

Hanna Hinrika Cramer, Clémence Corminboeuf, Christophe Werlé, and Walter Leitner

CO₂ to X/Y/Z? Selectivity Control in Catalytic Carbon Dioxide Reduction

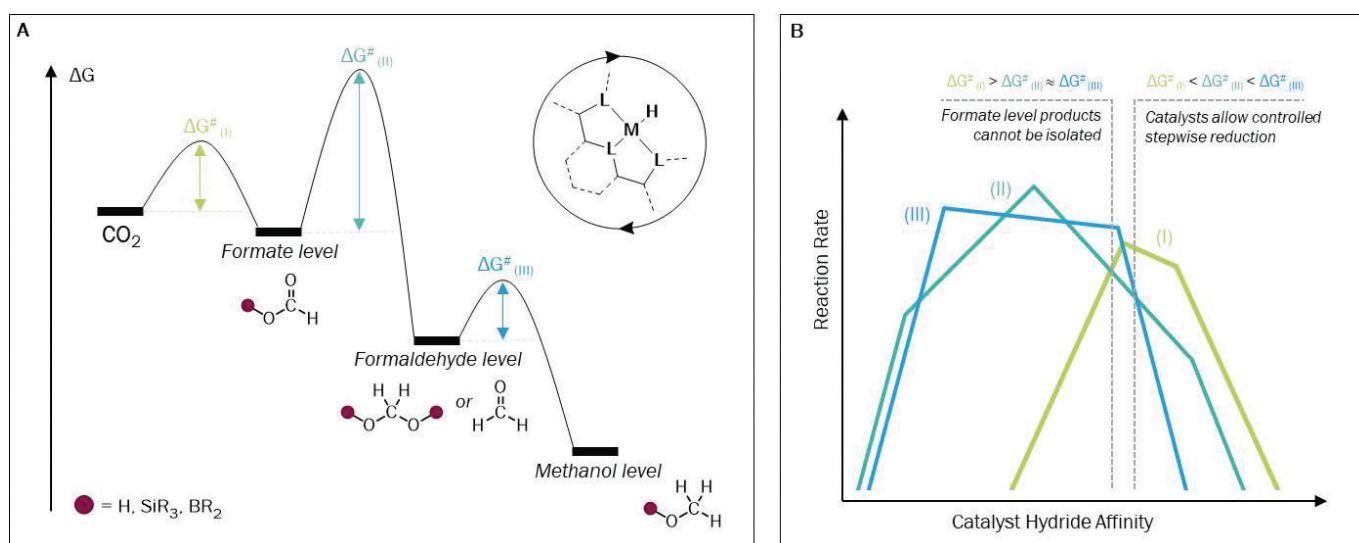


Fig. 1: Generalized reaction profile of the stepwise reduction of CO₂ to formate, formaldehyde, and methanol level products catalyzed by a transition metal hydride complex (A); relation between catalyst hydride affinity, kinetic barriers, and selectivity (B).

CO₂ is the main molecular contributor to global warming, and its emission must be drastically reduced to reach the goal of a sustainable chemical industry. At the same time, we can view it not only as an unwanted waste molecule but also as a non-fossil carbon source that can be transformed into a large variety of value-added products. Its benefits as a feedstock chemical include low toxicity, non-flammability, and low costs. But most importantly, large-scale CO₂ utilization allows moving from a linear- to a circular carbon economy that reintroduces emitted CO₂ into the chemical value chain. Of particular interest are CO₂ reduction products that have a higher energy content, including formic acid, formaldehyde, methanol, methane, as well as C>1 molecules. Many of them find diverse large-scale applications: As two examples, methanol is well-known as a versatile platform chemical – its relevance already manifested in the “Methanol economy” envisioned by Asinger in 1987 – and formaldehyde has a broad synthetic utility for further functionalization to products with higher molecular complexity [1].

Thermodynamic and kinetic challenges

So how do we efficiently access these targets from CO₂? From a molecular perspective, the main challenge is that CO₂ lies in a thermodynamic sink and thus is a very stable molecule. This necessitates using high-energy coreactants, such as hydrogen, hydroboranes, or hydrosilanes. Additionally, CO₂ reduction has a high kinetic barrier, and a suitable catalyst is essential to facilitate product formation. Transition metal hydride complexes are of particular importance as homogeneous catalysts: Ligands with great steric and electronic versatility provide the transition metal with the ideal environment for one specific product, which leads to high control over the reactivity. Since the carbon atom of CO₂ is prone to nucleophilic attack, a typical catalytic cycle involves a hydride transfer to the carbon atom, while the catalyst is then regenerated by its reaction with the hydride source. The first two-electron reduction leads to formate derivatives, while the second step as a net-four-electron reduction gives formaldehyde-level products. Further reduction leads to the methanol level with net-six-electron reduction products (Figure 1A).

This gives rise to a key problem: While we want to selectively access one product at a high rate, the overreduction of the targeted molecule needs to be suppressed, which is a significant challenge in catalyst development. Thermodynamically, reductions to formaldehyde- and particularly to methanol-level

Dr. Hanna Hinrika Cramer
Max Planck Institute for Chemical Energy Conversion
Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany
Princeton University, 08544 Princeton, NJ, USA
hc2460@princeton.edu

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products provide a much stronger driving force than the generation of formates. Yet, the catalytic reduction of CO₂ to the formate level is comparatively facile, but methanol and particularly formaldehyde are much more challenging to obtain. This is because of two reasons: The high kinetic barrier $\Delta G^{\ddagger}_{(1)}$ of formate-to-formaldehyde reduction hampers the formate reduction, and the comparatively low kinetic barrier $\Delta G^{\ddagger}_{(1)}$ of formaldehyde-to-methanol reduction makes isolation of formaldehyde derivatives difficult. Development and improvement of processes to selectively access any of these products is therefore an ongoing challenge.

Reaction conditions as control parameters

Besides the catalyst, the reaction conditions also significantly influence which product is observed; including temperature, solvent, concentration, and pressure. While typically, catalysts are optimized towards one specific product, these external parameters offer an additional tool for selectivity control. In my Ph.D. work at the Max Planck Institute for Chemical Energy Conversion in Mülheim an der Ruhr, we were particularly interested in this phenomenon and studied whether the responsiveness to the reaction conditions might enable catalytic systems to selectively access more than one CO₂ reduction level – following the concept of “adaptive catalysis” [2]. This involved both identifying a suitable catalyst and optimizing the reaction conditions for each product level of interest. In our work, we identified a catalytic system based on a cobalt pincer hydride complex that could selectively reach all three product levels in the reduction with the same reducing agent [3]. In particular, lower (ambient) CO₂ pressures, higher temperatures (80 °C), and higher concentrations (absence of solvent) were beneficial for reduction beyond the formate level, and fine adjustment of the conditions then allowed to access each product in good to excellent selectivity.

Mechanistic studies were based on stoichiometric experiments and computational chemistry, and they showed that this unique behavior was due to two key factors: First, increasing kinetic barriers in the order formate < formaldehyde < methanol led to a higher required temperature for reducing beyond the formate level. Second, competing hydride transfer steps either to CO₂ or to formates make the reaction sensitive to CO₂ pressure and concentration: They both determine the relative abundance of the two substrates in the catalytic reaction. Hence, well-balanced kinetic barriers in the three reduction processes are a promising way to control product selectivity in CO₂ reduction [4].

Catalyst hydride affinity as a selectivity descriptor

But what kind of catalysts enable this behavior – and in general, which catalysts prefer which product platform? Ideally, we would be able to identify trends in catalyst design that are linked with the observed activity and selectivity. One key descriptor is the hydride affinity of the transition metal complex – a measure of the metal-hydride interaction strength. For an overall fast catalytic turnover, the rates of all elementary steps

must be well balanced, and following Sabatier’s principle, the hydride must bind to the metal center neither too strongly nor too weakly to facilitate efficient catalytic reduction [5]. But how does this relate to several subsequent reduction steps and the selectivity of an individual catalyst? It is possible to identify systems for rapid turnover for one product, but sluggish reactivity for another?

To address this, we teamed up with the Laboratory of Computational Molecular Design at the EPFL in Switzerland and computationally evaluated a library of diverse 3d transition metal pincer complexes as potential catalysts [6]. Insights about their selectivity arose from analyzing the kinetic profiles for the reduction of CO₂ to formate-, formaldehyde-, and methanol-level products, respectively. The key result was that not only the activity but also the selectivity is linked to the metal-hydride bond strength of the catalyst – which again depends largely on the electron-donating ability of the respective pincer ligand. The hydride affinity could be used to establish linear correlations with relative energies of all relevant intermediates and transition states. Data analysis via “volcano plots” visualizes the optimal catalyst with the highest activity for each product (Figure 1B). Since the reaction is a cascade with three steps, the most active catalysts for all products must be suitable for catalyzing the initial CO₂ reduction – but beyond that, the magnitude of the hydride affinity is key in determining the selectivity. Specifically, catalysts with a higher hydride affinity have increasing kinetic barriers in the order of formate < formaldehyde < methanol. This makes them more prone to access each product selectively under the right choice of reaction conditions. When the hydride affinity becomes lower, however, the initial CO₂ reduction is the slowest step, and the two subsequent reduction steps are both significantly faster. In this case, any formate-level products will be further reduced, and stopping the reaction at this level is not possible anymore. So, in conclusion, choosing a catalyst with the right metal-hydride interaction strength should allow for enhancing the selective formation of any of the desired products.

Based simply on the magnitude of the hydride affinity as the key descriptor, the computational model provides an activity/selectivity estimate of any catalyst not only within, but also beyond the chosen catalyst data set – allowing to evaluate the expected reactivity for potential future catalytic systems. Back in Mülheim an der Ruhr, we aimed to experimentally validate the computational implications with a series of cobalt and nickel pincer catalysts. We were able to observe the predicted selectivity trends and achieved an improved yield for the most challenging formaldehyde level, which demonstrated the practical applicability of our model and its benefit in catalyst development.

To summarize, selectivity in CO₂ reduction depends on both the reaction conditions and catalyst hydride affinity, and this allows appropriate “adaptive” catalysts to selectively reach multiple products under the right conditions. Identifying trends in these two control parameters might require very detailed mechanistic studies. Still, it is essential to design catalysts that precisely meet the requirements for the targeted product – and helps to contribute to using an abundant waste molecule as recyclable and versatile carbon feedstock.

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Dr. Hanna Hinrika Cramer



Dr. Hanna Hinrika Cramer grew up in the vast countryside of Ostfriesland, Germany, and pursued her BSc. and MSc. studies in chemistry at the Carl-von-Ossietzky University of Oldenburg. She discovered her passion for inorganic and computational chemistry during this time, which motivated her to visit the Max Planck Institute for Chemical Energy Conversion in Mülheim an der Ruhr for a research internship with Prof. Frank Neese. Inspired by the institute's approach of using in-depth mechanistic studies for developing sustainable energy systems, she chose to return to the Ruhr area for her Ph.D. work with Prof. Walter Leitner and Dr. Christophe Werlé. Supported by a fellowship of the German Academic Scholarship Foundation (Studienstiftung des deutschen Volkes), she investigated selectivity control mechanisms in 3d-metal catalyzed carbon dioxide reduction combining organometallic catalysis with quantum chemistry. Since she wanted to learn more computational tools for catalyst development, she worked with Prof. Clémence Corminboeuf as a visiting Ph.D. student at the EPFL, Switzerland, while at the same time enjoying the beauty of the Swiss Alps and Lake Geneva during many hiking and Scuba diving trips. After completing her doctoral studies in June 2022, she currently aims to tackle a different sustainability problem – single-use plastic waste – by catalyst development for chemically recyclable polyolefins as postdoctoral researcher at Princeton University with Prof. Paul Chirik.

ZITATE ZUM KLIMAWANDEL

*„Die Erde hat Fieber – und das Fieber steigt.“
„Wenn wir keinen Planeten mehr haben, geht es der
Wirtschaft nicht gut.“*

Albert ‚Al‘ Gore

*„Der wichtigste Artenschutz ist und bleibt der Klima-
schutz.“*

Philip Vohrer

*„Ja, wir könnten jetzt was gegen den Klimawandel tun,
aber wenn wir dann in 50 Jahren feststellen würden,
dass sich alle Wissenschaftler doch vertan haben und
es gar keine Klimaerwärmung gibt, dann hätten wir völ-
lig ohne Grund dafür gesorgt, dass man selbst in den
Städten die Luft wieder atmen kann, dass die Flüsse
nicht mehr giftig sind, dass Autos weder Krach machen
noch stinken und dass wir nicht mehr abhängig sind
von Diktatoren und deren Ölvorkommen. Da würden
wir uns schön ärgern.“*

Marc-Uwe Kling

*„Der Klimawandel ist die größte Bedrohung der Zukunft.
Jeder Staat muss mitwirken, die Ursachen zu bekämp-
fen und die Folgen zu mindern.“*

Klaus Töpfer

*„Es ist fast so, als hätten wir ein Feuer entfacht, um uns
zu wärmen, und dabei übersehen, dass auch das Mobi-
liar verbrennt.“*

James Lovelock

*„Fokussiere all deine Energie nicht auf das Bekämpfen
des Alten, sondern auf das Erschaffen des Neuen.“*

Sokrates

*„Erst wenn der letzte Baum gerodet, der letzte Fluss ver-
giftet, der letzte Fisch gefangen ist, werdet ihr feststel-
len, dass man Geld nicht essen kann.“*

Weisheit der Cree

*„Der heutige Mensch ist der Natur gefährlicher gewor-
den, als sie ihm jemals war.“*

Hans Jonas

*„Die Erde ist nicht nur unser gemeinsames Erbe, sie ist
auch die Quelle des Lebens.“*

Dalai Lama

*„Man sollte nie daran zweifeln, dass eine kleine Gruppe
kluger, engagierter Bürger die Welt verändern kann. In
der Tat ist das der einzige Weg, der jemals Erfolg hatte.“*

Margaret Mead

Quelle: <https://www.careelite.de/klimaschutz-zitate-sprueche/>