^2\)) occupying antibonding d-orbitals relative to Ni\(^0\) ([Ar] 3d\(^8\) 4s\(^2\)) and the smaller energy gap between Fe and P valence orbitals than between Ni and P valence orbitals, which allows for greater hybridization. Indeed, this increase in M-P bond strength for Fe is responsible for the shorter M-M distance on Fe\(_2\)P at ~3.05 Å compared to 3.18 Å for Ni\(_2\)P.

**Electrochemistry**

Working electrodes were prepared by mounting an Fe\(_2\)P catalyst pellet in a sandwich-type liquid electrolyte cell (described earlier\(^{36}\)), where the counter and working electrode are separated by a Nafion 115 membrane. Linear sweep voltammetry was conducted in the presence and absence of CO\(_2\) to determine the Fe\(_2\)P CO\(_2\) reduction and hydrogen evolution activity, respectively. The results are shown in Figure 3A. At potentials less reducing than -0.10 V vs. RHE, CO\(_2\) activates a higher total current density in comparison with the Ar-saturated phosphate. This indicates that at mildly reducing potentials (0.00 to -0.10 V vs. RHE), CO\(_2\) reduction activity dominates over HER. Although the competing HER is kinetically favored with increasing driving force (< - 0.10 V vs. RHE), the presence of CO\(_2\) decreases the total current density. This suggests that one or more CO\(_2\)RR intermediates binds strongly to the catalyst surface suppressing the HER activity, as supported by theoretical calculations below. This is direct evidence for a common active site or shared intermediate for CO\(_2\)RR and HER. The same behavior is seen on nickel phosphides.\(^{36}\)
Figure 3.3. iR-corrected linear sweep voltammetry, chronoamperometry, faradaic efficiency, and steady-state current density

A) iR-corrected linear sweep voltammetry of Fe$_2$P at 0.5 mV s$^{-1}$. Tests were conducted in argon-purged 0.5 M phosphate buffer at pH 7.5 (grey), where current density is due to HER, and in CO$_2$-saturated 0.5 M KHCO$_3$ at the same pH (green), where current is due to CO$_2$RR and HER. Binding of CO$_2$RR intermediates to the catalyst surface partially suppresses HER, decreasing current density. B) Chronoamperometry at potentials ranging from 0 to -0.2 V on Fe$_2$P, in CO$_2$-saturated 0.5 M KHCO$_3$. C) Faradaic efficiency for CO$_2$RR products on an Fe$_2$P catalyst, with a 0.5 M KHCO$_3$ electrolyte. The remaining Faradaic efficiency is hydrogen. D) Steady-state total current density in gray and total CO$_2$ current density in blue (product of the CO$_2$RR FE and current density).

Representative chronoamperometry traces from 16-h experiments in 0.5 M KHCO$_3$ with a constant CO$_2$ flow of 5 sccm are shown in Figure 3B. The high porosity of the catalyst causes an initial induction period of up to two hours during which the iron-phosphorous-oxide catalyst surface is reduced and equilibrated with adsorbed intermediates concurrently with CO$_2$RR.$^{30}$ A steady-state current is reached thereafter and maintained for the remainder of the experiment. Repeating the chronoamperometry after electrolyte
replacement and at any of the selected potentials with the same catalyst pellet reproduces the induction period and steady-state current. This indicates that the induction period is caused by a reversible phenomenon consistent with the equilibration of a porous surface with reaction intermediates under applied potential.

**CO₂ Reduction Reaction Products**

After a constant reduction potential was applied for 16 h, the liquid products were analyzed by HPLC and ¹H NMR. Fe₂P catalyzed the reduction of CO₂ and water to five products: formate (C₁), ethylene glycol (C₂), methylglyoxal (C₃), 2,3-furandiol (C₄), and hydrogen. All of these products, except for ethylene glycol, have been reported as CO₂RR products on nickel phosphide catalysts. The Faradaic efficiency (FE) for total CO₂RR and for HER as a function of the applied potentials are shown in **Figure 3C** and the HER FE in **Figure S5**. The total CO₂RR FE (53%) peaks at 0.00 V vs. RHE and decreases with negative bias: 33% at -0.05 V, 22% at -0.10 V, 3% at -0.15 V and 4% at -0.20 V.

Previously, ethylene glycol was reported as a minor product on only two other catalysts and required large overpotential: metallic copper at potentials negative of -0.67 V vs. RHE;² and on gold nanoparticles with ionic liquids at -0.58 V vs. RHE.⁴³ Comparatively, Fe₂P catalyzes significant production of ethylene glycol (18% of CO₂RR) at a potential as low as 0.00 V vs. RHE (**Figure 3C**). The ratio of ethylene glycol to other CO₂RR products increases to 65% at both -0.05 V and -0.10 V, although the overall selectivity shifts to favor hydrogen evolution.

**Figure 3D** compares the total CO₂RR current density for all carbon products to the total current density (HER + CO₂RR) as a function of potential. As expected, the total current
density obeys the Butler-Volmer equation\textsuperscript{49} with exponentially increasing current density vs applied potential. In contrast, the total CO\textsubscript{2}RR current density, increases between 0.00 V and -0.10 V to a maximum of 46 $\mu$A/cm\textsuperscript{2}, then decreases significantly to a local minimum at -0.15 V (12 $\mu$A/cm\textsuperscript{2}), followed by a slight increase at -0.20 V, the end of range. As will be shown later, this response agrees with our theoretical predictions of the adsorption energies as a function of potential. The general trend favoring CO\textsubscript{2}RR over HER at low overpotentials indicates thermodynamic control, while at negative bias, HER outcompetes CO\textsubscript{2}RR due to kinetic control, analogous to the nickel phosphides including Ni\textsubscript{2}P.\textsuperscript{36} However, the current maximum at -0.10 V is unique to Fe\textsubscript{2}P.

GC-DFT predicts an inversion in the trend of the adsorption energy at -0.10 V of the dissociation products of adsorbate water molecules (H* and OH*) bound to the reconstructed P*. Figure \textbf{1} reveals an extremum in adsorbate binding energy centered at -0.10 V that governs all adsorbates on Fe\textsubscript{2}P, not just H* and OH*. For the Fe\textsubscript{3} hollow site on the reconstructed surface increasingly negative bias causes H*, OH* and P* to bind more tightly until -0.10 V is reached, then reverses binding more loosely at -0.20 V. By contrast, on the unreconstructed surface, increasingly negative bias has the opposite effect, with H*, OH* and P* binding weaker at -0.10 V compared to both more positive and more negative bias. Accordingly, the strength of P* bonding to the Fe\textsubscript{3} hollow site and to H* and OH* on the reconstructed site are important predictors of whether CO\textsubscript{2}RR or HER is dominant at a given potential. We develop this further in the next section.
We note that the absolute value of the adsorption energies of adsorbates can be offset as they are referenced to H$_2$(aq) as opposed to solvated protons whose energy depends on the local pH of the system. Adsorption energies referenced to dissolved H$_2$ may be directly correlated to HER activity. For a discussion, see ESI.

**The Effect of Applied Bias on CO$_2$RR vs HER selectivity**

*Table 1* shows the equilibrium (thermodynamic) reduction potentials (E$^0^*$ at pH 7.0 vs. RHE) and the number of electrons required to reduce CO$_2$ to various products observed over Ni$_2$P and Fe$_2$P. E$^0^*$ was taken from literature data$^{50,51}$ or calculated by Mavrovouniotis’s method of individual group contributions.$^{52,53}$ From this, it can be seen that ethylene glycol is predicted to be the most thermodynamically favored product by at least 0.18 V over all other products including H$_2$. Thus, it is expected to form if kinetic factors are not important (activation barriers, reactant availability).

**Table 3.1.** Standard electrochemical potentials at pH 7.0 of CO$_2$RR half-reaction products

<table>
<thead>
<tr>
<th>Product</th>
<th>Half-Reaction</th>
<th>E$^0^*$ (V vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>2 (e$^-^\cdot$ + H$^+$) ⇌ H$_2$</td>
<td>0.00</td>
</tr>
<tr>
<td>Formic acid</td>
<td>CO$_2$ + 2 (e$^-^\cdot$ + H$^+$) ⇌ HCOOH</td>
<td>-0.02</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>2 CO$_2$ + 10 (e$^-^\cdot$ + H$^+$) ⇌ C$_4$H$_4$O$_2$ + 2H$_2$O</td>
<td>+0.20</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>3 CO$_2$ + 12 (e$^-^\cdot$ + H$^+$) ⇌ C$_3$H$_4$O$_2$ + 4H$_2$O</td>
<td>+0.02</td>
</tr>
<tr>
<td>2,3-furandiol</td>
<td>4 CO$_2$ + 14 (e$^-^\cdot$ + H$^+$) ⇌ C$_4$H$_4$O$_3$ + 5H$_2$O</td>
<td>+0.01</td>
</tr>
</tbody>
</table>

**Figure 4** summarizes the chemical steps that our experiments and theory predict to be involved in the reaction mechanism, while *Table S3* gives their equilibrium potentials. **Figure S6** details all the steps we have considered. Analogous to the CO$_2$RR mechanism on nickel phosphides, the first proposed reaction intermediate is *formate, *OC(H)O. GC-DFT was used to calculate two reaction pathways to this intermediate on Fe$_2$P – a
stepwise mechanism of CO$_2$ adsorption followed by *hydride transfer, vs a concerted *hydride transfer into CO$_2$ to form *formate. Both pathways use the reconstructed surface and the hydride source is Fe$_3$P–H (denoted H*) on the reconstructed P* site.

Figure 3.4. Proposed mechanism for formation of CO$_2$RR products

The stepwise pathway begins with adsorption of aqueous CO$_2$ at Fe to form an Fe-C bond (~2.13 Å) and bending of CO$_2$. This is accompanied by the formation of a nearby Fe-O bond (~2.17 Å) to a second Fe that stabilizes the resulting negative charge. Our calculations indicate this intermediate (schematically drawn in Figure 4, atomic detail in Figure S7) has an adsorption energy of -1.61 eV at 0 V (Figure 5). Formation of the Fe-C bond weakens and lengthens the Fe-Fe bonding distances by as much as 0.03 nm, as shown in Figure S12. Maximum affinity of CO$_2$ on the surface at -0.10 V bias is predicted to be $E_{\text{ads}} = -1.72$ eV (Figure 5), following a similar trend to the predicted H adsorption energies on the P* site. Subsequently, *hydride transfer to the adsorbed CO$_2$ with further bending and release of one O* to produce *formate completes the stepwise pathway. Our calculations show the hydride transfer reaction energy for the stepwise pathway is thermoneutral or slightly positive, but it displays the opposite trend with
applied bias as the concerted pathway, and is more energetically unfavorable by about 1.6 eV (dashed green trace in Figure 5). Literature reports indicate that the chemisorption of CO$_2$ at surfaces is kinetically unfavorable due to a large barrier to bending CO$_2$.$^{54}$

A concerted pathway is predicted to occur by adsorption of CO$_2$ into the H* bond to form *formate anion bound through one oxygen atom (Figure 5). See ESI Figure S7 for structural details. A comparison of formate adsorption to the Fe and P* sites via Fe-O and P-O bonds shows that the Fe–OC(H)O adsorption is significantly more stable than the Fe$_3$P–OC(H)O adsorption by 2 eV or greater (Figure 5). As such, we postulate that the CO$_2$RR mechanism likely proceeds through the concerted pathway with formation of Fe–OC(H)O intermediate. This interaction is predicted to be monodentate as no energy minimum was found for interaction of the second O atom of formate to any other surface atom.

Figure 3.5. Computed adsorption energies vs. applied electrical bias
Computed adsorption energies (eV) of CO$_2$ and formate on the P* and Fe sites of the reconstructed surface vs. applied electrical bias (V vs. RHE) obtained using GC-DFT. The adsorption energies are relative to aqueous CO$_2$ and H$_2$. The green and pink dashed lines denote reaction energies of the stepwise and concerted hydride transfer reactions (HT) as a function of applied potential, respectively
The bonding of formate to the surface is strengthened by an additional 0.37 eV at an applied potential of -0.1 V relative to 0.0 V; the desorption energy at -0.1 V is 1.5 eV (dashed magenta line in Figure 5). As the negative bias increases further to -0.2 V, this bond weakens by 0.74 eV. This appreciably weaker adsorption energy of formate at -0.20 V bias offers a likely explanation for the experimental drop in CO$_2$RR current in this range, regardless of how it forms. The concerted reaction is considerably more favorable energetically relative to its stepwise counterpart across the range of applied potentials considered. Moreover, a concerted mechanism of HT with CO$_2$ insertion and immediate stabilization of the resultant negatively charged oxygen has a lower kinetic barrier compared to bending CO$_2$.$^{54}$ In fact, to form Fe-*OCHO in a stepwise approach, a net of 4 bonds would need to be dissociated or formed: the dissociation of P-H and Fe-C bonds and the formation of C-H and Fe-O bonds, vs only two bonds via the concerted mechanism. Therefore, based on both the energy of reaction intermediates and their kinetic barriers the concerted pathway to *formate is the likely first step of the mechanism. In the next section we examine how the decrease in *formate affinity on the surface can account for the loss in total CO$_2$RR current as the applied bias is increased above -0.2 V.

**Nature of bonding of adsorbates to the surface.**

A comparison of the projected density of states (PDOS) at the respective applied potentials (Figure S9) clarifies the origin of the CO$_2$RR current peak at -0.1 V. The PDOS reveals that the applied negative bias shifts the Fe–O* antibonding states down in energy as the Fermi level increases with bias. This is due to renormalization of
antibonding states that now interact with the additional occupied states filled as the Fermi level rises. PDOS plots along with Bader charges are reported in the ESI, with additional thorough discussion of the effect of applied bias on the PDOS. This prediction is an advantage of use GC-DFT.

Electrochemical models that attempt to account for the effects of the applied bias typically assume that the main effect of the bias is a rigid shift of the Fermi level and that no renormalization of surface electronic states occurs. However, GC-DFT predicts that the states renormalize under the applied potential because electrons of the newly occupied states (at cathode) or the newly depopulated states (at anode) interact with and modify all other electronic states of the electrode and adsorbates. This is a more realistic model of the biased interfaces of electrochemical systems. In other words, the change in occupancy creates electric fields that polarize nearby adsorbate and electrode electronic states. This is especially true for highly polarizable states, such as lone pairs.

Renormalization under the applied potential results in different shifts of the bonding and antibonding states which manifests itself in shape changes of the electronic bands, including peaks merging, splitting, growing and shrinking.

To quantify these observations, we present a unique type of system analysis in Figure 6 that tracks relative energy changes of particular bands (orbitals) as a function of the applied potential. Here, the difference between a band center (first moment of the PDOS) and the Fermi level for each electronic state of interest is plotted as a function of the potential, Eqn [1]:

$$
\Delta \varepsilon_{(ab-b),i} = \varepsilon_{ab,i} - \varepsilon_{b,i} = \\
\int_{E_f-1.0}^{E_f+1.0} E \, D_i(E) dE - \int_{E_{f-1.0}}^{E_{f+1.0}} E \, D_i(E) dE,
$$

[1]
Here, $\Delta \varepsilon_{(ab-b),i}$ represents an energy gap between states (orbitals) near the Fermi level, which are obtained by projecting the DOS. $\varepsilon_{ab,i}$ is the number-averaged center of states above the Fermi level (usually antibonding-type), and $\varepsilon_{b,i}$ is the number-averaged center of states below the Fermi level (usually bonding-type) for a state $i$. A range of 1.0 eV straddling the Fermi level was chosen to quantify the effects on the frontier orbitals because a larger range dilutes the effects, while a smaller range neglects important bonding and antibonding states.

**Figure 3.6.** Energy gap between orbitals near the Fermi level

Energy gap between orbitals (antibonding – bonding) near the Fermi level, $\Delta \varepsilon_{((ab-b))}$, vs applied bias for: a) Fe3(P–H)* on reconstructed surface, and b) *OC(H)O bound to Fe on reconstructed surface. Values of $\Delta \varepsilon_{((ab-b))}$ are normalized at 0 V to determine the relative stability at -0.1 V and -0.2 V vs RHE. Negative values represent a smaller gap and thus lower orbital overlap and weaker bonding, whereas positive $\Delta \varepsilon_{((ab-b))}$ values indicate increased bonding character. Fe + P indicates the overall density of states in the catalyst bulk. Fe3-P* refers to the density of states on the reconstructed active site only. a) shows that on the reconstructed surface a more negative bias increases Fe3–P* bonding (red) and weakens the (P–H)* hydride bond (cyan). b) shows that with *OC(H)O bound to the reconstructed surface the formate states (green), Fe–O* states (purple), and hydride states (blue) all exhibit weaker binding under negative bias and even more so from -0.1 to -0.2 V. The C–H bond of *formate (black) first strengthens modestly at -0.1 V, then significantly weakens at -0.2 V. In contrast, bonding of the neighboring Fe3–P* site (orange) in (b) is weakened at -0.1 V but is stronger at -0.2 V.

$\Delta \varepsilon_{(ab-b)}$ is analogous to the gap between the bonding and antibonding molecular orbitals (MOs) formed by the overlap of atomic orbitals (AOs). As such, similar
concepts from molecular orbital theory can be utilized to understand the influence of the applied bias on the portion of the electronic structure that is responsible for Fe$_2$P’s electrocatalytic character. Within MO theory, an increase in the overlap of in-phase and out-of-phase AOs results in larger constructive and destructive interference, and thus a larger energy gap between the resultant bonding and antibonding MOs. Similarly, these concepts apply to the frontier states of the extended system that gives rise to the splitting quantified by $\Delta \varepsilon_{(ab-b)}$, wherein an increase in $\Delta \varepsilon_{(ab-b)}$ signifies an increase in the energy gap between the band centers of the filled and unfilled states of each type (i). By analogy to the splitting between bonding and antibonding MO orbitals, an increase in $\Delta \varepsilon_{(ab-b)}$ indicates that the particular bonding states are stabilized as a result of renormalization. Other methods that neglect renormalization assume a rigid shift of the Fermi level relative to the PDOS which fails to quantify changes in bonding. Consequently, those methods are not suitable for this type of analysis. Additionally, this interpretation of $\Delta \varepsilon_{(ab-b)}$ only applies when the relevant antibonding states lie above the Fermi level.

The plot of $\Delta \varepsilon_{(ab-b)}$ versus applied potential shows that the gap between Fe$_3$–P* states (red in Figure 6A) associated with the reconstruction increases with negative bias above -0.1V, indicating this bond strengthens. Conversely, the gap between (P–H)* states (cyan in Figure 6A) decreases with negative bias above 0 V, indicating the (P–H)* bond weakens. The inverse correlation is consistent with the expected behavior for bonding by P* to its nearest neighbor atoms. The weakening of the (P–H)* bond at negative bias indicates it becomes more ionic, (P’H’)*, as electrons are added to the system. This bond becomes more hydridic using terminology from the catalysis literature.
Following adsorption of formate, the plot of $\Delta \varepsilon_{(ab-b)}$ vs $V$ shows that (Figure 6B, obtained from the density of states in Figure S11): 1) the overall lattice Fe-P bonding is not affected much at all, while the Fe-P* bonding is strengthened analogous to the case on the reconstructed surface; 2) the valence states of carbon in *OC(H)O are weakly destabilized at -0.1 relative to 0 V, and strongly destabilized at -0.2 V; 3) The latter weakening of bonding with negative bias also occurs for states of *OC(H)O and Fe-O* especially prominent at -0.2 V, indicating weakening of bonding within *formate and its binding to the surface Fe as electrons are added to the system. Not only does this orbital analysis match the parabolic trend of the predicted adsorption energies (Figure 5), but also matches with the peak in CO$_2$ current observed experimentally at -0.1 V.

Furthermore, both trends are paired with the opposite energy offset at the nearby Fe$_3$–P* states (orange in Figure 6B), which are slightly weaker bonded at -0.1 V and more strongly bonded at -0.2 V. Accordingly, we attribute the peak in total CO$_2$RR current at -0.1 V to the competing influence of increasing (P-H)* hydricity, favoring hydride transfer and weakening of formate binding affinity at more negative bias.

In sum, the weakening of surface-adsorbate interactions results from a combination of two effects: changes in the adsorbate-surface electronic distribution at different applied potentials, and the repulsive Coulomb potential between the negatively charged cathode and polarizable adsorbate atoms. This explains the reversal in the observed trends in adsorption energies (weaker) and CO$_2$ reduction current (greater) between -0.1 and -0.2 V. In addition, cations attracted to the biased cathode may superimpose additional field effects over those considered here, but which are beyond the scope of this work.
Origin of the C\textsubscript{2} product selectivity

The ~30% increase in adsorption energy of *formate at -0.10 V suggests that it has a longer lifetime on the catalyst, potentially allowing for a second HT to formaldehyde which is a precursor to C-C coupling via the aldol mechanism, analogous to what was previously hypothesized on Ni\textsubscript{2}P.\textsuperscript{36} Indeed, the data in Figure 3 show that at negative bias of -0.05 and above the C\textsubscript{2} product dominates relative to all carbon products (C\textsubscript{1}, C\textsubscript{3} and C\textsubscript{4}). This differs from the nickel phosphide catalysts where C\textsubscript{3} and C\textsubscript{4} products are favored at all potentials and C\textsubscript{2} is not observed at all.\textsuperscript{36} A possible explanation for this difference may be found in the branching reactions separating the C\textsubscript{2} and C\textsubscript{3} pathways in the proposed mechanism (Figure 4). The C\textsubscript{2} branch point requires a third *hydride addition, while the C\textsubscript{3} branch point requires *formaldehyde addition. We know from Figure 6A that the surface hydride, (P-H)*, becomes more weakly bound, hence more labile and hydridic (P+H-), as the bias increases negative of 0 V (by 90 to 115 meV between -0.1 and -0.2 V). This increased hydride reactivity will favor the C\textsubscript{2} pathway relative to C\textsubscript{3} and C\textsubscript{4} if the proposed mechanism is correct.

3.3 Conclusions

This study investigated use of iron phosphide as catalyst for CO\textsubscript{2} reduction. Fe\textsubscript{2}P converts CO\textsubscript{2} primarily to ethylene glycol and to smaller amounts of formate, methylglyoxal, and furandiol in aqueous potassium bicarbonate solution, at potentials as low as 0 V vs. RHE. This contrasts with strong preference for C\textsubscript{3} and C\textsubscript{4} products on Ni\textsubscript{2}P and NiP\textsubscript{2}.\textsuperscript{36} The maximum combined CO\textsubscript{2}RR Faradaic Efficiency of 53% was obtained at 0.00 V vs. RHE. This is the first report of ethylene glycol synthesis at substantial FE in aqueous media at these low overpotentials. As the kinetic driving force
is increased (increasing reductive bias) hydrogen evolution becomes favored, reaching more than 95% FE at -0.20 V, consistent with the behavior observed with other transition metal phosphides.

The catalyst was thoroughly characterized before and after electrocatalysis and shows no indication of bulk instability. Small amounts of Fe dissolution from the native oxide was shown to be present in all experiments but control experiments showed that this soluble Fe did not change the catalyst activity in the same direction. This demonstrated that soluble iron species does not contribute to the overall change in reaction product distribution which is therefore attributed to the bulk catalyst composition and structure.

State-of-the-art GC-DFT modeling was employed to characterize the effects of the applied bias and solvent on surface speciation and reactivity. The Fe$_2$P (0001) surface was found to be the most thermodynamically stable, in agreement with previous reports.

We found that a phosphorus adlayer formation is largely favored both in the absence of an applied reductive bias and becomes even more so under reductive potentials. Hydride and hydroxide adsorption on the phosphorus adlayer and adsorptions of carbon-containing intermediates on Fe are strongly potential dependent, with an optimal value at -0.10 V vs. RHE. This potential is also well correlated to the experimental observation of the maximal partial CO$_2$RR current density at -0.10 V. Based on the experimentally observed reaction in the presence vs. absence of CO$_2$ in the electrolyte and corroborated by the GC-DFT results, we propose that the P* reconstructed surface of the Fe$_3$P$_2$ termination on Fe$_2$P [0001] facets is the active site in both the HER and CO$_2$RR.

GC-DFT is developed to allow prediction of the consequences of an applied bias. It successfully describes changes in both the hydride free energy and changes of the
adsorbate-surface affinity, both of which allow development of the mechanism, its 
HER/CO$_2$RR selectivity and the branching between C$_2$ and C$_3$/C$_4$ pathways with applied 
bias.

In comparison with the iso-structural Ni$_2$P, adsorption energies indicate that hydrides are 
more labile. This result is consistent with the preferential formation of smaller chains of 
C$_1$ and C$_2$ products on Fe$_2$P, in contrast with C$_3$ and C$_4$ on Ni$_2$P due to the rapid chain 
growth termination by hydrogenation of glycolaldehyde (the C$_2$ intermediate required to 
form C$_3$ and C$_4$ products). A higher hydride lability on Fe$_2$P also explains why the 
kinetically favored hydrogen evolution reaction is substantially preferred on this catalyst 
at comparable potentials.

These results highlight the importance of precisely tuning surface hydride binding 
affinity to obtain the desired products (C$_3$ vs. C$_4$ and H$_2$) and underscores the imperative 
importance of surface reconstruction when designing new pnictide catalysts. This insight 
is fundamental for the discovery of new materials for the conversion of CO$_2$ into organic 
chemicals.

3.4 Methods

Catalyst synthesis: Iron metal powder (Fisher Scientific) was annealed under 1% 
hydrogen (balance Ar) flow for 4 h at 450 °C to remove surface oxides. The reduced iron 
powder was mixed with 1.5% molar excess of red phosphorous (Alfa Aesar, 98.9%, 100 
mesh), for a total of 10 g of sample per batch. The powder was ground with an agate 
mortar and pestle for 20 min, transferred to a quartz tube, then flushed with argon and 
evacuated to less than 100 mTorr three times. The quartz tubes were sealed and heated at 
a rate of 0.5°C min$^{-1}$ stepwise to 250°C, 450°C, 550°C and finally to 800°C. The
temperature was maintained for 6 h at each intermediate step to avoid hotspot formation due to the exothermic reaction, and 24 h at the final temperature. The sample was left to cool down naturally in the furnace to 60°C. Powder X-ray diffraction (PXRD) was used to determine what/if additional amounts of phosphorous or iron were needed; these were added and the synthesis repeated until the catalyst was phase-pure. After synthesis, the Fe₂P powder was washed in 3% HCl, stirring under argon for 2h, to remove any soluble phosphates. The catalyst was then rinsed and centrifuged five times with water, and then twice with ethanol, followed by drying at room temperature under vacuum.

Electrochemistry: All potentials for experiments done in this work are referenced to RHE at the pH used throughout this paper. Electrochemical measurements were performed in a custom-made glass-reinforced nylon-6,6 cell, with silicon O-rings and PEEK fittings (IDEX-HS) as previously described. The working and counter electrodes were separated by a Nafion 115 membrane (Fuel Cell Store). Platinum black deposited on Pt foil (Alfa Aesar, 99.9%) was the counter electrode and an ALS Hg/H₂SO₄ was used as reference electrode, calibrated before each experiment against a pristine Ohaus SCE electrode. This SCE was periodically calibrated against a freshly flame-annealed Pt electrode in 0.5 M H₂SO₄, under 1 atm H₂. The working electrode was prepared by mixing 1.400 g of the catalyst with 10% (w/w) neutralized Nafion suspension, being supported on an Al-mesh backing (20x20 mesh size, McMaster-Carr) and pressing at 22 ton onto an aluminum die (Ø = 2 cm). The die, containing the pressed catalyst pellet, became the working electrode and current collector, with only the Fe₂P surface exposed to the electrolyte. CO₂ (Air Gas, instrument grade, with a Supelco hydrocarbon trap) was supplied through the bottom of the cell to both the working and
counter electrodes, through a fritted gas dispersion tube (Ace Glass, 5-8 µm pore size) at a flow rate of 5 sccm (certified MKS P4B mass flow controllers). The electrolysis was run for 16 h at a time, with the headspace of the working electrode compartment sampled every hour for gas chromatography. Liquid samples were collected at the end of the electrolysis (see further below). Each CO$_2$RR FE value reflects the average of at least 3 replicates.

Electrochemical measurements were performed with a Gamry 5000E potentiostat. Before each electrolysis experiment, the electrolyte (0.5 M KHCO$_3$, Sigma Aldrich ACS reagent grade, Chelex-treated) was pre-saturated with CO$_2$ for an hour. Then, a gas chromatogram was taken to ensure that there was no air present in the headspace. A potentiostatic electrochemical impedance spectrum at 0V vs. RHE from 1 Hz to 1 MHz was run to determine the uncompensated resistance (typically between 6 and 10 ohm, see Figure S1). Chronoamperometry was then performed for 16 h with manual IR compensation. Between experiments, the electrochemical cell was rinsed with Millipore water, and the working electrode catalyst pellet was soaked in Millipore water for 10 min, to prevent carryover of product between experiments, and then dried under a vacuum for 10 min, to avoid oxidation of the catalyst surface. The catalyst pellet was re-used for multiple experiments at varying potentials. By doing this, the longevity of the electrodes, particularly the working electrode, was ensured, with no significant difference in product distribution observed as the electrode was re-used. Additional experimental replicas, using freshly made catalysts, were run at all potentials to ensure that the product distribution was consistent across the investigated potential region. The electrochemical surface area was determined as described in the Section 2 of the ESI.
Gas chromatography: Detection and quantification of possible headspace products (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene) was performed by an auto-sampling online HP 5890 Series II GC, with a 500 µL sample loop. The GC was fitted with a 6’ packed HayeSep D, and a 6’ packed MoleSieve 13X column, with thermal conductivity and flame ionization detectors connected in series. Samples were taken before chronoamperometry to ensure that the cell was CO₂ saturated and had no air leaks, and then every hour once chronoamperometry was started. Calibration curves were constructed from certified gas standards (Gasco) by CO₂ dilution using mass flow controllers. The hydrogen calibration was done with in situ generated gas through electrolysis of water on platinum, under argon (supplied by an MFC), and diluted post-reaction with CO₂.

High-performance liquid chromatography (UV/RID): Liquid products were identified and quantified by a Perkin-Elmer Flexar HPLC, equipped with an auto-sampler, refractive index (RID, and UV-vis detector. An HPX-87H Aminex column (BioRad) was used, with injection volumes of 10 µL. The run time was 60 min at a flow rate of 0.3 mL/min and at 65 ºC. Calibration was conducted with standards of concentrations between 0.1-5 mM. The standards were: furandiol, methylglyoxal, and ethylene glycol, in 0.5 M KHCO₃, detected using the RID. Acetic acid and formic acid, standards were prepared at concentrations of 0.01-5 mM and detected by UV at 210 nm. Product assignment was confirmed by ¹H NMR, as described in detail in the SI (Figure S3).

X-ray photoelectron spectroscopy (XPS): The surface of Fe₂P before and after reaction was analyzed by a Thermo K-Alpha XPS spectrometer. The chamber was evacuated to
5x10^{-9} Torr base pressure. The spectra were collected with a flood gun for charge compensation and an X-ray beam of 400 μm was used.

Computational Methods: DFT calculations with periodic boundary conditions were performed using the JDFTx code.\textsuperscript{56} The generalized gradient approximation (GGA) was employed to compute the exchange-correlation energy using the Bayesian Error Estimate Functional with van der Waals correlations (BEEF-vdW), which was shown to provide a better description of CO\textsubscript{2} reactivity compared to the revised Perdew-Burke-Ernzerhof functional.\textsuperscript{57,58} The SG15 Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials were used to model truncation of the core electrons of the system.\textsuperscript{59,60} The bare Fe\textsubscript{2}P (0001) surface was modeled using a 4 layer supercell consisting of alternating layers with Fe\textsubscript{3}P\textsubscript{2} and Fe\textsubscript{3}P stoichiometries, making a total of 48 Fe and 24 P atoms in the supercell. The lattice parameters were optimized for the clean surface and fixed for all adsorbate and reconstruction calculations. A 2 × 2 × 1 Monkhorst-Pack grid was used for k-point sampling of the Brillouin zone. Geometries were optimized with a 20 Rydberg plane wave energy cutoff energy. The electronic energies were converged to within 1 × 10^{-8} Hartrees. Magnetic states were allowed to relax to their ferrimagnetic state, as was expected for Fe\textsubscript{2}P. The charge-asymmetry corrected, local-response, nonlocal-cavity solvation model (CANDLE) was implemented to account for solvation effects on molecules and surfaces.\textsuperscript{61} An electrolyte consisting of 0.5 M Na\textsuperscript{+} and 0.5 M F\textsuperscript{-} was embedded into the solvent model.

All constant-potential grand-canonical DFT (GC-DFT) calculations were performed using the same settings. The algorithm implemented by JDFTx variationally minimized
the grand free energy at a set constant potential by varying the electron count within the unit cell as well as by balancing fluid bound charges.
3.5 References


(40) International Crystal Structure Database.


Chapter 4: A Theoretical and Experimental Study of the Ni$_2$P Surface Under Electrochemical Conditions

Abdulaziz Alherz$^\dagger$, Karin U. D. Calvinho$^\dagger$, Shinjae Hwang, Anders B. Laursen, Zachary J. L. Bare, G. Charles Dismukes and Charles B. Musgrave

$^\dagger$These authors contributed equally.

Abstract

Ni$_2$P has been shown to lower the barriers for water splitting and CO$_2$ reduction reactions, yet little is known about the dynamic behavior of its surface as a response to bias and solvent at different electrochemical conditions. In this work, we model the biased Ni$_2$P-electrolyte interface using grand-canonical density functional theory calculations and characterize its behavior using operando Raman spectroscopy at various electrolyte and pH conditions. Our calculations predict a stable phosphorus-enriching reconstruction that involves P adsorption at Ni$_3$ hollow sites as applied potentials between +0.2 V to -0.5 V vs RHE. Additionally, our calculations predict the speciation of water onto the reconstructed surface site (P*). The quantification of the effects of the applied bias on adsorption energies reveals a parabolic trend in adsorption energies centered at -0.2 V for all adsorbates, in agreement with experimental observations that catalyst surface oxidation increases over time at 0 V vs RHE, is constant at -0.2 V, and is decreases at -0.5 V. The P reconstruction, as well as H and OH surface adsorption, are experimentally confirmed with operando Raman spectroscopy, which is validated with phonon calculations. The deeper understanding of the surface this study provides will inform mechanistic predictions and the rational design of catalysts, which are critical to
improving the catalytic performance of the hydrogen evolution reaction and CO₂ reduction.

4.1 Introduction

Electrochemical CO₂ reduction and water splitting are some of the most promising methods for producing green chemicals and storing renewable energy. Nickel phosphides have been shown to be among the most active earth-abundant catalysts for hydrogen evolution in acidic or basic conditions \(^1\)–\(^5\) and are the most energy-efficient known catalysts for converting CO₂ to up to C₄ products. \(^6\) However, recent studies show that Ni₂P likely reconstructs under working conditions \(^1\),\(^7\)–\(^9\), which has implications for accurately determining the active sites and reaction mechanisms of CO₂ reduction and the hydrogen evolution reaction (HER). In turn, this information is crucial for the design of new and improved catalysts, as reconstructions can change the surface reactivity by blocking sites from adsorbates, as well as providing new sites with different surface reactivity. Additionally, some surface reconstructions may be favored under different electric biases. Thus, it is essential, albeit challenging, to experimentally probe the evolution of the catalyst surface under relevant reaction conditions. \(^10\) Furthermore, state-of-the-art theoretical models are crucial to understand the interplay between the effects of the solvent, reaction intermediates, and the applied potential on the evolution of the catalytic surface.

Operando Raman spectroscopy is particularly well-suited for evaluating catalysts in aqueous solutions, as water scatters light weakly. \(^11\) This technique has been shown to be exceptionally useful to understand phenomena such as the detection of adsorbates, surface reconstruction, and the evolution of reaction intermediates. \(^12\) For instance, Lum
and Ager showed that residual oxides are stable for up to 5 hours on oxide-derived copper, and play a key role in shifting reaction selectivity to C₂ and C₃ products. In another hallmark study, Dutta et al. used operando Raman to demonstrate that the selectivity of CO₂ conversion to formate is maximal on SnOₓ with a mixed oxidation state. While operando Raman spectroscopy has been applied to understand nickel phosphide electrosynthesis, no study has examined Ni₂P under conditions relevant for HER and CO₂RR. In addition to providing insight into these important transformations, such a study could guide the revision of established theoretical screening tools, which fall short of capturing the observed activity, and identify the active sites responsible for NiP’s remarkable HER and CO₂RR reactivity.

Analogous to its effect on the surface reconstruction, the interaction of the electrolyte with the catalyst influences the reaction mechanism by stabilizing charged and polar species, including transition states, transporting ions, modifying the local pH, or blocking active sites. Moreover, solvent and electrolyte species at the catalyst interface modify the surface electronic structure, as well as cause unexpected chemical reduction or oxidation of the surface prior to the application of bias and also as a response to the applied bias. Therefore, to model these effects and provide a fundamental description of the mechanism computational tools capable of modeling the effects of solvent and applied potential on the surface electronic structure must be utilized to accurately predict the catalytic behavior of the electrochemical surface-solvent interface.

We thus employ the Grand-Canonical Electronic Density Functional Theory (GC-DFT) method combined with the CANDLE solvation model to analyze the effects of applied potential on Ni₂P catalyst activity. This state-of-the-art approach models the change in
the number of electrons in the Ni₂P cathode surface required to maintain the applied potential by self-consistently solving for the number of electrons that minimizes the grand free energy at a specified chemical potential that corresponds to the applied bias. While more computationally expensive than standard DFT methods appropriate for modeling systems with a fixed number of electrons, GC-DFT enables a considerably more accurate and realistic description of the surface electronic densities as a function of applied potential, revealing unprecedented detail of the effect of bias on the electronic structure and the unique nonlinear trends in adsorption energies with applied bias which traditional DFT methods otherwise are incapable of predicting. This analysis is performed in coordination with operando Raman spectroscopy, which characterizes the catalytic surface as it responds to potential and pH changes. Together these approaches provide a powerful strategy that informs our understanding of the dynamic catalytic environment at the atomic level, which is crucial for revealing a detailed description of the hydrogen evolution and CO₂ reduction reaction mechanisms.

We report the computed stabilities of surfaces that are incrementally reconstructed by P adsorption at the Ni₃ hollow sites at different applied potentials to determine that the P* enriched surface is stable at all conditions. The stability of the P reconstructed surface is further improved by the favorable dissociative adsorption of water as H and OH adsorbed onto the P* site. As previously shown by Wexler et al,18 P* is the active site that provides hydrides to facilitate HER; the same is expected for CO₂RR. One additional remarkable outcome of this study is the prediction of an oxidized surface in the form of multiple P-OH bonds, despite the reducing potentials. This is corroborated by operando Raman spectroscopy.
4.2 Results

**Surface Reconstruction of Ni$_2$P (0001)**

Reconstruction of the Ni$_2$P surface in the form of additional adsorbed P adatoms (P*) on the Ni$_3$ hollow sites was examined using DFT. The effects of reconstruction are crucial for not only characterizing the surface, but also for correctly modeling heterogeneous reaction pathways. Reconstructions can produce previously unexplored topologies that create possibly active catalytic sites or hinder pathways by sterically blocking active sites. They can also occur via various mechanisms, such as by incorporation of residual atoms produced during synthesis or (electro-)chemical speciation of the top-most layer of the surface. Our Raman results suggest that the surface reconstructs prior to any applied electrical bias, which indicates that it results from the synthesis conditions.

Our initial calculations validate Wexler’s prior results regarding the surface termination and reconstruction of the Ni$_2$P surface. The [0001] facet of Ni$_2$P consists of alternating layers along the z-direction with Ni$_3$P and Ni$_3$P$_2$ stoichiometries, averaging to the net stoichiometry of Ni$_2$P. A lower surface energy by ~0.12 J/m$^2$ is obtained by terminating the Ni$_2$P surface with a Ni$_3$P$_2$ layer (see ESI). The Ni$_3$ hollow site is blocked by the adsorbed P atoms of the P* reconstruction. This, however, provides a new active site, P*, which facilitates hydride transfers to protons for generating H$_2$, and is likely responsible for the reduction of CO$_2$. As previously predicted, a P*-enriched surface is more energetically favorable than the clean Ni$_2$P surface, with an adsorption energy of -1.16 eV at 0 V vs RHE relative to the white phosphorus reference. P-enriched reconstruction is predicted for various binary phosphide materials, such as nickel phosphides, iron phosphides, and cobalt phosphide nanosheets. P* adsorbs less
strongly on Ni$_2$P relative to its Fe$_2$P analog (~1 eV at 0 V vs RHE). Because P* is the active site for hydride transfer reactions, several implications can be drawn by comparing the P* adsorption strength between Fe$_2$P and Ni$_2$P. A strongly adsorbed P*, as is the case for Fe$_2$P, correlates to weakly bound surface hydrides and thus a more hydridic surface that is more selective towards HER than CO$_2$RR. In contrast, weakly bound P* forms more stable, and thus, weaker surface hydrides. Consequently, these catalysts are likely to be more fine-tuned towards selective CO$_2$ reduction, as exemplified in the excellent Faradaic efficiency of Ni$_2$P catalysts towards C$_3$+ products.

We further examine the extent of the effect of applied bias on Ni$_2$P reconstruction, as demonstrated in the reconstruction progression displayed in Figures 1a-c. Due to the size of the slab supercell model chosen to balance computational expense with accurate predictions, our investigation is limited to reconstructions in increments of 25% of the total number of Ni$_3$ hollow sites as shown in Figure 1d. DFT calculations excluding bias effects predict favorable reconstruction. GC-DFT calculations at various reductive applied indicate that any reductive bias results in a considerably more favorable adsorption relative to calculations excluding bias effects, as shown in Figures 1d-e. For example, the adsorption energy per P* for the unbiased surface is computed to be -0.21 eV and -1.16 eV at 0 V vs RHE of applied bias. There are slight favorable interactions between the reconstructed sites across all applied potentials below 50% reconstruction, as the adsorption energy per adsorbed P* is more negative when the percentage increases from 0% to 50%. At reconstructions above 50%, unfavorable interactions appear to govern the reconstructed P* sites, as indicated by the slight increase in the adsorption energy per atom ($E_{\text{ads/atom}}$) in Figure 2e. Nevertheless, P* adsorption
remains highly favorable even at full P* coverage of the Ni₃ hollow sites. Hence, we believe that the entire surface is likely to reconstruct in this manner provided that this reconstruction is not kinetically hindered. While reconstruction is favored at all reductive biases explored, GC-DFT also predicts that the adsorption energy of P* as a function of bias is parabolic and centered at -0.2 V at which it has an adsorption energy of -1.34 eV. A similar parabolic behavior has also been observed on the Fe₂P surface.

![Diagram of Ni₃P surface reconstruction](image)

Figure 4.1. Illustration of the extent of the Ni₃P surface reconstruction. a) unreconstructed surface, b) 50%, and c) 100% Ni3 hollow site reconstruction. Ni atoms are depicted in grey, P atoms in lilac. d) Plot of the total adsorption energy of all P*s on the Ni3 hollow sites. e) Plot showing the average adsorption energy of P* per reconstructed site. At no applied bias, the adsorption energy is much lower, yet still favorable. There is very little favorable interactions as the concentration of P* increases. Under an applied bias interactions between P* sites are most favorable at ~50% reconstruction. While evidence of slight destructive interactions are present, indicated by the rise in Eads/atom with increasing % Reconstruction, they remain largely favorable on the surface. Reconstruction at any percentage is most favored at -0.2 V vs RHE.

Next, we investigate the speciation of aqueous solvent on the surface and describe this activity at various applied biases. We compute adsorption energies of H and OH on the Ni₂P surface at two distinct sites: Ni₃ hollow and P* sites. H and OH adsorptions are
computed relative to the solvated proton and water molecule references, respectively, with additional discussion of the reference states described in the ESI. The adsorption energies reported in Figure 2 indicate that P* outcompetes H and OH adsorption onto the Ni$_3$ hollow site at all examined potentials by more than 0.3 eV, thus providing further evidence that this site reconstructs. The adsorption energy of H on the Ni$_3$ hollow as a function of applied bias exhibits an inversion from the behavior that is observed for P* adsorption, which is centered at approximately -0.2 V at which it is most favorable.

Figure 4.2. Computed adsorption energies as a function of bias
Computed adsorption energies (eV) as a function of bias (V vs. RHE, pH = 7.5) spanning +0.2 V to -0.5 V vs RHE for P* on the Ni$_3$ hollow, as well as adsorption of multiple H and OH at the Ni$_3$ hollow and P* sites. The adsorbates all exhibit parabolic adsorption energy trends with bias centered at approximately -0.2 V or -0.3 V as either the most favorable (on the Ni3 hollow sites) or least favorable (on P* sites) adsorptions. Strong adsorption of P on the Ni$_3$ site shows that the surface reconstruction is thermodynamically favored and outcompetes proton and OH adsorption. H adsorption energies are computed using solvated protons (pH = 7) as the reference state. OH adsorption energies are computed using the energy of OH radical as the reference state as customary, determined by $\mu$(OH) = $\mu$(H2O) – $\frac{1}{2}$$\mu$(H2)

Adsorption onto the P* site is intriguing as it has significant implications on active site behavior as well as the underlying CO$_2$RR mechanism. H adsorption is
favorable across applied potentials ranging from +0.2 V to –0.5 V vs RHE. Furthermore, we predicted favorable adsorption of an additional H onto the same P* site, which as a result of adsorption of the second H adsorption moves from the Ni$_3$ hollow to a Ni-Ni bridge site to balance the coordination of P*, which remains tetrahedral as demonstrated in Figures 3a-b. Adsorptions of one and two equivalents of hydroxyls (Figures 3c-d), on the other hand, are predicted to be less favorable. However, this could be the result of our choice of reference to compute the adsorption energies, as we demonstrate below experimental evidence of both P*H$_2$ and P*(OH)$_2$ bonds. Our choice of reference does not account for induced local pH effects caused by the applied bias, which shift $E_{\text{ads}}$. Reductive bias typically results in a more basic local pH due to the consumption of protons and release of OH$^-$ in HER and CO$_2$RR, where the increase in hydroxide concentration near the surface increases the chemical potential of OH$^-$, resulting in more favorable adsorptions than our reference state predicts. Nevertheless, the adsorption energy trend with applied bias strongly correlates with the experimental observations discussed below.

![Figure 4.3](image)

**Figure 4.3. Geometries of Hs/OHs adsorbed on P**

Geometries of a) H adsorbed on P*, b) two H's adsorbed on P*, c) OH adsorbed on P*, and d) two OH's on P* at 0 V vs RHE, where P* is the reconstructed site. Note that in cases (b) and (d) with two adsorbates, P* moves from the Ni$_3$ hollow site to a Ni-Ni bridge site to maintain its 4-fold coordination.
Figure 4.4. Raman spectra of Ni$_2$P film on nickel foil with no electrolyte CO$_2$-saturated 0.1 M KHCO$_3$ (pH 6.8), 1 M NaOH (pH 14), and 0.5 M H$_2$SO$_4$ (pH 0.3). All spectra shown here were collected at open circuit potential.

**Experimental validation**

A Ni$_2$P film was synthesized on a nickel foil by reaction with hypophosphite at 350°C under an inert atmosphere. The formation of phase pure Ni$_2$P was confirmed through PXRD (Figure S1).

Raman spectra of the Ni$_2$P surface without electrolyte, and with acidic, neutral, and basic electrolytes at open circuit potential (OCP) are shown in Figure 3. Detailed assignments and references are reported in Table 1. The as-prepared Ni$_2$P spectrum displays the characteristic symmetric stretch and antisymmetric deformation modes of PH$_2$. This is in accordance with the P* reconstruction predicted by DFT on Ni$_3$ hollow sites, and evidence that it is stable even in the absence of applied potential. Other surface
phosphorus sites are coordinatively saturated and cannot accommodate two adsorbates. However, the P* adsorbed on the Ni$_3$ triangle site moves to a bridging Ni$_2$ site and assumes a favorable tetrahedrally coordinated geometry upon binding of two H$^+$ adsorbates. Additionally, the formation of PH$_2^*$ is predicted to be favorable by more than 1.5 eV, in agreement with our observation. The DFT calculated frequency for the symmetric PH$_2$ stretch (2319 cm$^{-1}$) also agrees with the experimentally measured value (2330 cm$^{-1}$). With the aid of phonon calculations, we confirm that the experimentally observed Raman modes at 2330 cm$^{-1}$ and 1052 cm$^{-1}$ indeed correspond to the symmetric vibrational stretching modes of P*H$_2$ and P*(OH)$_2$, respectively, within only 11 cm$^{-1}$ (<1%).

### Table 4.1. Raman spectra assignment based on DFT-calculated vibrational frequencies and reference experimental data

<table>
<thead>
<tr>
<th>Raman data (cm$^{-1}$)</th>
<th>DFT Calc. (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Ref. Exp. Data (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2330</td>
<td>2319</td>
<td>v(PH$_2$)sym</td>
<td>2327</td>
<td>21</td>
</tr>
<tr>
<td>1638</td>
<td></td>
<td>H$_2$O bending</td>
<td>1643</td>
<td>22</td>
</tr>
<tr>
<td>1594</td>
<td></td>
<td>v(Ni-H)assym multi-bonded</td>
<td>1600</td>
<td>23</td>
</tr>
<tr>
<td>1149</td>
<td></td>
<td>PH$_2$ scissor</td>
<td>1167</td>
<td>21</td>
</tr>
<tr>
<td>1065</td>
<td></td>
<td>CO$_3^{2-}$</td>
<td>1069</td>
<td>24</td>
</tr>
<tr>
<td>1052</td>
<td>1054</td>
<td>v(PO$_2$) sym stretch</td>
<td>1048</td>
<td>25</td>
</tr>
<tr>
<td>1016</td>
<td></td>
<td>HCO$_3^-$</td>
<td>1017</td>
<td>24</td>
</tr>
<tr>
<td>986</td>
<td></td>
<td>SO$_4^{2-}$</td>
<td>983</td>
<td>26</td>
</tr>
<tr>
<td>682</td>
<td></td>
<td>Ni-H deformation</td>
<td>692</td>
<td>23</td>
</tr>
</tbody>
</table>

Additionally, in accord with the prediction of the favorable adsorption of H on the Ni$_3$ hollow, the antisymmetric stretch of multi-bonded H on Ni appears at 1594 cm$^{-1}$, and the Ni-H in plane deformation at 682 cm$^{-1}$. The presence of H on the Ni$_3$ hollow indicates that the P reconstruction of the surface is partial. No Ni-O mode is observed.
In the Ni$_2$P spectra with KHCO$_3$, H$_2$SO$_4$, and NaOH, the presence of characteristic vibration frequencies from the surface and the electrolytes indicates that Raman scattering is collected on the interface between the electrode and the electrolyte. The PH$_2$ symmetric stretch is present in acidic, neutral, and basic pH, indicating that the P reconstruction is stable across all examined pHs. In acidic and basic media, the adsorption of hydroxide to form P*(OH)$_2$ is evidenced by the 1052 cm$^{-1}$ band. However, in neutral pH, the characteristic stretches from the adsorbed bicarbonate and carbonate ions, at 1065 and 1016 cm$^{-1}$ respectively, overlap with the P*(OH)$_2$ modes, so it is not possible to verify its formation. Adsorption of SO$_4^{2-}$ in the H$_2$SO$_4$ solution is evidenced by the 982 cm$^{-1}$ mode.

Next, we examine the Raman spectra of Ni$_2$P in the 900 to 1100 cm$^{-1}$ region as a function of potential over time, at different pHs (Figure 4). With H$_2$SO$_4$ at -0.5 V vs. RHE, the peaks corresponding to P*(OH)$_2$ and adsorbed SO$_4^{2-}$ disappear over time, as expected, due to surface reduction and Coulombic repulsion of anions at reducing potentials. However, at -0.2 V vs RHE, the P*(OH)$_2$ and SO$_4^{2-}$ peak areas remain approximately constant over the 40 min chronoamperometry. In contrast, at 0.0 V vs. RHE, which we note is still a reducing potential, (~ -0.2 V vs. OCP), a surprising increase in both the P*(OH)$_2$ and SO$_4^{2-}$ peak areas is observed, indicating that the surface oxidizes and anions accumulate near the electrode surface. A similar trend is observed with the HCO$_3^-$ and CO$_3^{2-}$ anion peaks; they are not present at the most strongly reducing potential applied (-0.5 V vs RHE), likely due to Coulombic repulsion, yet increase over time at 0.0 V and -0.2 V vs. RHE. In contrast, at pH 14, the P*(OH)$_2$ signal is low, and no significant change is observed above the noise level.
Finally, by examining the PH$_2$ symmetric stretch at 2330 cm$^{-1}$ (displayed on Figure 5), we observed that the peak height remains approximately constant over time at all pHs and potentials applied. This indicates that the adsorption of two hydrides on the reconstructed phosphorus is favored, stable and exists across the applied bias range of 0.00 to -0.5 V vs RHE, regardless of pH. Additionally, this indicates that the formation of PH$_2$ is faster than the processes of surface oxidation and anion accumulation near the surface discussed previously. This observation agrees with the calculated adsorption energies for PH$_2$ being largely favored over P*(OH)$_2$.

![Figure 4.5](image.png)

**Figure 4.5.** Raman spectra of Ni$_2$P under applied potential over time focusing on the 900-1100 cm$^{-1}$ region where modes corresponding to P(OH)$_2$, SO$_4^{2-}$, CO$_3^{2-}$, and HCO$_3^-$ appear.
108

Figure 4.6. Raman spectra of Ni₂P under applied potential over time focusing on PH₂ symmetric stretch at ~2330 cm⁻¹

Under an applied potential, over the course of the hydrogen evolution and the CO₂ reduction reactions, OH⁻ ions are released near the surface, increasing the local pH. The increased local pH consequentially raises the chemical potential of OH⁻, driving the adsorption reaction of P*(OH)₂ forward, according to the relationship:

$$E_{ads P- (OH)₂} = \mu_{P- (OH)₂} - \mu_{P*} - 2\mu_{OH^-},$$

where $E_{ads}$ becomes more negative, i.e. more favored, as the concentration of OH⁻ increases. Hence, throughout electroreduction, a slow increase in local pH due to CO₂RR and HER may favor the formation of P*(OH)₂ bonds at the detriment of PH₂. This explains why the kinetics of P*(OH)₂ formation at 0 V (at pH 0 and pH 7) and at -0.2 V (pH 7) are slow. At more strongly reducing potentials, the Coulombic repulsion of OH⁻ may outweigh the thermodynamic drive for forming P*(OH)₂ bonds.

In our previous HER and CO₂RR studies on nickel phosphides¹,⁶,²⁷, when a potential is held constant, we consistently observed a high initial current, followed by a slow
deactivation (up to 2 hours) until the reductive current reached a plateau. Upon replenishing with fresh electrolyte, the initial current was recovered, indicating that the process is reversible and may be dependent on local pH. The new operando Raman evidence of slow P*(OH)2 bond formation provides support to the hypothesis that the suppression of reductive current and the formation of P*(OH)2 may be connected. Hydroxyl groups may be binding to the reconstructed phosphorus more strongly than the hydride groups responsible for the reductive activity in HER and CO2RR, thereby blocking the active sites and reversibly poisoning the catalyst. The inhibitory effect may be more pronounced on HER than on CO2RR, explaining why HER is almost completely suppressed while the Faradaic efficiency is maximized at 0 V vs RHE, the same potential where the P*(OH)2 bonding is most evident. Understanding the implications of the P-OH bonds on CO2RR activity would enlighten our understanding of cathodic electrocatalysts. Based on the combined insight gained from our coupled experimental and theoretical study, we postulate that the observed trends of parabolic adsorption energies and surface oxidation under reductive conditions we observe may not be unique to phosphide electrocatalysts. Consequently, the community should revisit simple(r) electrocatalysts to further understand the fundamental effects of applied bias and the implications these phenomena have on catalyst stability and activity.

4.3 Conclusions
This work reports experimental and theoretical evidence that the Ni2P surface is reconstructed by P* enrichment of the Ni3 hollow sites. GC-DFT calculations indicate that the application of a reductive bias further stabilizes the reconstruction relative to
open-circuit potential, and the observed P-OH$_2$ and P-H$_2$ symmetric and asymmetric modes in Raman spectroscopy validate the existence of the P* reconstructed site. Reconstruction likely occurs during synthesis, as these modes can be observed before application of the reductive bias.

Quantifying the solvent and solute effects on the surface remains a daunting challenge. H adsorption in the form of protons, hydrides, or hydrogen atoms has always been taken for granted as most electrocatalytic systems rely on reduction via H bonds. However, we now confirm the oxidation of the surface at reductive potentials in the form of P*OH and P*(OH)$_2$ bonds at mildly reducing potentials and across the pH scale. These reduction potentials also correspond to the highest Faradaic efficiency of this catalyst towards C$_3$ and C$_4$ products, which indicates that the OH groups may aid CO$_2$RR or serve to hinder HER, which is facilitated at more reductive biases when OH groups are released.

This raises more questions about the current understanding of electrocatalytic systems, mainly whether the P(OH)$_2$ bond formation is strictly applicable to Ni$_2$P or can be extended to other electrochemical systems. Future works must also consider to what extent can this phenomenon influence the CO$_2$RR mechanism, and how can such a phenomenon be exploited to control catalyst selectivity.

Furthermore, we strongly encourage future electrocatalysis work to be modelled by appropriate methods that correctly model the surface, applied potential, solute(s), and solvent interactions – both long-range and chemical speciation – near the electrode, as the most widely-used models over the past decade employ unjustifiable assumptions, such as modeling the applied bias with a rigid shift of the Fermi level and modeling
electrocatalysis under vacuum conditions, and costly attempts to fix them, such as the inclusion of an explicit non-speciating layer of solvent molecules.

4.4 Methods

**Synthesis:** A 2 mm thick, 4×4 cm nickel foil (99.5% metal basis, Alfa Aesar), was polished consecutively with increasingly fine grit sanding paper ending at 1500-grit. The foil was then sonicated in 5% HCl(aq), rinsed with acetone, ethanol (96%), and finally ultrapure water, followed by drying in a drying oven for at least 30 min. Next, a conformal oxide layer was grown by heating the foil in air at 500°C for 2 h. The oxidized foil was transferred to tube-furnace fitted with a 2-inch diameter quartz tube. Sodium hypophosphite was placed in an alumina boat upstream from another alumina boat containing the Ni foil and an excess phosphine getter (made from a 1×3 inch 1 mm thick Ni foam) was placed downstream from the foil. The two boats were placed so that the Ni foil was at the oven’s hot zone. The tube was purged with Ar for 20 min to eliminate air, then the temperature was raised to 350°C and held for 30 min. After synthesis, the foil was washed using ultra-sonication in 5% (w/v) hydrochloric acid to remove any phosphates, then ultrapure water, ethanol, and acetone.

**WARNING:** The phosphidation reaction (2 NaH₂PO₂ → Na₂HPO₄ + PH₃) generates highly toxic and pyrophoric phosphine gas (some phosphine dimer is also formed) and must be performed in a fume hood only by trained personnel adhering to safety regulations.

**XRD:** Powder X-Ray diffraction was performed at room temperature on a Bruker D8 Advance system with a Cu K-alpha 0.15418 nm source. The step size used for the diffraction patterns was 0.02°, and the scan speed was 0.013°/s.
**Raman:** Operando Raman was conducted at room temperature using a Renishaw inVia Raman microscope, equipped with a 532 nm Nd:YAG excitation source. All spectra were recorded using 50× magnification lenses, with focal distance of ~1 cm (50L). Optical alignment was verified using a Si single crystal. Based on the laser wavelength and water refractive index, the probing depth was calculated to be at least 300 nm, but some studies indicate that it may be as extensive as several micrometers.28,29 For the operando spectra, we used an electrochemical Raman cell with Ag/AgCl micro-reference electrode and platinum wire counter electrode from redox.me. Before each experiment, the reference electrode potential was measured against a pristine calomel electrode, which is periodically calibrated against SHE. A Gamry potentiostat interface 5000E was used to apply constant potential for 40 min, while Raman spectra was recorded with 10 accumulations, 100% power, in 7.5-minute intervals.

**DFT:** DFT calculations with periodic boundary conditions were performed using the JDFTx code. The exchange-correlation energy was calculated using the Generalized Gradient Approximation (GGA) by employing the Bayesian Error Estimate Functional with van der Waals correlations (BEEF-vdW). The SG15 Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials were used to model truncation of the core electrons of the system. The Ni$_2$P (0001) surface facet was modeled using a 4-layer unit cell, consisting of alternation Ni$_3$P and Ni$_3$P$_2$ stoichiometries with a Ni$_3$P$_2$ termination, for a total of 48 Ni and 24 P atoms in the clean surface unit cell. The lattice parameters were optimized for the clean surface and fixed for all subsequent reconstruction and adsorbate calculations. One unit cell has four equivalents of the Ni$_3$ hollow site; thus, a completely reconstructed surface includes 48 Ni and 28 P atoms.
A 2 × 2 × 1 Monkhorst-Pack grid was used for k-point sampling of the Brillouin zone. Geometries were optimized with a 20 Ryd planewave cutoff energy. The electronic energies were converged to $1 \times 10^{-8}$ Hartrees, and ionic steps were converged to $1 \times 10^{-6}$ Hartrees. Although nonmagnetic, the magnetic states of the Ni$_2$P surface were allowed to relax, expectedly resulting in negligible magnetic moments. The charge-asymmetry corrected, local-response, nonlocal-cavity solvation model (CANDLE) was implemented to account for solvation effects on molecules and surfaces. An electrolyte consisting of 0.5 M Na$^+$ and 0.5 M F$^-$ was embedded into the solvent model.

The Grand Canonical Electronic DFT (GC-DFT) method was used to include applied bias effects into the Schrodinger equation. This models the applied bias as a fixed chemical potential, which allows a more realistic description of the free flow of electrons through the electrode by self-consistently solving for the number of electrons that minimizes the grand free energy while also balancing the bound fluid charges. All constant potential GC-DFT calculations were performed using the same settings.

**Derivation of Surface Energies:**

**Reconstruction Plots:**

\[
\gamma(T,P) = \frac{1}{2N} \left( G(T,P) - \sum_{i=1}^{N} N_i \mu_i(T,P) \right) \quad \text{Eq. 1}
\]

\[
\mu_i(T,P) = \mu_i^0 + \Delta \mu_i(T,P) \quad \text{Eq. 2}
\]

\[
\Delta \mu_i(T,P) = RT \ln \frac{P}{p_i} \quad \text{Eq. 3}
\]

\[
\mu_{hc} = \frac{1}{2} (\mu_{Ni}^{init} - \mu_{F}) \quad \text{Eq. 4}
\]
\[ y(T, P) = \frac{1}{2A} \left( g(T, P) - \frac{N_n}{2} \lambda N_n + \mu_f \right) \]  

Eq. 5

\[ \Delta \mu_H = -RTpH \ln(10) \]  

Eq. 6

Speciation Plots:
4.5 References


(10) Li, X.; Wang, S.; Li, L.; Sun, Y.; Xie, Y. Progress and Perspective for In Situ Studies of CO 2 Reduction. J. Am. Chem. Soc. 2020, jacs.0c02973. https://doi.org/10.1021/jacs.0c02973.


Electronic Supplementary Information

Selective CO$_2$ reduction to C$_3$ and C$_4$ oxhydrocarbons on nickel phosphides at overpotentials as low as 10 mV

Karin U. D. Calvinho$^a$, Anders B. Laursen$^a$, Kyra M. K. Yap$^a$, Timothy A. Goetjen$^a$, Shinjae Hwang$^a$, Nagarajan Murali$^a$, Bryan Mejia-Sosa$^b$, Alexander Lubarski$^a$, Krishani M. Teeluck$^a$, Eugene S. Hall$^a$, Eric Garfunkel$^a$, Martha Greenblatt$^a$, and G. Charles Dismukes$^{a,b,*}$

$^a$Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey, 08854
$^b$Waksman Institute of Technology, Rutgers, The State University of New Jersey, 190 Frelinghuysen Road, Piscataway, New Jersey, 08854
*$^{*}$Corresponding author (e-mail: dismukes@rutgers.edu).
†These authors contributed equally.
1. Powder X-Ray Diffraction

Powder X-Ray diffraction was conducted at room temperature on a Philips Xpert system, spinning at 100 rpm, in a Bragg-Brentano geometry, using Cu K-alpha 0.15418 nm x-rays, calibrated daily with a Si standard. The step size used for the diffraction patterns shown was 0.02°, and the scan speed 0.013°/s. The sample holder was 3 mm deep and ½” in diameter, completely filled with as-synthesized powder. Post-reaction PXRD was conducted on catalyst pellets containing 1 (w/w) % neutralized Nafion. The pellets, 2 cm in diameter and 2 mm thick, were extracted from the reactor, rinsed with ultrapure water, and mounted onto a sample holder. After the measurements, the patterns were translated to correct for the offset sample height.

Figure S7 Powder X-ray diffraction of Ni₃P as-synthesized (top trace), after at least 3 hours of CO₂RR (middle trace) and simulated ICDD reference pattern (bottom trace). Pristine Ni₃P is crystalline and phase-pure. After reaction, no crystalline impurity is formed and crystallinity of the bulk structure of Ni₃P is preserved.
Figure S8: Powder X-ray diffraction of $\text{Ni}_{12}\text{P}_5$ as-synthesized (top trace), after at least 3 hours of CO$_2$RR (middle trace) and simulated ICDD reference pattern (bottom trace). Pristine $\text{Ni}_{12}\text{P}_5$ is crystalline and phase-pure. After reaction, no crystalline impurity is formed and crystallinity of the bulk structure of $\text{Ni}_{12}\text{P}_5$ is preserved.
Figure S9: Powder X-ray diffraction of Ni$_2$P as-synthesized (top trace), after at least 3 hours of CO$_2$RR (middle trace) and simulated ICDD reference pattern (bottom trace). Pristine Ni$_2$P is crystalline and phase-pure. After reaction, no crystalline impurity is formed and crystallinity of the bulk structure of Ni$_2$P is preserved.
Figure S10 Powder X-ray diffraction of Ni₅P₄ as-synthesized (top trace), after at least 3 hours of CO₂RR (middle trace) and simulated ICDD reference pattern (bottom trace). Pristine Ni₅P₄ is crystalline and phase-pure. After reaction, no crystalline impurity is formed and crystallinity of the bulk structure of Ni₅P₄ is preserved.
Figure S11: Powder X-ray diffraction of NiP$_2$ as-synthesized (purple trace), after 3 hours of CO$_2$RR (blue trace) and simulated ICDD reference pattern for the monoclinic (red trace) and cubic (mint green trace) polymorphs. Pristine NiP$_2$ is in the monoclinic crystalline polymorph. After reaction, while the crystalline structure is mostly preserved, 9% (calculated by the peak area ratio) of the monoclinic phase is converted to the cubic phase of NiP$_2$. Additionally, four new diffraction peaks appear. XPS indicates the presence of surface hydroxides and phosphates. The impurity peak at 38° matches one of the 100% intensity peaks, the (101), in Ni(OH)$_2$ (ICDD 00-014-0117), but the other 100% intensity (001) peak at 19° is missing. The lower intensity Ni(OH)$_2$ peaks coincide with the NiP$_2$ peaks and would not be resolved in the diffractogram. The three remaining impurity peaks match Ni$_3$(PO$_4$)$_2$ (ICDD 01-070-1796), including the major (111) line at 20° and other peaks expected to be minor. Since the intensities expected of the phosphate and hydroxide pattern do not match perfectly the peaks that appear after reaction, the assignment of the impurity structure is uncertain by PXRD alone.
2. Scanning Electron Microscopy

The scanning electron micrographs shown below (Figure S6 and S7) were obtained using a Zeiss Sigma Field Emission SEM in-lens detector. The samples were supported on conductive carbon tape.

Figure S12: SEM images of as-synthesized nickel phosphide loose powders showing roughly spherical, polydisperse particles (top row). The second row of images shows the morphology of the particles after being pressed into pellets. After at least three CO\textsubscript{2}RR turnovers per surface atom, the catalysts were imaged as pressed pellets (bottom row).

Figure S13: Cross-section SEM of a post-reaction Ni\textsubscript{2}P pellet. From (a), the mean thickness of the pellet is 575 µm. The cylinder that appears on the lower right corner of image is from the aluminum mesh used for the pellet’s mechanical support and faces away from the electrolyte. Inset (b) shows that, near the surface, the particles are packed more tightly than in the center of the pellet, (c).
3. Determination of uncompensated resistance

Figure S14: Potentiostatic electrochemical impedance spectroscopy of Ni$_2$P at 0 V vs RHE in 0.5 M KHCO$_3$ gives a solution resistance of 6.75 Ω. This measurement was done before reaction and is representative of the behavior observed for all of the tested nickel phosphides.
4. Electrochemical surface area measurements

Electrochemical capacitance was utilized to determine the surface area of each of the nickel phosphides. To measure capacitance, the potential was cycled between 0.11 and -0.04 V vs RHE at different scan rates in CO₂-saturated 0.5M KHCO₃. The cyclic voltammograms for Ni₂P can be seen in Figure S9. The capacitive current was measured at 0.04 V, where the faradaic current is minimal, and plotted versus scan rate. The slope of the linear fit is the capacitance of the sample. The electrochemical surface area (ECSA) was calculated using the ratio of the capacitance measured and the specific capacitance for metal phosphides (40 µF/cm², as reported by Kibsgaard et al¹). A roughness factor was then obtained by dividing the ECSA by the geometric area of the sample.

![Cyclic Voltammogram]

Figure S15: Electrochemical capacitance measurement to determine the surface area of Ni₂P. The capacitive current is determined from cyclic voltammograms in a region with minimal Faradaic current (in this case 0.04 V). In the inset, the capacitive current is plotted as a function of scan rate.

Table S1: Roughness factors calculated from the electrochemical surface area

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Roughness Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃P</td>
<td>276</td>
</tr>
<tr>
<td>Ni₁₀P₅</td>
<td>158</td>
</tr>
<tr>
<td>Ni₃P</td>
<td>312</td>
</tr>
<tr>
<td>Ni₅P₄</td>
<td>214</td>
</tr>
<tr>
<td>NiP₂</td>
<td>349</td>
</tr>
</tbody>
</table>
5. Linear Sweep Voltammetry

Figure S16: Linear sweep voltammetry of Ni₃P, Ni₁₂P₅, Ni₅P₄, and NiP₂ in CO₂ saturated 0.5 M KHCO₃ (blue) and argon-purged 0.5 M phosphate buffer solution. The scan rate used was 0.5 mV/s and the solution resistance was compensated through positive feedback.
6. Chronoamperometry

Figure S17: Representative IR-compensated chronoamperometry measurements in CO$_2$-purged (5 sccm) 0.5 M KHCO$_3$. 

7. Gas Chromatography

Detection and quantification of possible headspace products (Hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene) was performed by an auto-sampling online HP 5890 Series II GC, with a 500 µL sample loop. The GC was fitted with a 6’ packed HayeSep D, and a 6’ packed MoleSieve 13X column, with thermal conductivity and flame ionization detectors connected in series. Argon was used as the carrier gas. The temperature was held at 50°C for 5 minutes for the desorption of permanent gases, then increased at a rate of 20 °C/min for 10 min for desorption of C₂ hydrocarbons, CO and CO₂, finishing with a 2 minute hold at 250 °C to ensure full elution of possible water vapor. Quantification limits were 2 ppm for C₂H₆ and C₂H₄, 5 ppm for CH₄, 50 ppm for H₂, 200 ppm for O₂ and N₂, and 600 ppm for CO₂ and CO.

Samples were taken before reaction to check for air presence and then every 30 minutes thereafter. Calibration curves were constructed from certified gas standards (Gasco) by CO₂ dilution using MKS P4B mass flow controllers (MFCs). The hydrogen calibration was done with in situ generated gas through electrolysis of water on platinum, under argon purge, and diluted post-reaction with CO₂.

Figure S18: (A) Typical chromatograph resulting from a mixed calibration standard (Gasco 105L-508). The quantification limits are 100 ppm (B) Calibration curve for hydrogen, the only product detected in the gas phase.
8. Liquid Product Analysis by $^1$H NMR/COSY

$^1$H NMR spectra were recorded using a Bruker Avance III 700 MHz NMR spectrometer equipped with a cryoprobe. 400 μL samples from the CO$_2$ reduction electrolyte were taken after the reaction from the working electrode compartment. The samples were combined with 100 μL of D$_2$O. Correlation spectra (COSY) were also recorded on the samples to assist in the $^1$H.

While the assignment of the formic acid peak was straightforward, the same was not true for the other two products. Based on the molecular structure, one would expect to see doublet peaks for 2,3-furandiol with coupling constants of $J = 1.75$ Hz. However, owing to the linewidths in aqueous solvent, they appear as singlets. For methylglyoxal, the complications arise from its high reactivity: in water, methylglyoxal forms mono-hydrates, di-hydrates, dimers and trimers. The $^1$H NMR of methylglyoxal in aqueous solution and its derivatives has been reported by Nemet et al$^2$; the corresponding predicted shifts are reported in the table below.

![Figure S19: $^1$H NMR of an electrolyte sample from the electroreduction of CO$_2$ on Ni$_3$P$_4$.](image)

<table>
<thead>
<tr>
<th>Species</th>
<th>Predicted Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-furandiol</td>
<td></td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td></td>
</tr>
</tbody>
</table>

Table S2: Predicted $^1$H NMR shifts for 2,3-furandiol and methylglyoxal species.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Predicted delta (ppm)</th>
<th>Compound</th>
<th>Predicted delta (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Compound" /></td>
<td>6.145 (d), J = 0.0025 ppm</td>
<td><img src="image2.png" alt="Compound" /></td>
<td>2.095 (s)</td>
</tr>
<tr>
<td><img src="image3.png" alt="Compound" /></td>
<td>7.030 (d), J = 0.0025 ppm</td>
<td><img src="image4.png" alt="Compound" /></td>
<td>5.726 (s)</td>
</tr>
<tr>
<td><img src="image5.png" alt="Compound" /></td>
<td>2.067 (s)</td>
<td><img src="image6.png" alt="Compound" /></td>
<td>1.231 (s)</td>
</tr>
<tr>
<td><img src="image7.png" alt="Compound" /></td>
<td>9.560 (s)</td>
<td><img src="image8.png" alt="Compound" /></td>
<td>2.098 (s)</td>
</tr>
<tr>
<td><img src="image9.png" alt="Compound" /></td>
<td>2.083 (s)</td>
<td><img src="image10.png" alt="Compound" /></td>
<td>4.890 (s)</td>
</tr>
<tr>
<td><img src="image11.png" alt="Compound" /></td>
<td>5.441 (s)</td>
<td><img src="image12.png" alt="Compound" /></td>
<td>5.825 (s)</td>
</tr>
<tr>
<td><img src="image13.png" alt="Compound" /></td>
<td>2.100 (s)</td>
<td><img src="image14.png" alt="Compound" /></td>
<td>1.301 (s)</td>
</tr>
<tr>
<td><img src="image15.png" alt="Compound" /></td>
<td>5.378 (s)</td>
<td><img src="image16.png" alt="Compound" /></td>
<td>4.415 (s)</td>
</tr>
<tr>
<td><img src="image17.png" alt="Compound" /></td>
<td>1.112 (s)</td>
<td><img src="image18.png" alt="Compound" /></td>
<td>1.286 (s)</td>
</tr>
<tr>
<td><img src="image19.png" alt="Compound" /></td>
<td>4.871 (s)</td>
<td><img src="image20.png" alt="Compound" /></td>
<td>1.391 (s)</td>
</tr>
<tr>
<td><img src="image21.png" alt="Compound" /></td>
<td>3.476 (d)</td>
<td><img src="image22.png" alt="Compound" /></td>
<td>3.476 (d)</td>
</tr>
<tr>
<td><img src="image23.png" alt="Compound" /></td>
<td>3.996 (d)</td>
<td><img src="image24.png" alt="Compound" /></td>
<td>3.996 (t)</td>
</tr>
<tr>
<td><img src="image25.png" alt="Compound" /></td>
<td>4.415 (s)</td>
<td><img src="image26.png" alt="Compound" /></td>
<td>4.464 (s)</td>
</tr>
</tbody>
</table>
9. Liquid Chromatography - Mass Spectrometry

Reaction products were analyzed by injecting 10 μL of electrolyte into an Agilent 1200 series HPLC coupled to an Agilent 6490 QQQ mass spectrometer equipped with an ion-spray source. Products were separated utilizing an Aminex HPX-87H column, using isocratic elution with 5 mM sulfuric acid in LCMS-grade water at a flow rate of 0.2 mL min⁻¹. Mass spectral operating parameters were set as described by Bennette et al.⁵ The MS scan was performed in negative ion mode over a range of mass-to-charge ratios between 30 and 195 m/z. The acquired data was analyzed using Agilent Mass Hunter software v. 1.04.

Figure S20: LC-MS of a -0.1 V vs RHE Ni2P sample. The unretained peak is at 19 min, followed by 2,3-furandiol and methylglyoxal. As methylglyoxal undergoes self-condensation in solution, several peaks are observed for it. Assignment of the LC-MS mass-to-charge ratios is shown in the table below.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecular Formula</th>
<th>MW</th>
<th>m/z</th>
<th>Retention time (min)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆H₆O₄</td>
<td>142.1</td>
<td>141</td>
<td>45.5</td>
<td>Methylglyoxal dimer (condensation product of methylglyoxal)</td>
</tr>
<tr>
<td></td>
<td>CH₂O₅S</td>
<td></td>
<td></td>
<td>35.5</td>
<td>Sulfuric acid + formic acid</td>
</tr>
<tr>
<td></td>
<td>C₆H₆O₅</td>
<td>158.1</td>
<td>157</td>
<td>26.7</td>
<td>Condensation product of methylglyoxal</td>
</tr>
<tr>
<td></td>
<td>C₅H₄O₅</td>
<td>144.1</td>
<td>161</td>
<td>18.2, 20.8</td>
<td>2,3-furandiol and carbonic acid ester + H₂O</td>
</tr>
<tr>
<td></td>
<td>C₆H₆O₅</td>
<td>158.1</td>
<td>175</td>
<td>26.5</td>
<td>Condensation product of methylglyoxal + water</td>
</tr>
<tr>
<td></td>
<td>C₇H₆O₆</td>
<td>186.1</td>
<td>185</td>
<td>18.5</td>
<td>2 x methylglyoxal + formic acid (condensation product of methylglyoxal)</td>
</tr>
</tbody>
</table>

Table S3: Interpretation of LCMS based on reference 6
10. High Performance Liquid Chromatography

Figure S21: Example of chromatographs for a CO$_2$RR sample on Ni$_2$P at -0.1 V vs RHE obtained with the refractive index detector (left) and the UV absorbance detector (right), arranged in series.

Figure S22: Calibration curves (from left to right) for 2,3-furandiol, methylglyoxal and formic acid. The mean error associated with the HPLC quantification was determined to be <2%.
11. Method for 2,3-furandiol quantification

Due to the difficulty in purchasing analytical standards of 2,3-furandiol, we quantitatively determined the concentration of the analyte in one CO₂RR electrolyte sample via ¹H-NMR using a Bruker Avance III 700 MHz. This NMR spectrometer was equipped with a cryoprobe. The sample was then considered a 2,3-furandiol standard and diluted to build a calibration curve for the HPLC-RID, used as the routine quantification tool. The retention time of 2,3-furandiol was confirmed through LCMS. For the NMR calibration, five solutions of 510 µL were prepared to determine a curve for the 2,3-furandiol product. The CO₂RR electrolyte containing 2,3-furandiol was diluted to 400 µL in 0.5 M KHCO₃ in electrolyte:bicarbonate ratios of 1:0, 1:1, 1:2, 1:3, and 0:1 (blank), to which 100 µL of D₂O and 10 µL of acetonitrile were added. The acetonitrile, which has a single peak at 2.00 ppm, was utilized as an internal standard to quantify 2,3-furandiol in the liquid products through the baseline-subtracted peak area ratio. The acetonitrile did not interfere with the 2,3-furandiol peaks, which occur at 6.26 and 7.03 ppm respectively. The concentration of 2,3-furandiol in the electrolyte was calculated from the equation of the linear fit, shown below to be 140 µmol/L.

![Calibration Curve](image)

Figure S23: Concentration of 2,3-furandiol in a CO₂RR electrolyte sample as measured by NMR as a function of sample dilution.
12. Faradaic Efficiency

The Faradaic Efficiency for the liquid CO\textsubscript{2} reduction products was calculated using the equation:

\[
FE_{\text{CO2RR}} = \frac{\text{Concentration} \cdot V_{\text{electrolyte}} \cdot \# \text{electrons} \cdot F}{\text{Charge}}
\]

where the concentration was measured by HPLC; the volume of electrolyte measured after each experiment (around 6 mL); the number of electrons is 2 for formate, 12 for methylglyoxal and 14 for furandiol; F is Faraday’s constant and the charge was integrated over the full time of the experiment. Each value in the table below reflects the average of at least three measurements.

To determine the hydrogen Faradaic Efficiency, on-line measurements were conducted, and the following equation was used:

\[
FE_{\text{H2}} = \frac{\text{mols of H2} \cdot \# \text{electrons} \cdot F}{\text{current} \cdot \text{time}}
\]

Where the number of mols of hydrogen was determined by GC, the number of electrons is 2, the current is recorded at the instant of automated sampling, and the time is what is required to fill up the GC sample loop (3 s at 5 sccm). Each value in the table below reflects the average of at least 5 measurements.

Table S4: Faradaic efficiency for all catalysts at the potentials tested \pm standard deviation between at least three chronoamperometry experiments.

<table>
<thead>
<tr>
<th>Potenti\textsubscript{al} (V vs RHE)</th>
<th>Formate Faradaic Efficiency (%)</th>
<th>2,3-furandiol Faradaic Efficiency (%)</th>
<th>Methylglyoxal Faradaic Efficiency (%)</th>
<th>CO\textsubscript{2}RR FE (%)</th>
<th>Hydrogen Faradaic Efficiency (%)</th>
<th>Total FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{3}P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>4.0 0.0</td>
<td>2.0 0.0</td>
<td>2.3 0.0</td>
<td>89. 34</td>
<td>98. 2</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>4.0 0.0</td>
<td>2.0 0.0</td>
<td>2.3 0.0</td>
<td>89. 34</td>
<td>98. 2</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{12}P\textsubscript{s}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>4.0 0.0</td>
<td>2.0 0.0</td>
<td>2.3 0.0</td>
<td>89. 34</td>
<td>98. 2</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>4.0 0.0</td>
<td>2.0 0.0</td>
<td>2.3 0.0</td>
<td>89. 34</td>
<td>98. 2</td>
<td></td>
</tr>
</tbody>
</table>
| Potenti  
(V vs RHE) | Formate Faradaic Efficiency (%) | 2,3-furandiol Faradaic Efficiency (%) | Methylglyoxal Faradaic Efficiency (%) | CO$_2$R FE (%) | Hydrogen Faradaic Efficiency (%) | Total FE (%) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.5 ± 0.0 4.6 ± 0.0 42. ± 0.6</td>
<td>1 ± 2 5 ± 7 3 ± 8 48.4 ± 13.</td>
<td>0.7 3 ± 2 94.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>1.6 ± 0.0 71.1 ± 1.1 27. ± 0.4</td>
<td>1 ± 3 6 ± 5 1 ± 3 100.3 ± 0.0 8 ± 3</td>
<td>0.0 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.10</td>
<td>0.6 ± 0.0 9.9 ± 0.2 3.1 ± 0.0</td>
<td>1 ± 1 4 ± 6 7 ± 5 13.7</td>
<td>86. ± 3.7 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.20</td>
<td>0.5 ± 0.0 8 ± 0.2 2.5 ± 0.0</td>
<td>0 ± 0 8 ± 7 5 ± 7 15.4</td>
<td>84. ± 5.1 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.30</td>
<td>0.2 ± 1 3 ± 2 2 ± 0.0</td>
<td>5 ± 3 3 ± 4 5 ± 1 10.</td>
<td>92. ± 15. 97.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.40</td>
<td>0.3 ± 0.0 7 ± 0.1 4.5 ± 0.0</td>
<td>8 ± 4 7 ± 1 8 ± 5 12.0</td>
<td>88. ± 14. 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.50</td>
<td>0.3 ± 0.0 7 ± 0.1 4.5 ± 0.0</td>
<td>8 ± 4 7 ± 1 8 ± 5 12.0</td>
<td>88. ± 14. 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ni$_3$P

| Potenti  
(V vs RHE) | Formate Faradaic Efficiency (%) | 2,3-furandiol Faradaic Efficiency (%) | Methylglyoxal Faradaic Efficiency (%) | CO$_2$R FE (%) | Hydrogen Faradaic Efficiency (%) | Total FE (%) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.5 ± 0.0 4.6 ± 0.0 42. ± 0.6</td>
<td>1 ± 2 5 ± 7 3 ± 8 48.4 ± 13.</td>
<td>0.7 3 ± 2 94.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>1.6 ± 0.0 71.1 ± 1.1 27. ± 0.4</td>
<td>1 ± 3 6 ± 5 1 ± 3 100.3 ± 0.0 8 ± 3</td>
<td>0.0 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.10</td>
<td>0.6 ± 0.0 9.9 ± 0.2 3.1 ± 0.0</td>
<td>1 ± 1 4 ± 6 7 ± 5 13.7</td>
<td>86. ± 3.7 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.20</td>
<td>0.5 ± 0.0 8 ± 0.2 2.5 ± 0.0</td>
<td>0 ± 0 8 ± 7 5 ± 7 15.4</td>
<td>84. ± 5.1 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.30</td>
<td>0.2 ± 1 3 ± 2 2 ± 0.0</td>
<td>5 ± 3 3 ± 4 5 ± 1 10.</td>
<td>92. ± 15. 97.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.40</td>
<td>0.3 ± 0.0 7 ± 0.1 4.5 ± 0.0</td>
<td>8 ± 4 7 ± 1 8 ± 5 12.0</td>
<td>88. ± 14. 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.50</td>
<td>0.3 ± 0.0 7 ± 0.1 4.5 ± 0.0</td>
<td>8 ± 4 7 ± 1 8 ± 5 12.0</td>
<td>88. ± 14. 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ni$_3$P$_4$

| Potenti  
(V vs RHE) | Formate Faradaic Efficiency (%) | 2,3-furandiol Faradaic Efficiency (%) | Methylglyoxal Faradaic Efficiency (%) | CO$_2$R FE (%) | Hydrogen Faradaic Efficiency (%) | Total FE (%) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.5 ± 0.0 4.6 ± 0.0 42. ± 0.6</td>
<td>1 ± 2 5 ± 7 3 ± 8 48.4 ± 13.</td>
<td>0.7 3 ± 2 94.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>1.6 ± 0.0 71.1 ± 1.1 27. ± 0.4</td>
<td>1 ± 3 6 ± 5 1 ± 3 100.3 ± 0.0 8 ± 3</td>
<td>0.0 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.10</td>
<td>0.6 ± 0.0 9.9 ± 0.2 3.1 ± 0.0</td>
<td>1 ± 1 4 ± 6 7 ± 5 13.7</td>
<td>86. ± 3.7 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.20</td>
<td>0.5 ± 0.0 8 ± 0.2 2.5 ± 0.0</td>
<td>0 ± 0 8 ± 7 5 ± 7 15.4</td>
<td>84. ± 5.1 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.30</td>
<td>0.2 ± 1 3 ± 2 2 ± 0.0</td>
<td>5 ± 3 3 ± 4 5 ± 1 10.</td>
<td>92. ± 15. 97.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.40</td>
<td>0.3 ± 0.0 7 ± 0.1 4.5 ± 0.0</td>
<td>8 ± 4 7 ± 1 8 ± 5 12.0</td>
<td>88. ± 14. 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.50</td>
<td>0.3 ± 0.0 7 ± 0.1 4.5 ± 0.0</td>
<td>8 ± 4 7 ± 1 8 ± 5 12.0</td>
<td>88. ± 14. 100.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NiP
### Table S5: Partial current densities for all catalysts

Currents were recorded after 3 hours of chronoamperometry and multiplied by the faradaic efficiency for each product.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential (V vs RHE)</th>
<th>$j_{\text{Total}}$ (µA/cm²)</th>
<th>$j_{\text{Formate}}$ (µA/cm²)</th>
<th>$j_{\text{Methylglyoxal}}$ (µA/cm²)</th>
<th>$j_{\text{Furanald}}$ (µA/cm²)</th>
<th>$j_{\text{CO}2\text{RR}}$ (µA/cm²)</th>
<th>$j_{\text{HER}}$ (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃P</td>
<td>0</td>
<td>-0.15</td>
<td>-6.01</td>
<td>-3.46</td>
<td>-3.05</td>
<td>-12.52</td>
<td>-132.76</td>
</tr>
<tr>
<td></td>
<td>-0.1</td>
<td>-0.85</td>
<td>-37.32</td>
<td>-15.63</td>
<td>-28.61</td>
<td>-81.56</td>
<td>-777.99</td>
</tr>
<tr>
<td></td>
<td>-0.2</td>
<td>-0.42</td>
<td>-15.12</td>
<td>-7.60</td>
<td>-12.26</td>
<td>-34.99</td>
<td>-358.68</td>
</tr>
<tr>
<td></td>
<td>-0.3</td>
<td>-0.42</td>
<td>-7.10</td>
<td>-10.54</td>
<td>-7.90</td>
<td>-25.54</td>
<td>-394.80</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>-0.86</td>
<td>-23.54</td>
<td>-34.67</td>
<td>-24.65</td>
<td>-82.86</td>
<td>-774.68</td>
</tr>
<tr>
<td></td>
<td>-0.5</td>
<td>-1.75</td>
<td>-15.75</td>
<td>-32.73</td>
<td>-21.70</td>
<td>-70.18</td>
<td>-1685.25</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>-0.08</td>
<td>-0.38</td>
<td>-12.15</td>
<td>-17.90</td>
<td>-30.43</td>
<td>-50.46</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.33</td>
<td>-1.46</td>
<td>-107.24</td>
<td>-108.57</td>
<td>-217.27</td>
<td>-114.53</td>
</tr>
<tr>
<td>Ni₁₂P₃</td>
<td>-0.1</td>
<td>-0.08</td>
<td>-1.18</td>
<td>-5.91</td>
<td>-2.13</td>
<td>-9.22</td>
<td>-74.09</td>
</tr>
<tr>
<td></td>
<td>-0.2</td>
<td>-0.45</td>
<td>-11.03</td>
<td>-39.09</td>
<td>-29.10</td>
<td>-79.22</td>
<td>-374.55</td>
</tr>
<tr>
<td></td>
<td>-0.3</td>
<td>-1.80</td>
<td>-1.26</td>
<td>-24.84</td>
<td>-1.98</td>
<td>-28.08</td>
<td>-1701.00</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>-1.41</td>
<td>-6.63</td>
<td>-18.47</td>
<td>-9.17</td>
<td>-34.26</td>
<td>-1357.83</td>
</tr>
<tr>
<td></td>
<td>-0.5</td>
<td>-2.37</td>
<td>-6.87</td>
<td>-21.57</td>
<td>-9.01</td>
<td>-37.45</td>
<td>-2360.52</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>-0.04</td>
<td>-0.59</td>
<td>-16.57</td>
<td>-1.82</td>
<td>-18.98</td>
<td>-18.14</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.03</td>
<td>-0.50</td>
<td>-8.42</td>
<td>-22.25</td>
<td>-31.17</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni₂P</td>
<td>-0.1</td>
<td>-0.14</td>
<td>-0.86</td>
<td>-4.48</td>
<td>-14.06</td>
<td>-19.40</td>
<td>-122.45</td>
</tr>
<tr>
<td></td>
<td>-0.2</td>
<td>-0.04</td>
<td>0.00</td>
<td>-1.78</td>
<td>-4.23</td>
<td>-6.01</td>
<td>-33.18</td>
</tr>
<tr>
<td></td>
<td>-0.3</td>
<td>-0.56</td>
<td>-2.92</td>
<td>-11.52</td>
<td>-14.22</td>
<td>-28.67</td>
<td>-518.26</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>-2.77</td>
<td>-68.63</td>
<td>-63.10</td>
<td>-198.43</td>
<td>-330.16</td>
<td>-2446.48</td>
</tr>
<tr>
<td></td>
<td>-0.5</td>
<td>-3.50</td>
<td>-47.29</td>
<td>-27.32</td>
<td>-41.69</td>
<td>-116.31</td>
<td>-3222.93</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>-0.42</td>
<td>-4.63</td>
<td>-189.32</td>
<td>-143.03</td>
<td>-336.98</td>
<td>-67.55</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-0.23</td>
<td>-5.94</td>
<td>-21.16</td>
<td>-20.88</td>
<td>-47.98</td>
<td>-182.35</td>
</tr>
<tr>
<td>Ni₃P₄</td>
<td>-0.1</td>
<td>-1.71</td>
<td>-41.72</td>
<td>-64.47</td>
<td>-170.49</td>
<td>-276.68</td>
<td>-1405.62</td>
</tr>
<tr>
<td></td>
<td>-0.2</td>
<td>-2.06</td>
<td>-7.62</td>
<td>-80.55</td>
<td>-70.45</td>
<td>-158.62</td>
<td>-1808.68</td>
</tr>
<tr>
<td></td>
<td>-0.3</td>
<td>-2.57</td>
<td>-18.25</td>
<td>-103.83</td>
<td>-81.47</td>
<td>-203.54</td>
<td>-2248.75</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>-3.82</td>
<td>-24.84</td>
<td>-34.78</td>
<td>-73.76</td>
<td>-133.38</td>
<td>-3718.47</td>
</tr>
<tr>
<td></td>
<td>-0.5</td>
<td>-4.59</td>
<td>-28.46</td>
<td>-28.00</td>
<td>-59.67</td>
<td>-116.13</td>
<td>-4296.24</td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>-0.21</td>
<td>-0.46</td>
<td>-127.70</td>
<td>-82.14</td>
<td>-210.30</td>
<td>-0.21</td>
</tr>
<tr>
<td></td>
<td>-0.1</td>
<td>-0.44</td>
<td>-0.44</td>
<td>-373.89</td>
<td>-71.77</td>
<td>-446.10</td>
<td>-17.28</td>
</tr>
<tr>
<td>NiP₂</td>
<td>-0.2</td>
<td>-1.71</td>
<td>-0.34</td>
<td>-30.10</td>
<td>-15.39</td>
<td>-45.83</td>
<td>-1609.11</td>
</tr>
<tr>
<td></td>
<td>-0.3</td>
<td>-3.60</td>
<td>-1.08</td>
<td>-275.30</td>
<td>-47.14</td>
<td>-323.53</td>
<td>-3134.49</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>-9.68</td>
<td>-0.97</td>
<td>-54.22</td>
<td>-38.73</td>
<td>-93.91</td>
<td>-8965.10</td>
</tr>
<tr>
<td></td>
<td>-0.5</td>
<td>-15.64</td>
<td>-1.56</td>
<td>-26.59</td>
<td>-29.72</td>
<td>-57.87</td>
<td>-15405.4</td>
</tr>
</tbody>
</table>
14. Control Experiments

To determine if any organic products detected during the experiments could have originated from the degradation of the membrane, the body of the cell (Nylon 66), or the ionomer used in the electrode preparation, we performed a selection of control experiments. First, the cell was assembled, filled out with 0.25 M pyrophosphate buffer, and purged with argon. A typical Ni$_2$P pellet containing 1% Nafion was used as the working electrode. A sample of the electrolyte was taken after 1h of purge, then 24h, with no potential applied. No carbon-containing products were detected by HPLC nor by NMR.

Next, using the same experimental configuration, electrolysis was performed at -0.20 V vs RHE for 6h to determine if any products could have resulted from reductive degradation of the cell, membrane, or ionomer. Again, no organic compounds were detected by NMR, nor by HPLC.

Finally, we performed isotope labeling experiments, described below in Section 14, which show that the C$_1$, C$_3$, and C$_4$ products originate from dissolved inorganic carbon.
15. **13C Isotopic Labeling**

To confirm that the origin of the products described was indeed dissolved inorganic carbon (CO₂ or HCO₃⁻) and not a contamination from other sources, such as the membrane or the electrolyzer body, we conducted an electrolysis experiment on Ni₂P at 0.00 V vs RHE using 13C labeled bicarbonate. 1.000 g of NaH¹³CO₃ (98 atom % ¹³C, 99% chemically pure, Sigma Aldrich) was diluted with 25 mL of argon-purged ultra-pure water to form a 0.475 M labeled bicarbonate solution. The cell was immediately filled with 7 mL of solution in each compartment, purged with argon for 20 min at 5 sccm, and sealed with an airlock. We then proceeded to electrolyze the solution for 38h. The total amount of products formed was quantified via HPLC: 0.22 mM of formate, 2.51 mM of 2,3-furandiol and 1.73 mM of methylglyoxal.

Surface-Assisted Laser Desorption/Ionization time-of-flight mass spectrometry (SALDI TOF-TOF-MS) was performed to quantify the ratio of ¹³C to ¹²C in the products formed. The instrument used was a Bruker Daltonics Autoflex III Smartbeam mass spectrometer equipped with a 355 nm Nd:YAG laser. Samples were exposed to 500 laser shots fired at a frequency of 100 Hz at typically 25-45% of full laser power in a random walk pattern to produce integrated spectra. The instrument was operated in reflectron mode with a mass range of 50-1200 Da. The samples were prepared by pipetting 1 µL of electrolyte onto a specially prepared gold-sputtered stainless-steel plate. The background was verified to be negligible and the signal-to-noise ratio was at least 10 for all peaks shown. All data were analyzed with Bruker Daltonics flexAnalysis software and mMass. The mass spectrometer was calibrated internally using the gold.

As shown in Figure S18 and Table S5, both methylglyoxal and furandiol are labeled with ¹³C, indicating that the source of carbon for both the products is dissolved inorganic carbon. The calculated ratio of ¹²C/¹³C on furandiol is 1.77%, consistent with the nominal 2 atom % ¹²C on the sodium bicarbonate used as the carbon source. However, methylglyoxal is particularly very reactive in water, and forms oligomers and hydrates as indicated in the table below, complicating the quantification of ¹³C incorporation in that product.

![Figure S24: SALDI-TOF of sample from electrolysis of NaH¹³CO₃ on Ni₂P at 0.00 V vs RHE](image-url)
As formate was not detected by mass spectrometry due to its low concentration and molecular mass, we performed $\textsuperscript{13}$C NMR on the labeled electrolyte sample and confirmed that $\textsuperscript{13}$C was quantitatively incorporated into the formate product. This indicates that $\text{H}^{\textsuperscript{13}}\text{COO}^-$ was also formed from either $\textsuperscript{15}\text{CO}_2(\text{aq})$ or $\text{H}^{\textsuperscript{13}}\text{CO}_3^-$. Because of the sample’s high pH (9.82), furandiol and methylglyoxal underwent aldol condensation, forming oligomers that precipitated, and hence were not detectable by $\textsuperscript{13}$C NMR of the solution.

**Figure 25:** $\textsuperscript{13}$C NMR of Ni$_3$P 0.00 V vs RHE electrolyte sample (plus 20% D$_2$O) with $\textsuperscript{13}$C labeled bicarbonate. The 170.98 peak corresponds quantitatively to the formate/bicarbonate ratio expected from...
the HPLC experiments, showing that HCOO\(^-\) is formed from the reduction of CO\(_2\) or HCO\(_3\)^-\). The spectrum was acquired with a Varian VNMRS 500 MHz, using decoupled-NOE 10000 scans at room temperature, with 3s relaxation delay.
16. Correlation between CO$_2$RR current density and phosphorus content

Figure S20 shows the linear relationship between the sum of the current density at all tested potentials with the phosphorus content of the catalyst, i.e. phosphorus rich compositions present an increased CO$_2$RR activity. While the precise determination of the role of phosphorus in the CO$_2$ reduction mechanism is beyond the scope of this paper, DFT calculations on Ni$_2$P and Ni$_5$P$_4$ show that phosphorus (rather than nickel) is the site with weak hydrogen adsorption$^7$. Therefore, the overall higher activity of the phases with higher P content is consistent with the proposed mechanism, where three important steps involve reversible hydrogen transfer.

Figure S26: The sum of CO$_2$RR current density for all potentials depicted in the manuscript Fig. 4(A) is linearly correlated with the phosphorus content of the catalyst (P:Ni ratio)
17. **Turnover Frequency Calculations**

Turnover frequency (TOF) is defined by:

$$TOF = \frac{\text{product formation rate (mol} \cdot \text{s}^{-1})}{\text{# surface sites (mol)}}$$

For the numerator, the product formation rate was measured using GC (for hydrogen) and HPLC (for formate, methylglyoxal and 2,3-furandiol) as described in Sections 7 and 10.

For the denominator, the number of surface sites, including nickel and phosphorus atoms, was estimated using the method outlined below as the exact active site for the reaction is unknown.

First, the molar volume \(V_m\) of the compounds was calculated from its formula weight \(F_w\) and density \(\rho\):

$$V_m \left(\frac{\text{cm}^3}{\text{mol}}\right) = \frac{F_w \left(\text{g} \cdot \text{mol}^{-1}\right)}{\rho \left(\text{g} \cdot \text{cm}^{-3}\right)}$$

The average surface occupancy was approximated using the equation below, where \(N_A\) is Avogadro’s number:

$$\text{Average surface occupancy (atoms} \cdot \text{cm}^{-2}) = \left(\frac{\# \text{ atoms per formula unit} \cdot N_A}{V_m} \right)^{\frac{2}{3}}$$

Finally, the number of surface sites was calculated using the product:

$$\# \text{surface sites (mol)} = \frac{\text{Surface occupancy} \cdot \text{Roughness Factor} \cdot \text{Geometric Area}}{N_A}$$

The geometric area is 3.14 cm\(^2\) for all electrodes and the roughness factor is reported in Table S1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(F_w) (g·mol(^{-1}))</th>
<th>(\rho) (g·cm(^{-3}))</th>
<th>Atoms per formula unit</th>
<th>Surface Occupancy ((10^{15} \text{ atoms-cm}^{-2}))</th>
<th>Surface sites (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(_3)P</td>
<td>207.04</td>
<td>7.82</td>
<td>4</td>
<td>2.02</td>
<td>2.91</td>
</tr>
<tr>
<td>Ni(_{12})P(_5)</td>
<td>859.13</td>
<td>7.54</td>
<td>17</td>
<td>2.01</td>
<td>1.65</td>
</tr>
<tr>
<td>Ni(_5)P</td>
<td>148.35</td>
<td>7.44</td>
<td>3</td>
<td>2.02</td>
<td>3.28</td>
</tr>
<tr>
<td>Ni(_9)P(_4)</td>
<td>417.33</td>
<td>6.32</td>
<td>9</td>
<td>1.89</td>
<td>2.11</td>
</tr>
<tr>
<td>NiP(_2)</td>
<td>120.63</td>
<td>4.57</td>
<td>3</td>
<td>1.67</td>
<td>3.04</td>
</tr>
</tbody>
</table>
18. Thermodynamic analysis of the CO$_2$ reduction mechanism

The table below contains the equilibrium potential for the reduction of CO$_2$(g) to several organic compounds at pH 7, corresponding to the half-reaction:

$$mCO_2(g) + n(H^+ + e^-) \rightarrow C_aH_xO_y + oH_2O$$

The values reported here are calculated from the standard free energy of formation ($\Delta G^0$) of the products and reactants, according to the equation:

$$E^{\circ} = [-1/nF] \cdot [\Delta fG^0(\text{product}) - \Delta fG^0(\text{reactant})],$$

where $n$ is the number of electrons added and $F$ is Faraday’s constant.

Table S7: Standard Gibbs free energy of formation ($\Delta G^0$) of reagents and common CO$_2$ reduction products and equilibrium potential of the CO$_2$RR half-reaction to that product. $M$, $n$, and $o$ refer to the stoichiometric coefficients for CO$_2$, electrons/protons and water, respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta fG^0$ (kJ/mol)</th>
<th>Source</th>
<th>$m$</th>
<th>$n$</th>
<th>$o$</th>
<th>$E^{\circ}$ (V vs RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ (g)</td>
<td>-394.4</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O (l)</td>
<td>-237.1</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH$^-$ (aq)</td>
<td>-229.99</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide (g)</td>
<td>-137.2</td>
<td>9</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-0.10</td>
</tr>
<tr>
<td>Formate (aq)</td>
<td>-356.0</td>
<td>8</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>-0.02*</td>
</tr>
<tr>
<td>Formaldehyde (aq)</td>
<td>-129.7</td>
<td>8</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>-0.07</td>
</tr>
<tr>
<td>Glyoxal (l)</td>
<td>-189.7</td>
<td>9</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>0.03</td>
</tr>
<tr>
<td>Methanol (aq)</td>
<td>-174.5</td>
<td>8</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>0.03</td>
</tr>
<tr>
<td>Acetate (aq)</td>
<td>-399.6</td>
<td>8</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>0.23*</td>
</tr>
<tr>
<td>Glycolaldehyde (l)</td>
<td>-288.7</td>
<td>10</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>-0.03</td>
</tr>
<tr>
<td>Methane (g)</td>
<td>-50.79</td>
<td>8</td>
<td>1</td>
<td>8</td>
<td>2</td>
<td>0.17</td>
</tr>
<tr>
<td>Acetaldehyde (l)</td>
<td>-127.6</td>
<td>9</td>
<td>2</td>
<td>10</td>
<td>3</td>
<td>0.05</td>
</tr>
<tr>
<td>Acetylene (g)</td>
<td>209.9</td>
<td>9</td>
<td>2</td>
<td>10</td>
<td>4</td>
<td>-0.05</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>-508.6</td>
<td>9</td>
<td>2</td>
<td>10</td>
<td>2</td>
<td>0.20</td>
</tr>
<tr>
<td>Pyruvate (aq)</td>
<td>-352.0</td>
<td>9</td>
<td>3</td>
<td>10</td>
<td>3</td>
<td>0.04</td>
</tr>
<tr>
<td>2-hydroxy-2-propenal (l)</td>
<td>-212.9</td>
<td>11</td>
<td>3</td>
<td>12</td>
<td>4</td>
<td>0.02</td>
</tr>
<tr>
<td>Ethanol (aq)</td>
<td>-177.0</td>
<td>8</td>
<td>2</td>
<td>12</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>Ethylene (g)</td>
<td>68.4</td>
<td>9</td>
<td>2</td>
<td>12</td>
<td>4</td>
<td>0.08</td>
</tr>
<tr>
<td>Glyceraldehyde (l)</td>
<td>-442.2</td>
<td>10</td>
<td>3</td>
<td>12</td>
<td>3</td>
<td>-0.03</td>
</tr>
<tr>
<td>Methylglyoxal (l)</td>
<td>-253.96</td>
<td>10</td>
<td>3</td>
<td>12</td>
<td>4</td>
<td>0.02</td>
</tr>
<tr>
<td>2,3-Furandiol (l)</td>
<td>-400.99</td>
<td>11</td>
<td>4</td>
<td>14</td>
<td>5</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethane (g)</td>
<td>-32.89</td>
<td>8</td>
<td>2</td>
<td>14</td>
<td>4</td>
<td>0.14</td>
</tr>
<tr>
<td>Hydroxyacetone (l)</td>
<td>-295.0</td>
<td>10</td>
<td>3</td>
<td>14</td>
<td>2</td>
<td>-0.31</td>
</tr>
<tr>
<td>Acetone (g)</td>
<td>-152.7</td>
<td>9</td>
<td>3</td>
<td>16</td>
<td>5</td>
<td>0.10</td>
</tr>
<tr>
<td>Allyl alcohol (l)</td>
<td>-92.0</td>
<td>10</td>
<td>3</td>
<td>16</td>
<td>5</td>
<td>0.06</td>
</tr>
<tr>
<td>Propionaldehyde (g)</td>
<td>-276.4</td>
<td>9</td>
<td>3</td>
<td>16</td>
<td>5</td>
<td>0.18</td>
</tr>
<tr>
<td>1-propanol (l)</td>
<td>-351.3</td>
<td>9</td>
<td>3</td>
<td>18</td>
<td>5</td>
<td>0.20</td>
</tr>
<tr>
<td>Propane (g)</td>
<td>-23.4</td>
<td>9</td>
<td>3</td>
<td>20</td>
<td>6</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Tabulated $\Delta f G^0$ values of some products and reaction intermediates were not available. Thus, they were estimated using the individual group contributions method from Mavrovouniotis$^{10}$ and Jankowski$^{11}$. In Table S8, the standard free energy of the CO$_2$ conversions is shown for every detected intermediate. After the endergonic reduction of CO$_2$ to formate and formaldehyde, the conversions to methylglyoxal and furandiol are exergonic at standard conditions.

Table S8: Standard Gibbs free energy ($\Delta f G^0$) of the proposed reaction mechanism of CO$_2$ conversion to formic acid, methylglyoxal, and 2,3-furandiol.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta f G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HCOO}^-$</td>
<td>38.4</td>
</tr>
<tr>
<td>$\text{H}_2\text{C} = \text{O} + (\text{H}^+ + 2\text{e}^-) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C} = \text{O} + 2\text{OH}^-$</td>
<td>3.4</td>
</tr>
<tr>
<td>$3\text{H}_2\text{C} = \text{O} \rightarrow \text{H}_2\text{C} = \text{O} + \text{H}_2\text{O}$</td>
<td>$-102.0$</td>
</tr>
<tr>
<td>$\text{H}_2\text{C} = \text{O} + \text{H}_2\text{C} = \text{O} + \text{OH}^- \rightarrow \text{Furandiol} + \text{H}_2\text{O} + (\text{H}^+ 2\text{e}^-)$</td>
<td>$-24.4$</td>
</tr>
</tbody>
</table>
19. Mechanism verification

The distinction between CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{-} as the source of carbon products is a major question in the CO\textsubscript{2} electroreduction field. While it is virtually impossible to isolate HCO\textsubscript{3}\textsuperscript{-} and CO\textsubscript{2} because of the equilibrium between them in aqueous media we attempted to answer this question by using different buffers and purge gases for electrolysis that would result in different relative concentrations of the species of interest. Electrolysis was performed for 14 h at 0.00V vs RHE on Ni\textsubscript{2}P.

\[ \text{H}^+(aq) + \text{HCO}_3^-(aq) \rightleftharpoons \text{CO}_2(aq) + \text{H}_2\text{O}(l) \]

The results summarized in Table S9 show that in very low concentrations of CO\textsubscript{2}, using argon-purged bicarbonate solution, the selectivity of the reaction is very similar to CO\textsubscript{2}-saturated HCO\textsubscript{3}\textsuperscript{-}, however the amount of reduction products formed decreases from 53.0 µmol to 10.6 µmol. Conversely, in the absence of bicarbonate but constant purge of CO\textsubscript{2} in pyrophosphate buffer, the selectivity changes to favor hydrogen evolution and formate production, however the total amount of CO\textsubscript{2} converted is more than double of the CO\textsubscript{2}-saturated KHCO\textsubscript{3}. The electrolyte effect on enhancing HER is consistent with the good hydrogen donating ability and good buffering capacity of pyrophosphate. Together, these results indicate that the main source of carbon in aqueous CO\textsubscript{2}, and that the bicarbonate ion acts as a “CO\textsubscript{2} buffer”, supplying CO\textsubscript{2} through the equilibrium above, rather than being reduced itself in the ionic form. This observation is consistent with a recent report from Hursán and Janáky.

Table S9: Reduction of aqueous solutions with different concentrations of CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{-} on Ni\textsubscript{2}P at 0.00 V vs RHE. Argon or CO\textsubscript{2} were purged at 5 sccm. The concentrations of CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{-} were estimated using Henry’s Law and the equilibrium constant for the aqueous HCO\textsubscript{3}\textsuperscript{-}/CO\textsubscript{2} equilibrium at room temperature and 1 atm. The influence of electrolyte concentration on CO\textsubscript{2} solubility was disregarded in the calculations, as these values are meant just for a rough comparison of species concentration. FE stands for Faradaic Efficiency, MG for methylglyoxal, and FD for furandiol.

<table>
<thead>
<tr>
<th></th>
<th>([\text{CO}_2\text{aq}]) (mM)</th>
<th>([\text{HCO}_3^-]) mM</th>
<th>FE HCO\textsubscript{O}' (%)</th>
<th>FE MG (%)</th>
<th>FE FD (%)</th>
<th>Total CO\textsubscript{2} RR FE (%)</th>
<th>HCO\textsubscript{O} (µmol)</th>
<th>MD (µmol)</th>
<th>FD (µmol)</th>
<th>Total µmols of CO\textsubscript{2} converted</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}-purged</td>
<td>0.5 M KHCO\textsubscript{3} (pH 7.5)</td>
<td>33</td>
<td>500</td>
<td>1.6</td>
<td>26.3</td>
<td>71.6</td>
<td>99.5</td>
<td>1.15</td>
<td>3.14</td>
<td>10.6</td>
</tr>
<tr>
<td>Ar-purged</td>
<td>0.5 M KHCO\textsubscript{3} (pH 9.8)</td>
<td>1.6 \times 10^{-4}</td>
<td>500</td>
<td>0.7</td>
<td>21.4</td>
<td>78.1</td>
<td>100.2</td>
<td>0.10</td>
<td>0.7</td>
<td>2.1</td>
</tr>
<tr>
<td>CO\textsubscript{2}-purged</td>
<td>0.25M pyrophosphate buffer (pH 7.5)</td>
<td>33</td>
<td>0.12</td>
<td>3.8</td>
<td>10.2</td>
<td>13.3</td>
<td>27.35</td>
<td>20.5</td>
<td>13.6</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Next, to verify the feasibility of the proposed mechanism (Figure 7 in the main text), sequential reduction of selected proposed intermediates was performed on Ni\textsubscript{2}P at 0.00 V vs RHE for 14 h. The solutions containing a 25 mM concentration of the intermediate (formate, formaldehyde or methylglyoxal) and 0.25 M pyrophosphate buffer (pH 7.5)
were continuously purged with argon to ensure that no dissolved oxygen or CO₂ remained in solution. Liquid products were quantified using HPLC. The results are summarized on Table S10 below and show that formate and formaldehyde were reduced to methylglyoxal and furandiol. Both products were formed on a 1:1 ratio, a selectivity that mirrors the one observed when reducing CO₂ in the same buffer. Finally, methylglyoxal is also reduced to furandiol. While these results support the mechanism, further investigation using DFT is underway and will be necessary to fully elucidate the mechanism, define the catalyst active sites, and the relative energy of the catalyst-bound intermediates.

Table S10: Reduction of CO₂ and the proposed reaction intermediates formate, formaldehyde, and methylglyoxal to furandiol. The reactions were performed at 0.00 V vs RHE on Ni₃P.

<table>
<thead>
<tr>
<th>Reagent and purge gas</th>
<th>HCOO⁻ produced (µmol)</th>
<th>Methylglyoxal produced (µmol)</th>
<th>Furandiol produced (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-purged PPBS</td>
<td>20.5</td>
<td>13.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Formate 25 mM (Ar-purged PPBS)</td>
<td>-</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Formaldehyde 25mM (Ar-purged PPBS)</td>
<td>-</td>
<td>3.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Methylglyoxal 25mM (Ar-purged PPBS)</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
</tr>
</tbody>
</table>
20. **Tafel Plots**

Figure S27: Tafel plots obtained by multiplying the faradaic efficiency for each product by the average current density at each potential.
21. Induction period

Figure S28: Four sequential 48-hour chronoamperometry traces at -0.5 V vs RHE on Ni₂P in CO₂-saturated 0.5 M KHCO₃. Between each experiment, the cell and the catalyst pellet were rinsed and reused with fresh electrolyte. The initial break-in period with higher reductive currents is consistently observed and might indicate reactant/product gradient formation that is caused by the porous structure of the electrode.
22. X-ray photoelectron spectroscopy

XPS analysis was performed on pristine electrodes (A-C) as well as after catalytic turnover (D-F). Here, catalytic turnover represents at least 3-4 full turnovers for CO$_2$RR per site as determined in the turnover frequency calculations. (A) is the detailed spectra of the C 1s and K 2p region, (B) is the detailed spectra of the Ni 2p region, (C) is the detailed spectra of the P 2p region, (D) is the detailed spectra of the C 1s and K 2p region, (E) is the detailed spectra of the Ni 2p region, and (F) is the detailed spectra of the P 2p region. Residuals are shown in green on the right y-axis using the same relative scale as the left y-axis.

![Figure S29 XPS of pristine (top) and post-reaction (bottom) Ni$_2$P](image)

![Figure S30: XPS of pristine (top) and post-reaction (bottom) Ni$_2$P$_3$](image)
Figure S32: XPS of pristine (top) and post-reaction (bottom) XPS Ni$_3$P$_4$. 
Figure S33: XPS of pristine (top) and post-reaction (bottom) NiP₂
23. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

ICP-OES was conducted on a Perkin Elmer Optima 7300 DV to detect the amount of phosphorus and nickel that leached into the solution due to catalyst corrosion. The samples were prepared by diluting 500 µL of the post-reaction electrolyte with 2500 µL of 5% (v/v) nitric acid in ultrapure water. Immediately prior to sample
analysis, a calibration was done with a serial dilution of a 100 ppm nickel and a 10 ppm phosphorus SPEX Certiprep certified analytical standards.

Table S11: Amount of nickel and phosphorus leached relative to the mass of catalyst on the cathode, after at least 3 hours of electrolysis, as measured by ICP-OES.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential (V vs RHE)</th>
<th>% Ni Leached</th>
<th>Standard Deviation</th>
<th>% P Leached</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(_2)P</td>
<td>0.05</td>
<td>0.001%</td>
<td>6.2E-07</td>
<td>0.025%</td>
<td>2.04E-05</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>0.001%</td>
<td>3.8E-07</td>
<td>0.041%</td>
<td>1.48E-05</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>0.000%</td>
<td>3.0E-07</td>
<td>0.094%</td>
<td>2.85E-05</td>
</tr>
<tr>
<td></td>
<td>-0.20</td>
<td>0.000%</td>
<td>1.3E-07</td>
<td>0.096%</td>
<td>1.54E-05</td>
</tr>
<tr>
<td></td>
<td>-0.30</td>
<td>0.000%</td>
<td>0.0E+00</td>
<td>0.043%</td>
<td>2.02E-05</td>
</tr>
<tr>
<td></td>
<td>-0.40</td>
<td>0.000%</td>
<td>2.5E-07</td>
<td>0.117%</td>
<td>2.58E-05</td>
</tr>
<tr>
<td></td>
<td>-0.50</td>
<td>0.000%</td>
<td>5.4E-07</td>
<td>0.091%</td>
<td>1.89E-05</td>
</tr>
<tr>
<td>Ni(_3)P</td>
<td>0.05</td>
<td>0.002%</td>
<td>4.5E-07</td>
<td>0.114%</td>
<td>6.85E-06</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>0.021%</td>
<td>7.2E-07</td>
<td>0.247%</td>
<td>8.89E-06</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>0.001%</td>
<td>3.3E-07</td>
<td>0.020%</td>
<td>2.82E-05</td>
</tr>
<tr>
<td></td>
<td>-0.20</td>
<td>0.000%</td>
<td>3.0E-07</td>
<td>0.090%</td>
<td>1.42E-05</td>
</tr>
<tr>
<td></td>
<td>-0.30</td>
<td>0.000%</td>
<td>4.8E-07</td>
<td>0.089%</td>
<td>6.23E-06</td>
</tr>
<tr>
<td></td>
<td>-0.40</td>
<td>0.001%</td>
<td>4.0E-07</td>
<td>0.121%</td>
<td>1.76E-05</td>
</tr>
<tr>
<td></td>
<td>-0.50</td>
<td>0.001%</td>
<td>3.4E-07</td>
<td>0.104%</td>
<td>1.89E-05</td>
</tr>
<tr>
<td>Ni(_2)P</td>
<td>0.05</td>
<td>0.000%</td>
<td>2.2E-07</td>
<td>0.058%</td>
<td>1.25E-05</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>0.001%</td>
<td>3.6E-08</td>
<td>0.229%</td>
<td>2.38E-05</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>0.000%</td>
<td>3.8E-07</td>
<td>0.040%</td>
<td>1.98E-05</td>
</tr>
<tr>
<td></td>
<td>-0.20</td>
<td>0.020%</td>
<td>1.1E-06</td>
<td>0.049%</td>
<td>5.13E-06</td>
</tr>
<tr>
<td></td>
<td>-0.30</td>
<td>0.005%</td>
<td>2.8E-07</td>
<td>0.083%</td>
<td>8.60E-06</td>
</tr>
<tr>
<td></td>
<td>-0.40</td>
<td>0.008%</td>
<td>4.7E-07</td>
<td>0.018%</td>
<td>1.90E-06</td>
</tr>
<tr>
<td></td>
<td>-0.50</td>
<td>0.019%</td>
<td>1.1E-06</td>
<td>0.493%</td>
<td>5.13E-05</td>
</tr>
<tr>
<td>Ni(_3)P</td>
<td>0.05</td>
<td>0.005%</td>
<td>6.4E-07</td>
<td>0.199%</td>
<td>8.57E-06</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>0.000%</td>
<td>8.9E-08</td>
<td>0.144%</td>
<td>4.88E-06</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>0.011%</td>
<td>5.4E-07</td>
<td>1.095%</td>
<td>6.57E-05</td>
</tr>
<tr>
<td></td>
<td>-0.20</td>
<td>0.020%</td>
<td>1.4E-06</td>
<td>0.810%</td>
<td>3.08E-05</td>
</tr>
<tr>
<td></td>
<td>-0.30</td>
<td>0.016%</td>
<td>2.0E-07</td>
<td>0.233%</td>
<td>1.86E-06</td>
</tr>
<tr>
<td></td>
<td>-0.40</td>
<td>0.017%</td>
<td>5.6E-07</td>
<td>0.163%</td>
<td>1.47E-05</td>
</tr>
<tr>
<td></td>
<td>-0.50</td>
<td>0.007%</td>
<td>8.0E-07</td>
<td>0.120%</td>
<td>6.83E-06</td>
</tr>
<tr>
<td>i(_2)P</td>
<td>-0.05</td>
<td>0.003%</td>
<td>6.0E-07</td>
<td>0.147%</td>
<td>1.60E-05</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>0.023%</td>
<td>1.6E-06</td>
<td>0.101%</td>
<td>5.05E-05</td>
</tr>
<tr>
<td></td>
<td>-0.20</td>
<td>0.003%</td>
<td>5.9E-07</td>
<td>0.255%</td>
<td>4.08E-06</td>
</tr>
<tr>
<td></td>
<td>-0.30</td>
<td>0.005%</td>
<td>7.9E-07</td>
<td>0.312%</td>
<td>2.40E-05</td>
</tr>
<tr>
<td></td>
<td>-0.40</td>
<td>0.009%</td>
<td>7.3E-07</td>
<td>0.136%</td>
<td>2.85E-06</td>
</tr>
<tr>
<td></td>
<td>-0.50</td>
<td>0.002%</td>
<td>1.5E-06</td>
<td>0.053%</td>
<td>2.81E-06</td>
</tr>
</tbody>
</table>
24. References


Appendix B: Chapter Two Supplemental Materials

Electronic Supplementary Information (ESI)

CO₂ electro-reduction on Cu₃P: Selective design of a formate pathway on Cu(I) and structural activity insights into H₂ selectivity

Anders B. Laursen,¹a Karin U. D. Calvinho,¹a Timothy A. Goetjen,ᵃ Kyra M. K. Yap,ᵃ Shinjae Hwang,ᵃ Hongbin Yang,ᵃ Eric Garfunkel,ᵃ and G. Charles Dismukesᵃᵇ⁻¹

ᵃ Department of Chemistry and Chemical Biology; Rutgers, the State University of New Jersey; 123 Bevier Road; Piscataway NJ 08854
ᵇ Waksman Institute of Microbiology, Rutgers, the State University of New Jersey; New Jersey; 190 Frelinghuysen Road; Piscataway NJ 08854
‡ These authors contributed equally
† Electronic Supplementary Information (ESI) available; [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x
Catalyst synthesis

Materials for catalyst synthesis was used as supplied without further purification. All electrolytes were made from PicoPure® water (18.2 MΩ resistivity) unless otherwise stated. Solvothermal reaction of phosphine compounds generates highly pyrophoric white phosphorous in small quantities which may spontaneously catch fire under air-exposure. This reaction should only be undertaken by trained personnel using appropriate safety equipment and safety protocols.

Trioctyl phosphine (TOP) and Triocetyl phosphine oxide (TOPO) were purchased from Strem Chemicals. TOP was stored in an Ar-filled glovebox and only air-exposed during transfer to the reaction vessel. Cu-foil from Alfa-Aesar (99.8% metal purity) was used. Viton-O-rings used to seal the solvothermal reactor were protected from the TOP/TOPO reaction mixture by wrapping in 1/4" width PTFE tape (McMaster). This tape is replenished between runs since some TOP/TOPO soaks into the tape and attacks the O-ring seal. In the absence of the PTFE protection layer the Viton seal material partially dissolves and contaminates the reaction solution.

Solvothermal reaction under reflux conditions was found to release low vapor pressure organic residue (collected post-reactor in an oil-bubbler). The Cu foil (Alfa-Aesar 99.8 %) was mechanically polished with a SiC polishing pad, subsequently sonicated three times (1x each in 1.0 M HCl, DI water, acetone), and then dried in air prior to synthesis. The Cu foil was placed in a three-neck reaction flask with 2.5 g tri-octylphosphine oxide (TOPO) and 12 mL tri-octylphosphine (TOP), which was sealed, and vacuum pumped to remove impurities in the TOP. The reaction flask was flushed with 143 sccm N2 and placed in a preheated sand bath at 310 °C for 45 min. The reaction temperature was controlled by a thermoprobe K-couple inserted through a Pyrex sheath into the reaction solution. After 45 min, the reaction flask was air-quenched to room temperature. The foil was cleaned (Cu3P NS/Cu foil) by sonication in a 3:1 EtOH:acetone mixture before drying at 60°C. The catalyst thin films were then analyzed by PXRD.

Catalyst characterization

Electrochemistry: A custom glass-fiber reinforced nylon-6,6 electrochemical cell, with silicon O-rings and PEEK fittings was used.54 The working electrode was separated from the counter electrode by a Nafion 115 membrane (Fuel Cell Store). Platinum black deposited on Pt foil (Alfa Aesar, 99.9%) was utilized as the counter electrode. A Hach Hg/Hg2SO4 reference electrode was used and calibrated daily against a pristine Accumet SCE electrode (which was periodically calibrated against freshly flame-annealed Pt electrode in 0.5 M H2SO4 under 1 atm H2, giving the Reversible Hydrogen Electrode. This avoids risks of Pt contamination during calibration of the reference electrode. The working electrode foil was connected to an adhesive aluminum tape strip on the back side. Aluminum was selected as a back contact because it is inert for CO2RR.99 The active area was masked off using a silicone gasket made from 0.01" fluoro-silicone sheets (McMaster). CO2 (Air Gas, instrument grade, with a Supelco hydrocarbon trap) was supplied through the bottom of the cell to both the working and counter electrodes at a flow rate of 5 sccm using mass flow controllers. Working electrode headspace was sampled every 30 minutes by gas chromatography (GC). Electrochemical measurements were performed with a Gamry 5000E potentiostat. Before each electrolysis, the electrolyte (0.1 M KHCO3, Chelex treated)99 was pre-saturated with CO2 for at least an hour. O2 absence was confirmed by GC. Electrochemical impedance spectra were collected at the open circuit from 1 Hz to 1 MHz. Uncompensated solution resistances were typically around 80 Ω. Between experiments, the electrochemical cell was rinsed with Millipore water and the surface oxide was removed from the working electrode with ammonium hydroxide before being re-used for multiple experiments at all potentials. In doing this, the longevity of the electrodes was confirmed, with no significant difference in product distribution observed as the electrodes were re-used. Additional replicates were made using fresh electrodes at all potentials to ensure that the product distribution was not affected across the investigated potential region.
**Powder X-Ray Diffraction (PXRD):** Powder X-Ray diffraction was conducted at room temperature on a Philips X’pert system, spinning at 100 rpm, in a Bragg-Brentano geometry, using Cu K-alpha 0.15418 nm x-rays, calibrated daily with a Si standard. The step size used for the diffraction patterns shown was 0.02°, and the scan speed 0.013°/s. The sample holder was 3 mm deep and ½” in diameter, completely filled with as-synthesized powder. Post-reaction PXRD was conducted on catalyst pellets containing 1 (w/w) % neutralized Nafion. The pellets, 2 cm in diameter and 2 mm thick, were extracted from the reactor, rinsed with ultrapure water, and mounted onto a sample holder. After the measurements, the patterns were translated to correct for the offset sample height.

**Scanning Electron Microscopy (SEM):** A benchtop Phenom instrument at 10keV acceleration was utilized to image samples. Samples were mounted on Al-stubs using carbon tape and cross-section samples precut using scissors. Cross-section regions were chosen where minimal compressive damage was seen to the film.

**Inductively Coupled Plasma – Optical Emissions Spectroscopy (ICP-OES):** ICP-OES was conducted on a Perkin Elmer Optima 7300 DV to detect the amount of phosphorus and copper that was dissolved from a pristine Cu₃P NS/Cu sample by aqua regia etching. The samples were prepared by diluting 500 µL of the post-reaction electrolyte with 2500 µL of 5% (v/v) nitric acid in ultrapure water. Immediately prior to sample analysis, a calibration was done with a serial dilution of a 100-ppm copper and 1000-ppm phosphorus SPEX Certiprep certified analytical standards.

**Scanning Transmission Electron Microscopy and Electron Energy Loss Spectroscopy (STEM & EELS):** High angle dark field imaging and EELS mapping were performed on a Nion UltraSTEM 100, operating at 60kV. Probe convergence and HAADF collection angle is 30 mrad and >80 mrad, respectively. Cu₃P nanosheets were removed from substrate and dispersed in acetone, before dropped casted on a lacy carbon TEM grid.
Electrolysis without surface phosphorus-oxide removal

Figure S 1Faradaic efficiency (FE) for H2 for electrodes without surface oxide removal. Results are shown for the average of several steady-state measurements as well as the last of the gas-samples in the sample run. FE is shown for 100mV interval potential step.
Pre- and Post-catalysis PXRD

**Fig. S 2** PXRD pattern for Cu$_3$P NS/Cu before (left) and after (right) catalysis.

**Fig. S 3** PXRD pattern for Cu$_2$O NP/Cu before (left) and after (right) catalysis.
Fig. S 4 PXRD pattern for Cu before (left) and after (right) catalysis.
Fig. S 5 HAADF low magnification image of Cu₃P hexagonal platelets from pristine surface.
Fig. S 6 HAADF high-resolution image of Cu₃P hexagonal nanosheet. Images shows that lattice fringes continue to the very surface indicating that there is a ~3nm thin low contrast and low crystallinity surface layer, identified by XPS as a copper phosphoxide layer.

Surface oxide etching procedure

Fig. S 7 (and Fig. S 1) shows the ammonia washed sample with and without ammonia hydroxide (25%) solution to remove surface copper phosphor-oxide layer. It is seen that even with 16 hours chrono-amperometry analysis for Cu₃P NS/Cu the electrical charge going towards the surface reduction rather than the HER or CO₂RR. We note that the CO₂RR is less than 2% so this cannot explain the difference. The FE difference would eventually be negligible once enough charge has been passed. This requires either much extended runs or even higher surface area catalysts with corresponding higher current densities for HER and CO₂RR.

The removal of surface phosphoxide by the surface etch removes this contribution nearly completely.
Electrochemical surface area measurements

Electrochemical capacitance was utilized to determine the surface area of each of the nickel phosphides. To measure capacitance, the potential was cycled between 0.11 and -0.04 V vs RHE at different scan rates in CO$_2$-saturated 0.1M KHCO$_3$. The capacitive current can be extracted from the cyclic voltammograms for Cu$_3$P and the result is plotted in Fig. S 8. The capacitive current was measured at 0.04 V, where the faradaic current is minimal, and plotted versus scan rate. The slope of the linear fit is the capacitance of the sample. The electrochemical surface area (ECSA) was calculated using the ratio of the capacitance measured and the specific capacitance for metal phosphides (40 µF/cm$^2$, as reported by Kibsgaard et al$^{100}$). A roughness factor was then obtained by dividing the ECSA by the geometric area of the sample.

Fig. S 7 shows Faradaic efficiency of Cu$_3$P NS/Cu at various potentials from -0.2 – -0.5 V vs RHE, in the presence and absence of ammonia etch just prior to electrocatalytic tests. Conditions are: 0.1M KHCO$_3$ pH 6.8 under CO$_2$ purging.
**Fig. S 8 ECSA determination of Cu$_3$P.**

Table S 1 Roughness factors calculated from the electrochemical surface area

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Roughness Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_3$P</td>
<td>53.57</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>61.67</td>
</tr>
<tr>
<td>Cu</td>
<td>4.92</td>
</tr>
</tbody>
</table>
Electrochemical Activity Analysis

Faradaic efficiencies for FA on the Cu2P NS/Cu catalyst was determined in triplicates whereas the H2 was determined by online GC at steady state (after > 30 min of electrolysis) with 5 or more determinations. The H2 determination showed a fairly large deviation between samples largely due to 1) the limited surface area of the catalyst giving a low H2 concentration, 2) intermittent water condensation in the cell’s exit lines partially blocking flows, 3) the presence of CO2 in the eluent gas flow increases noise in the H2 determination (even for the calibration, GC is calibrated with CO2 balance gas). All these factors are exacerbated at low H2 concentrations as seen in the table below.

Table S 2 Electrochemical activity for CO2RR on Cu2P NS/Cu. H2 could not be detected at -0.1V vs RHE due to the low current (and corresponding H2 rate) being below the GC detection limit given the 5 sccm CO2 flow rate.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Formate FE</th>
<th>St Dev</th>
<th>H2 FE</th>
<th>St Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1 V</td>
<td>0.89%</td>
<td>0.05%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>-0.2 V</td>
<td>0.6%</td>
<td>0.1%</td>
<td>95%</td>
<td>60%</td>
</tr>
<tr>
<td>-0.3 V</td>
<td>0.7%</td>
<td>0.1%</td>
<td>94%</td>
<td>36%</td>
</tr>
<tr>
<td>-0.4 V</td>
<td>1.8%</td>
<td>0.3%</td>
<td>93%</td>
<td>17%</td>
</tr>
<tr>
<td>-0.5 V</td>
<td>2%</td>
<td>1%</td>
<td>98%</td>
<td>18%</td>
</tr>
</tbody>
</table>

Fig. S 9 Chronoamperometric life-time analysis for benchmark Cu and Cu2O/Cu. Samples are run in a negative to positive potential sequence. The one-hour induction period observed on Cu2O is likely due to the reduction of the surface CuO species into Cu2O, as observed by XPS/Auger.
XPS analysis

Fig. S 10 XPS analysis of Cu$_3$P NS/Cu, Cu$_2$O/Cu, and Cu electrodes before and after catalysis. (A) Pristine Cu$_3$P NS/Cu 2p, (B) Post-catalysis Cu$_3$P NS/Cu 2p, (C) Pristine Cu$_2$O/Cu, (D) Post-catalysis Cu$_2$O/Cu, (E) Pristine Cu, (F) Post-catalysis Cu detail spectra.

The main difference between these species Cu show nearly no satellite species between (941.90 - 944.80eV)$^{87}$, whereas CuO shows a significant doublet satellite peak; while Cu$_2$O shows intermediate satellite features. Cu 2p$^{3/2}$ peak shifts of Cu and Cu$_2$O ($E_{\text{bind}}$, Cu$_2$O) is minimal whereas. Data shown in Fig. S 10 in ESI shows that the pristine Cu$_2$O/Cu sample contains large amounts of CuO ($E_{\text{bind}}$=934.8eV) likely at the surface (vide infra). Post-catalysis the sample 2p satellites are significantly reduced indicating the film is converted entirely to Cu$_2$O ($E_{\text{bind}}$=932.7eV). Cu foil showed only metallic Cu prior to catalysis (post sputtering), whereas after catalysis some CuO-species appears at $E_{\text{bind}}$=934.7eV, as well as significant satellite peaks characteristic of CuO 2p satellites.
Turnover Frequency Calculation

Surface atom density, Cu₃P:

\[
\left( \frac{24 \text{ atoms}}{\text{unit cell}} \right)^\frac{2}{3} \frac{A^3}{\text{unit cell} \cdot 10^{-24} \text{cm}^3/A^3} = 4.004 \cdot 10^{14} \text{ surface atoms/cm}^2
\]

Surface atom density, Cu₂O:

\[
\left( \frac{6 \text{ atoms}}{\text{unit cell}} \right)^\frac{2}{3} \frac{A^3}{\text{unit cell} \cdot 10^{-24} \text{cm}^3/A^3} = 1.814 \cdot 10^{15} \text{ surface atoms/cm}^2
\]

Surface atom density, Cu:

\[
\left( \frac{4 \text{ atoms}}{\text{unit cell}} \right)^\frac{2}{3} \frac{A^3}{\text{unit cell} \cdot 10^{-24} \text{cm}^3/A^3} = 1.928 \cdot 10^{15} \text{ surface atoms/cm}^2
\]

TOF:

\[
TOF = \frac{j \left( \frac{mA}{cm^2_{\text{geo}}} \right)}{1000 \left( \frac{A}{mA} \right) \cdot \text{Surface roughness (cm}^2_{\text{ECSA/cm}} \text{geo})} \cdot \frac{6.022 \cdot 10^{23}}{\text{mol}^{-1}} \cdot \frac{6 \text{ electrons per product} \cdot \text{Surface atom density (cm}^2_{\text{ECSA/cm}} \text{geo}) \cdot 96485 \left( \frac{C}{mol} \right)}{6 \text{ electrons per product} \cdot \text{Surface atom density (cm}^2_{\text{ECSA/cm}} \text{geo})}
\]

\[
H^- TOF_{Cu_3P} = \left[ \frac{mA}{cm^2_{\text{geo}}} \right] \cdot 0.145779 \left( \frac{cm^2_{\text{geo}}}{mA \cdot \text{sites}} \right) \text{ hydrides}
\]

\[
H^- TOF_{Cu} = \left[ \frac{mA}{cm^2_{\text{geo}}} \right] \cdot 0.328942 \left( \frac{cm^2_{\text{geo}}}{mA \cdot \text{sites}} \right) \text{ hydrides}
\]

\[
H^- TOF_{Cu_2O} = \left[ \frac{mA}{cm^2_{\text{geo}}} \right] \cdot 0.027896 \left( \frac{cm^2_{\text{geo}}}{mA \cdot \text{sites}} \right) \text{ hydrides}
\]

Turnover Number Calculation

\[
TON = \frac{\text{Charge passed through electrode (C)}}{\text{Surface area (cm}^2)} \cdot \text{Surface atom density (cm}^2_{\text{atom/cm}}) \cdot \text{Charge of electron (C/e)}
\]
Cu₃P facets and terminations

Fig. S 11 Cu₃P[001]-Cu₄ surface termination.

Fig. S 12 Cu₃P[001]-Cu₃P₃ surface termination.
Fig. S13 Cu₃P[001]-Cu₆ surface termination.

Fig. S14 Cu₃P[110]-Cu₆P₂ surface termination.
Fig. S15 Cu₃P[110]-Cu₃P₂ surface termination.
Fig. S16 Cu3P[110]-Cu6P2 surface termination.

Table S3 Cu3P P6cm crystal structure determined surface facet termination for [001] and [110].

<table>
<thead>
<tr>
<th>Facet</th>
<th>Termination</th>
<th>Number of P atoms</th>
<th>Number of Cu atoms</th>
<th>Area [Å²]</th>
<th>P/Cu area [Å⁻¹]</th>
<th>(Cu+P)/area [Å⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu3P</td>
<td>Cu4</td>
<td>0</td>
<td>4</td>
<td>20.971</td>
<td>0.04768</td>
<td>0.286101</td>
</tr>
<tr>
<td>[001]</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu3P</td>
<td>Cu3P3</td>
<td>3</td>
<td>3</td>
<td>61</td>
<td>0.3333</td>
<td>0.160933</td>
</tr>
<tr>
<td>[001]</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu3P</td>
<td>Cu6</td>
<td>0</td>
<td>6</td>
<td>20.971</td>
<td>0.00670</td>
<td>0.160933</td>
</tr>
<tr>
<td>[001]</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu3P</td>
<td>Cu6P3</td>
<td>2</td>
<td>6</td>
<td>49.710</td>
<td>0.3333</td>
<td>0.140816</td>
</tr>
<tr>
<td>[110]</td>
<td></td>
<td></td>
<td></td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu3P</td>
<td>Cu6P2</td>
<td>2</td>
<td>5</td>
<td>49.710</td>
<td>0.3333</td>
<td>0.160933</td>
</tr>
<tr>
<td>[110]</td>
<td></td>
<td></td>
<td></td>
<td>33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix C: Chapter Three Supplemental Materials

Electronic Supplementary Information
Electrocatalytic CO₂ Reduction on Isostructural Fe₂P vs. Ni₂P: Shifting Carbon Product Selectivity to Ethylene Glycol on Iron Phosphide

Karin U. D. Calvinhoᵃ†, Abdulaziz Alherzᵇ†, Kyra M. K. Yapᵃ†, Anders B. Laursenᵃ, Shinjae Hwangᵃ, Zachary J. L. Bareᵇ, Charles B. Musgraveᵇ,c*, G. Charles Dismukesᵃ,d*

ᵃDepartment of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey, 08854
ᵇDepartment of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO, 80309
ᶜRenewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, CO 80309
ᵈWaksman Institute of Technology, Rutgers, The State University of New Jersey, 190 Frelinghuysen Road, Piscataway, New Jersey, 08854

*Corresponding authors (e-mail: charles.musgrave@colorado.edu, dismukes@rutgers.edu).
†These authors contributed equally.
1. Powder X-Ray Diffraction

PXRD analysis was conducted at room temperature on a Philips X’Pert system, spinning at 20 rpm, in a Bragg-Brentano geometry, Cu K-alpha 0.15418 nm, calibrated with a Si single crystal before every measurement. The step size used for the diffraction patterns was 0.02°, and the scan speed was 0.013º s\(^{-1}\). The sample holder was 3 mm deep and \(\frac{1}{2}\)" in diameter.

*Figure 52.* PXRD pattern of as-synthesized Fe\(_2\)P catalyst (red) and the Fe\(_2\)P reference pattern. The comparison of the two patterns verifies that there is no contamination in the as-synthesized catalyst from a secondary phase or amorphous material, above the 2% device detection limit.
2. Fe$_2$P Layers: Fe$_3$P and Fe$_3$P$_2$, and Reconstruction

*Figure S2.* Layers of the Fe$_2$P surface catalyst. Each layer alternates between Fe$_3$P and Fe$_3$P$_2$ stoichiometry. The surface terminates more favorably with the Fe$_3$P$_2$ stoichiometry, topped with P* to signify reconstruction on the Fe$_3$ hollow sites.
3. Less Favorable P* Reconstruction Site

Figure S3. P* Reconstruction of a) Fe₃ hollow site and b) the distorted Fe₃ hollow site; or Fe₃P hollow site. Reconstruction (b) is less symmetric and less energetically favorable compared to the P* reconstruction of the Fe₃ hollow in (a). We adopt (a) to represent our reconstructed Fe₃P catalyst surface.
4. A note on the choice of reference states for GC-DFT calculated adsorption energies

As the local pH may strongly depend on the electrode geometry and other experimental factors, it is not feasible to accurately assess solvated protons as a reference point. Hence, while the adsorption energies of H* on the reconstructed site are positive with respect to dissolved H\textsubscript{2}, H* could still be favorably adsorbed on the reconstructed surface under local pH conditions. We emphasize that the trend of the results we predict is independent of the reference point and therefore, it is clear that all adsorbates interact with the Fe\textsubscript{3} hollow more strongly than with the reconstructed site.
5. Reconstruction comparisons on Ni$_2$P and Fe$_2$P

![Adsorption Energy (eV)]

Figure S4. Adsorption energies (eV) as a function of bias for P* on the M$_3$ site for Fe$_2$P and Ni$_2$P. In both cases, applying a bias increases the stability of reconstruction. As described in the main text, reconstruction of Fe$_2$P is more favorable than Ni$_2$P, which has some implications.
6. Current Density

Table S1. Partial current densities for all catalysts. Currents were recorded after 16 hours of chronoamperometry and multiplied by the Faradaic efficiency for each product.

<table>
<thead>
<tr>
<th>Potential (V vs RHE)</th>
<th>$J_{\text{Total}}$ (mA/cm$^2$)</th>
<th>$J_{\text{Formate}}$ (µA/cm$^2$)</th>
<th>$J_{\text{Ethylene Glycol}}$ (µA/cm$^2$)</th>
<th>$J_{\text{Methylglyoxal}}$ (µA/cm$^2$)</th>
<th>$J_{\text{Furandiol}}$ (µA/cm$^2$)</th>
<th>$J_{\text{CO}_2\text{RR}}$ (µA/cm$^2$)</th>
<th>$J_{\text{HER}}$ (µA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.01</td>
<td>-1.99</td>
<td>-1.37</td>
<td>-2.56</td>
<td>-1.03</td>
<td>-6.95</td>
<td>-6.12</td>
</tr>
<tr>
<td>-0.05</td>
<td>-0.06</td>
<td>-1.27</td>
<td>-13.57</td>
<td>-2.94</td>
<td>-2.92</td>
<td>-4.30</td>
<td>-58.73</td>
</tr>
<tr>
<td>-0.1</td>
<td>-0.21</td>
<td>-3.97</td>
<td>-29.63</td>
<td>-7.87</td>
<td>-4.50</td>
<td>-45.99</td>
<td>-159.49</td>
</tr>
<tr>
<td>-0.15</td>
<td>-0.37</td>
<td>-1.23</td>
<td>-5.38</td>
<td>-2.95</td>
<td>-2.88</td>
<td>-12.44</td>
<td>-361.02</td>
</tr>
<tr>
<td>-0.2</td>
<td>-0.55</td>
<td>-2.37</td>
<td>-13.72</td>
<td>-2.98</td>
<td>-2.76</td>
<td>-21.82</td>
<td>-529.24</td>
</tr>
</tbody>
</table>
7. Faradaic Efficiency

The Faradaic Efficiency for the liquid CO$_2$ reduction products was calculated using the equation:

\[ FE_{CO2RR} = \frac{\text{Concentration} \cdot V_{\text{electrolyte}} \cdot \#\text{electrons} \cdot F}{\text{Charge}} \]

where the concentration was measured by HPLC; the volume of electrolyte measured after each experiment (around 6 mL); the number of electrons is 2 for formate, 12 for methylglyoxal and 14 for furandiol; F is Faraday’s constant and the charge was integrated over the full time of the experiment. Each value in the table below reflects the average of at least three measurements.

To determine the hydrogen Faradaic Efficiency, on-line measurements were conducted, and the following equation was used:

\[ FE_{H_2} = \frac{\text{mols of } H_2 \cdot \#\text{electrons} \cdot F}{\text{current} \cdot \text{time}} \]

Where the number of mols of hydrogen was determined by GC, the number of electrons is 2, the current is recorded at the instant of automated sampling, and the time is what is required to fill up the GC sample loop (3 s at 5 sccm). Each value in the table below reflects the average of at least 5 measurements.

Table S2. Faradaic efficiency averages for all catalysts at the potentials tested and standard deviation (SD) from at least three chronoamperometry experiments.

<table>
<thead>
<tr>
<th>Potential (V vs RHE)</th>
<th>Formate FE (%) SD</th>
<th>Ethylene glycol FE (%) SD</th>
<th>Methylglyoxal FE (%) SD</th>
<th>2,3-furandiol FE (%) SD</th>
<th>Total CO$_2$RR FE (%) SD</th>
<th>H$_2$ FE (%) SD</th>
<th>Total FE (%) SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>15.2</td>
<td>0.1</td>
<td>10.5</td>
<td>0.11</td>
<td>19.6</td>
<td>0.02</td>
<td>7.90</td>
</tr>
<tr>
<td>0.05</td>
<td>2.04</td>
<td>0.2</td>
<td>21.5</td>
<td>0.35</td>
<td>4.67</td>
<td>0.04</td>
<td>4.64</td>
</tr>
<tr>
<td>0.10</td>
<td>1.93</td>
<td>0.0</td>
<td>14.4</td>
<td>0.20</td>
<td>3.83</td>
<td>0.03</td>
<td>2.19</td>
</tr>
<tr>
<td>0.15</td>
<td>0.33</td>
<td>0.0</td>
<td>1.44</td>
<td>0.01</td>
<td>0.79</td>
<td>0.00</td>
<td>0.77</td>
</tr>
<tr>
<td>0.20</td>
<td>0.43</td>
<td>0.0</td>
<td>2.49</td>
<td>0.02</td>
<td>0.54</td>
<td>0.00</td>
<td>0.50</td>
</tr>
</tbody>
</table>


Figure S5. Hydrogen Faradaic efficiency. Error bars represent the standard deviation for at least three replicas. Detailed quantification methods as previously described\(^2\).
8. Reaction pathways for Ethylene Glycol

The reaction schematic below shows all the steps we have considered the prediction of the CO$_2$RR mechanism on Fe$_2$P. Following the gray arrows, the electron transfer to CO$_2$ has been shown to require potential of -1.44 V$^1$. Following the proton-coupled electron transfer (PCET) pathway, Garza et al$^2$ have calculated the $\Delta G$ at 0V vs RHE to be 0.65 eV for the CO to HCO step. Conversely, the energetics for the hydride transfer pathway, even without added stabilization expected from interaction of the intermediates with the catalyst surface are more favorable (Table S7), with the highest $\Delta G^0$ being 38.4 kJ/mol (0.40 eV). Because we see the formation of ethylene glycol at 0V vs. RHE, the most likely pathway is the hydride transfer in green, as electron transfer and PCET require much higher applied potentials.

Figure S6. Steps considered in the prediction of the mechanism for CO$_2$RR to ethylene glycol. The gray arrows indicate steps based on electron transfer. The orange arrows are for proton-coupled electron transfer steps, and this is the pathway proposed for ethylene glycol formation on copper by Garza et al$^2$. In green, the hydride transfer pathway that we believe to be the one preferred on Fe$_2$P.
9. Reaction Thermodynamics

The table below contains the Gibbs free energy ($\Delta_r G^0$) of the reaction steps of the proposed Fe$_2$P-catalyzed reduction of CO$_2$ mechanism. After the endergonic reduction of CO$_2$ to formate and formaldehyde, the conversion to glycolaldehyde, ethylene glycol, methylglyoxal, and furandiol are exergonic at standard conditions. A list of formation energies for all the products and reactants can be found in our previous work$^3$. The $\Delta_r G^0$ values listed here are for free solvated reactants and products, i.e. not bound to a catalyst surface, and therefore are just a reflection of the uncatalyzed reaction thermodynamics.

Table S3. Standard Gibbs free energy ($\Delta_r G^0$) of the proposed reaction mechanism of CO$_2$ conversion to formic acid, glycolaldehyde, ethylene glycol, methylglyoxal, and 2,3-furandiol.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta_r G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + H$^+$ + 2e$^-$ $\rightarrow$ HCOO$^-$</td>
<td>38.4</td>
</tr>
<tr>
<td>$\xrightarrow{\text{Formic acid}}$</td>
<td></td>
</tr>
<tr>
<td>2H$^+$ + 2e$^-$ + H$_2$O $\rightarrow$ H$_2$O</td>
<td>3.4</td>
</tr>
<tr>
<td>$\xrightarrow{\text{Formaldehyde}}$</td>
<td></td>
</tr>
<tr>
<td>$\xrightarrow{\text{Glycolaldehyde}}$</td>
<td>-29.3</td>
</tr>
<tr>
<td>$\xrightarrow{\text{Ethylene glycol}}$</td>
<td>-219.9</td>
</tr>
<tr>
<td>3H$^+$ + 2e$^-$ + H$_2$O $\rightarrow$ H$_2$O</td>
<td>-102.0</td>
</tr>
<tr>
<td>$\xrightarrow{\text{Methylglyoxal}}$</td>
<td></td>
</tr>
<tr>
<td>H$_2$O + HCOO$^-$ $\rightarrow$ H$_2$O + H$^+$ + 2e$^-$</td>
<td>-24.4</td>
</tr>
<tr>
<td>$\xrightarrow{\text{Formaldehyde Methylglyoxal}}$</td>
<td>2,3-Furandiol</td>
</tr>
</tbody>
</table>
10. CO$_2$ Adsorption

![Diagram of CO$_2$ adsorption on Fe at 0V vs RHE, $E_{coh} = -1.72$ eV.]

*Figure S7.* CO$_2$ adsorption on Fe at 0V vs RHE, $E_{coh} = -1.72$ eV.
11. **Density of States**

Here we show densities of states of four systems at three different applied potentials. We believe these are the most important to our conclusions: a) P* adsorption at Fe₃ hollow (reconstruction), b) H**P* adsorption at Fe₃ hollow, c) **OCHO at P*, and d) *OCHO at Fe. For each subset of DOS, we report a table of oxidation state values of important atoms as determined by Bader Charge Analyses that help explain observed trends.

**Figure S8.** Projected DOS of P* on the Fe₃ hollow at a) 0 V, b) -0.1 V, and c) -0.2 V vs RHE. The figures show projected DOS of all the P states in green, Fe states in red, and P* states in cyan.

**Table S4.** Oxidation states of the reconstructed surface’s P* and Fe₃ site based on Bader Charge analysis.

<table>
<thead>
<tr>
<th>Oxidation States</th>
<th>0 V</th>
<th>-0.1 V</th>
<th>-0.2 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>P*</td>
<td>-0.242</td>
<td>-0.247</td>
<td>-0.275</td>
</tr>
<tr>
<td>Fe₃(avg)</td>
<td>+0.184</td>
<td>+0.196</td>
<td>+0.215</td>
</tr>
</tbody>
</table>

It is difficult to discern anything from the DOS figures, other than the fermi level is shifting up relative to other states due to increased bias. Bader Charge analysis indicates that increasing the bias results in a net charge transfer from Fe atoms of the Fe₃ site to P*.

**Figure S9.** Projected DOS of H**P* on the Fe₃ hollow at a) 0 V, b) -0.1 V, and c) -0.2 V vs RHE. The figures show projected DOS of all the P* states in green, Fe₃ states in red, and H** states in cyan.

**Table S5.** Oxidation states of H* adsorbed on the P-Fe₃ site based on Bader Charge analysis.
Bader charge analysis indicates that more electrons localize on $P^*$ with increased bias. This is accompanied by a partial increase in the oxidation state of the surrounding Fe$_3$ atoms. The analysis also strongly suggests that the adsorbed H$^{**}$ is a hydride, with a net negative charge exceeding -1.

**Table S6**. Oxidation states of **OCHO** adsorbed on $P^*$ on the Fe$_3$ site based on Bader Charge analysis.

<table>
<thead>
<tr>
<th>Oxidation States</th>
<th>0 V</th>
<th>-0.1 V</th>
<th>-0.2 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^*$</td>
<td>-1.413</td>
<td>-1.926</td>
<td>-1.928</td>
</tr>
<tr>
<td>$O$</td>
<td>-1.898</td>
<td>-1.895</td>
<td>-1.896</td>
</tr>
<tr>
<td>$C$</td>
<td>2.263</td>
<td>2.762</td>
<td>2.782</td>
</tr>
<tr>
<td>$H$</td>
<td>0.046</td>
<td>0.054</td>
<td>0.036</td>
</tr>
<tr>
<td><strong>OCHO</strong>(total)</td>
<td>-1.003</td>
<td>-1.005</td>
<td>-1.006</td>
</tr>
<tr>
<td>$P^*$</td>
<td>-0.467</td>
<td>-0.444</td>
<td>-0.450</td>
</tr>
</tbody>
</table>

Here the projected DOS shows that P-O antibonding states are already occupied (approximately -0.5 eV below the Fermi Level) at 0 vs RHE. This explains why adsorption is less favorable on this site compared to the Fe site. Increasing the bias from 0V to -0.2V does not occupy any more antibonding states, and only shifts the FL upwards slightly, explaining why the adsorption energy slightly changes with bias, as shown in Figure 6 of the main text.
Figure S11. Projected DOS of *OCHO on surface Fe at a) 0 V, b) -0.1 V, and c) -0.2 V vs RHE. The figures show projected DOS of all the H states in purple, Fe states in green, O* states in red, C states in blue, and the other O states in cyan.

Table S7. Oxidation states of *OCHO adsorbed on the Fe site based on Bader Charge analysis.

<table>
<thead>
<tr>
<th>Oxidation States</th>
<th>0V</th>
<th>-0.1V</th>
<th>-0.2V</th>
</tr>
</thead>
<tbody>
<tr>
<td>O*</td>
<td>-1.743</td>
<td>-1.763</td>
<td>-1.749</td>
</tr>
<tr>
<td>O</td>
<td>-1.909</td>
<td>-1.901</td>
<td>-1.911</td>
</tr>
<tr>
<td>C</td>
<td>+2.897</td>
<td>+2.907</td>
<td>+2.886</td>
</tr>
<tr>
<td>H</td>
<td>-0.035</td>
<td>-0.043</td>
<td>-0.024</td>
</tr>
<tr>
<td>*OCHO(total)</td>
<td>-0.790</td>
<td>-0.799</td>
<td>-0.798</td>
</tr>
<tr>
<td>Fe</td>
<td>+0.663</td>
<td>+0.633</td>
<td>+0.666</td>
</tr>
</tbody>
</table>

A comparison of the density of states at the respective applied potentials clarifies this unexpected behavior (Figure S10), where the Fe-O* antibonding states shift down in energy due to the renormalization of states as more states are occupied at more negative potentials. At 0 V vs. RHE, the Fe-O antibonding states are far above the Fermi level by ~0.7 eV, as shown in Figure S10A. However, at -0.2 V vs. RHE these antibonding states are only ~0.1 eV above the Fermi level (Figure S10B), even though the Fermi level is shifted up by only 0.2 eV. The traditional assumption using DFT methods with no applied potential shifts the states rigidly relative to the Fermi level so that each originally unoccupied states becomes closer to the Fermi only by the decrease in the applied bias, as noted by the dashed line in Figure S10A. However, GC-DFT predicts a larger shift of these antibonding states, because of its ability to compute minimum energy geometries and self-consistent renormalized electronic states as a function of the applied potential.
Converged geometries of the clean surface, reconstructed surface, and adsorbates at various adsorption sites are provided in POSCAR format and can be visualized using various free software, such as Ovito and VESTA. Lattice and atom coordinates must be converted from Angstrom to Bohr to be run in JDFTx.

Sample input file settings:

```
# INPUT GEOMETRY & LATTICE
include init.lattice
include init.ionpos
latt-scale 1 1 1
latt-move-scale 0 0 0

# KPOINTS
kpoint-folding 2 2 1
kpoint 0 0 0 1
#symmetries none

# PSEUDOPOTENTIALS
ion-species SG15/$ID_ONCV_PBE-1.1.upf
ion-species SG15/$ID_ONCV_PBE-1.0.upf

# ENERGY CUTOFF
elec-cutoff 20 #520 eV
#core-overlap-check none

# INITIALIZATION/READ WAVEFN
lcao-params 30
#initial-state jdft.$VAR

# CONVERGENCE ALGORITHM
electronic-minimize
  nIterations 200
  energyDiffThreshold 1e-08

# OPTIMIZE LATTICE / ATOMS (IONS)
#lattice-minimize
ionic-minimize

# SPIN / MAGNETIZATION
elec-smearing Fermi 0.001
elec-initial-magnetization 0 no
spintype z-spin
Nelec/2+10
elec-n-bands { Nelec/2+10 }
converge-empty-states yes
dft-functional gga-beefvdw

# SOLVATION DETAILS
fluid LinearPCM
pcm-variant CANDLE
fluid-solvent H2O
fluid-cation Na+ 0.5
fluid-anion F- 0.5

# APPLIED BIAS or EXPLICIT ELEC
#eqn: target-mu= -(Vref+V)/27.2114 = -PZC-V/27.2114
target-mu -0.1510

# DENSITY OF STATES
include init.DOS
```
dump-name jdft.$VAR
dump Ionic State EigStats
dump End Ecomponents
dump End ElecDensity
dump End EigStats
dump End BandEigs
dump End RhoAtom
dump End Lattice
dump Ionic IonicPositions
dump End Kpoints
dump End KEdensity
dump End Dtot BoundCharge
13. Inductively Coupled Plasma Optical Emission Spectrometry

To investigate catalyst stability, ICP-OES was conducted on a Perkin Elmer Optima 7300 DV to detect the amount of phosphorous and iron that leached into the solution due to catalyst corrosion. The samples were prepared by diluting 1.000 mL of the electrolyte after 16h of catalysis at a set potential with 2.000 mL of 5% (v/v) nitric acid in ultrapure water. Immediately prior to sample analysis, a calibration was done with serial dilutions of 100 ppm iron and 10 000 ppm phosphorous SPEX Certiprep certified analytical standards.

Table S8. Amount of iron and phosphorus leached relative to the mass of catalyst on the cathode, after at least 16 hours of electrolysis, as measured by ICP-OES.

<table>
<thead>
<tr>
<th>Potential (V vs RHE)</th>
<th>Fe in electrolyte (mM)</th>
<th>Standard deviation</th>
<th>% of Fe in pellet leached</th>
<th>P in electrolyte (mM)</th>
<th>% of P in pellet leached</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.23</td>
<td>0.61</td>
<td>0.09%</td>
<td>12.78</td>
<td>0.74%</td>
<td>4.81</td>
</tr>
<tr>
<td>-0.05</td>
<td>3.95</td>
<td>0.59</td>
<td>0.13%</td>
<td>16.91</td>
<td>0.93%</td>
<td>3.37</td>
</tr>
<tr>
<td>-0.1</td>
<td>4.07</td>
<td>0.66</td>
<td>0.15%</td>
<td>20.51</td>
<td>1.47%</td>
<td>3.49</td>
</tr>
<tr>
<td>-0.15</td>
<td>4.60</td>
<td>0.88</td>
<td>0.15%</td>
<td>22.33</td>
<td>1.47%</td>
<td>5.26</td>
</tr>
<tr>
<td>-0.2</td>
<td>6.11</td>
<td>0.60</td>
<td>0.17%</td>
<td>20.53</td>
<td>1.36%</td>
<td>1.35</td>
</tr>
</tbody>
</table>

The results summarized in Table S8 and Figure S12 indicate that less than 0.2% of Fe and less than 1.5% of P consistently leached from the electrode. This behavior is analogous to nickel phosphides, postulated to be due to the dissolution of a surface phosphor-oxide layer (formed by air-exposure) after which the catalyst is stable. This explanation is corroborated by the XPS data. Based on this, it is expected that the Fe and P dissolution does not indicate an inherent instability of the catalyst under working conditions. Here, the Fe concentration is furthermore seen to be dependent on the applied potential, with stronger reducing potentials resulting in increased Fe corrosion. This result contradicts the thermodynamic behavior of Fe described in the Pourbaix diagram at pH 7.5. However, at more reducing potentials, the gas-evolving HER increases exponentially causing bubble formation, which could lead to Fe2P particles dislodging from the pellet. Such dislodged particles would be free to spontaneously oxidize as the cathodic bias is lost, giving rise to an increase in Fe and P concentration in solution at strong bias.
Figure S12. ICP analysis of post-experiment solutions indicate that Fe leached from the electrode for all experiments, with its concentration in the electrolyte being dependent on potential.
**14. Potential role of dissolved iron species**

As detected by ICP, iron leaches into solution during reaction in concentrations ranging from 3 to 6 mM and could play a role in determining reaction selectivity. Based on the Pourbaix diagram, iron would likely be present as Fe$^{2+}$, a Lewis acid that can activate aldol-coupling reactions. The CO$_2$RR mechanism on nickel phosphides was proposed to rely on the condensation of formaldehyde through the formose reaction, which is known to be catalyzed by Lewis acids through coordination with oxygen atoms. Hence, it would be expected that the presence of Fe$^{2+}$ would accelerate aldol coupling through the activation of the reactive aldehyde. If, however, the surface concentration of surface bound formaldehyde is low, the Fe-activated aldehyde may instead react with a surface hydride to form the corresponding alcohol (see Figure 5). If this were to occur at the glycolaldehyde step, the reaction would terminate at ethylene glycol. Thus, the C$_3$ product could be relatively disfavored compared to the C$_2$ product. This is in agreement with studies into Lewis acid cations, such as Mg$^{2+}$ and Ca$^{2+}$ (at concentrations >7 mM), which have been reported to improve the CO$_2$ reduction activity of a catalyst, both in terms of catalytic efficiency and lifetime of the catalyst.

It has been speculated that the Lewis acid co-catalysts electrophilically assist in breaking one of the C-O bonds of CO$_2$, and thereby catalyze the first hydride transfer to CO$_2$, resulting in an overall increased reaction rate. Thus, the formation of ethylene glycol, which has not previously been observed on the Ni$_2$P catalyst where Ni leaching was negligible, could be attributed to the presence of cationic Fe in the electrolyte acting as a Lewis acid co-catalyst on the glycolaldehyde intermediate.

To test this hypothesis, we performed chronoamperometry on Ni$_2$P using the same methodology as described for Fe$_2$P. However, the 0.5 M KHCO$_3$ buffer was spiked with 6 mM of iron perchlorate. As Fe(ClO$_4$)$_3$ is hygroscopic, it was vacuum-dried at room temperature before solution preparation. After 16 h at -0.1 V, the electrolyte was analyzed by NMR and HPLC. The Faradaic efficiency was 36% for formate, 11% for methylglyoxal, and 4% for furandiol. No ethylene glycol formation was detected. While the presence of Fe ions in the electrolyte indeed changed the reaction selectivity from a C$_4$ to C$_1$ product, these results indicate Fe ions are not responsible for the formation of ethylene glycol. The appearance of this new product is, as detailed in the main article, a result of the more labile hydrides and the weaker formate adsorption on the Fe$_2$P surface.
15. X-ray photoelectron spectroscopy

The surface chemical state and composition of Fe₂P was evaluated by X-ray photoelectron spectroscopy (XPS) before and after reaction at -0.2 V vs. RHE for 4 h. The surface of Fe₂P before and after reaction was analyzed by a Thermo K-Alpha XPS spectrometer. The chamber was evacuated to 5x10⁻⁹ Torr base pressure. The spectra were collected with a flood gun for charge compensation and an X-ray beam of 400 μm was used. Figure S13 shows deconvoluted Fe₂P XPS spectra (referenced to adventitious carbon at a binding energy of 284.8 eV). In Figure S13A, the XPS spectra in the Fe 2p region features 3 sets of doublets attributable to three distinct Fe species with the expected spin-orbit coupling of Fe 2p₃/₂ and Fe 2p₁/₂. Each doublet features a corresponding satellite. The 3 species are attributed to Fe⁶⁺ from Fe₂P, Fe²⁺, and Fe³⁺ based on the NIST XPS binding energy database (see ESI for detailed assignments).¹¹ The latter two are likely from surface phosphorus oxides in agreement with previous studies suggesting that iron phosphides surface-oxidize upon air exposure after synthesis to form a partially hydrated surface with phosphate coating.¹² The surface iron phosphorus-oxide layer thickness is ~1-3 nm, estimated by photoelectron escape depth of FeOₓ (or FeOOH) on Fe(s).¹³,¹⁴ In Figure S13B, the P 2p spectra shows two sets of doublets corresponding to two different species with their spin-orbit coupling of 2p₃/₂ and 2p₁/₂. These two species can be ascribed to P⁵⁻ and PO₄³⁻ based on their binding energy compared to the NIST reference database.¹¹ We note that the composition (estimated by peak area) of Fe⁶⁺ relative to Fe²⁺ and Fe³⁺ increases upon catalytic turnover. Similarly, the P⁵⁻/PO₄³⁻ ratio is observed to increase after catalysis (see details in Table S9). This can be interpreted as a decrease in surface iron oxide/phosphate thickness attributed to the simultaneous electrochemical reduction and/or dissolution of the surface iron phosphorus-oxide.

Figure S13. A) Fe 2p and B) P 2p XPS spectra of Fe₂P pellet as-synthesized (top) and after reaction (bottom). Residuals are plotted x².
Table S9. XPS Peak assignment and references, as well as peak area ratios for Fe₂P and surface oxide.

<table>
<thead>
<tr>
<th>Peak assignment</th>
<th>Reference E (eV)</th>
<th>Ref. Compound</th>
<th>Ref. Compound</th>
<th>Measured E (eV) As made</th>
<th>Measured E (eV) Post-reaction</th>
<th>Peak Area As made</th>
<th>Peak area Post-reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2p Spectra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P⁺ 2p₃/₂</td>
<td>129.5</td>
<td>Fe₃P</td>
<td>11</td>
<td>129.5</td>
<td>129.5</td>
<td>3188.43</td>
<td>473.15</td>
</tr>
<tr>
<td>P⁺ 2p₁/₂</td>
<td>130.3</td>
<td>P</td>
<td>11</td>
<td>130.4</td>
<td>130.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-O 2p₃/₂</td>
<td>133.7</td>
<td>FePO₄</td>
<td>11</td>
<td>133.2</td>
<td>132.8</td>
<td>3129.01</td>
<td>347.34</td>
</tr>
<tr>
<td>P-O 2p₁/₂</td>
<td>134.6</td>
<td>CrPO₄</td>
<td>11</td>
<td>134.0</td>
<td>133.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P⁺/P-O peak area ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.02</td>
<td>1.36</td>
</tr>
<tr>
<td>Fe 2p Spectra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe²⁺ 2p₃/₂</td>
<td>707.1</td>
<td>Fe₃P</td>
<td>11</td>
<td>707.0</td>
<td>707.0</td>
<td>9404.32</td>
<td>1693.63</td>
</tr>
<tr>
<td>Fe⁺ 2p₁/₂</td>
<td>720.2</td>
<td>Fe/Cu</td>
<td>11</td>
<td>720.0</td>
<td>719.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺ 2p₃/₂</td>
<td>709.4-710.7</td>
<td>FeO</td>
<td>11</td>
<td>710.5</td>
<td>710.5</td>
<td>9519.25</td>
<td>1205.36</td>
</tr>
<tr>
<td>Fe⁺⁺ 2p₁/₂</td>
<td>724</td>
<td>FeO</td>
<td>15</td>
<td>723.7</td>
<td>723.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺ 2p₃/₂</td>
<td>710.4-711.6</td>
<td>Fe₂O₃</td>
<td>11</td>
<td>711.9</td>
<td>712.0</td>
<td>14219.62</td>
<td>592.26</td>
</tr>
<tr>
<td>Fe⁺⁺⁺ 2p₁/₂</td>
<td>726</td>
<td>Fe₂O₃</td>
<td>18</td>
<td>725.6</td>
<td>725.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe⁺⁺⁺[Fe²⁺⁺⁺+Fe³⁺⁺⁺] peak area ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
<td>0.94</td>
</tr>
</tbody>
</table>
16. Determination of uncompensated resistance

Figure S14 – Potentiostatic electrochemical impedance spectroscopy of Fe₃P at -0.2 V vs RHE in 0.5 M KHCO₃ gives a solution resistance of 8.6 Ω. This measurement was done before electrolysis, and is representative of the behavior observed for all trials on Fe₃P.
17. Electrochemical Surface Area

Electrochemical capacitance was utilized to determine the electrochemical surface area of Fe₃P. To measure the capacitance, the potential was cycled between 0.11 and 0.21 V vs. RHE, at different scan rates and in an electrolyte of CO₂-saturated 0.5 M KHCO₃. The cyclic voltammograms for Fe₃P are shown in Figure S15. The capacitive current was measure at 0.16 V, where the faradaic current is negligible, and was plotted versus the scan rate. The slope of the linear trend line is the capacitance of the surface area. The electrochemical surface area (ECSA) was calculated by the ratio of the capacitance measure to the specific capacitance for metal phosphides (40 µF/cm², as reported by Kibsgaard et al). The roughness factor was calculated by dividing the ECSA by the geometric area of the sample, resulting in 418 cm²/cm².

![Figure S15](image)

**Figure S15.** Electrochemical capacitance measurements taken to determine the ECSA of Fe₃P. In the inset, the capacitive current is plotted as a function of scan rate.
18. Liquid Product Analysis by $^1$H NMR

$^1$H NMR spectra were recorded using a Bruker Avance Neo 500 MHz spectrometer. 100 μL samples from the CO$_2$ reduction electrolyte were taken from the working electrode compartment after the reaction. The samples were combined with 400 μL of D$_2$O. A custom script for water suppression was used, and 256 scans were accumulated for every measurement. Details of the spectral assignment can be found in our previous work.$^3$

*Figure S16. Representative NMR spectrum of the electrolyte after catalysis at -0.1 V.*
19. References


Electronic Supplementary Information:
Theoretical and Experimental Insights into the Ni₂P Surface Under Electrochemical Conditions

Abdulaziz Alherz\textsuperscript{a}, Karin U. D. Calvinho\textsuperscript{b,}, Shinjae Hwang\textsuperscript{b}, Anders B. Laursen\textsuperscript{a}, Zachary J. Bare, Charles B. Musgrave\textsuperscript{b,}, G. Charles Dismukes\textsuperscript{a,c,*}

\textsuperscript{a}Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO, 80309
\textsuperscript{b}Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey, 08854
\textsuperscript{c}Waksman Institute of Technology, Rutgers, The State University of New Jersey, 190 Frelinghuysen Road, Piscataway, New Jersey, 08854

*Corresponding authors (e-mail: charles.musgrave@colorado.edu, dismukes@rutgers.edu).
†These authors contributed equally.
Figure 53: Powder X-ray diffraction pattern of Ni$_2$P film on nickel foil