Carbonate-Catalyzed CO_2 Hydrogenation to Multi-Carbon Products

Investigators

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Abstract

A grand challenge for the 21st century is to drastically reduce greenhouse gas emissions without compromising quality of life for a growing population. Using renewable energy to drive the synthesis of organic compounds from CO_2 and H_2O could provide a sustainable source of fuels and chemicals with no net CO_2 emissions. In order for this approach to gain traction, however, it is essential to develop sustainable syntheses that are cost-competitive with fossil fuels. The key technical challenge is to efficiently transform CO_2 into multi-carbon compounds because these targets generally have higher value, greater energy density, and more applications than C_1 compounds. At the molecular level, the challenge is to make C–C bonds. An appealing strategy is to produce H_2 by using renewable energy to electrolyze H_2O and then synthesize multi-carbon compounds by hydrogenating CO_2. Renewable H_2 can be produced today using electrolyzers powered by photovoltaics or wind turbines, albeit at a higher cost than natural gas–derived H_2; emerging photoelectrochemical technologies may lower the cost in the future. The key obstacle to using renewable H_2 to synthesize multi-carbon compounds is the absence of effective CO_2 hydrogenation methods. Despite decades of research, currently available CO_2 hydrogenation methods are only useful for synthesizing methane, CO, or methanol. All of these methods use metal or metal oxide surfaces as catalysts. The absence of efficient multi-carbon product synthesis in this paradigm is understandable given the enormous challenges of designing a single surface that activates H_2 and CO_2 and mediates C–C bond formation in a controlled manner.

The goal of this project is to develop a completely new approach to CO_2 hydrogenation that 1) directly produces multi-carbon products 2) uses simple carbonate salts (M_2CO_3 or MCO_3) as catalysts instead of transition metals or metal oxides. The target products include oxalate, acetate, ethylene, and ethanol. The use of carbonate (CO_3^{2-}) as a catalyst is inspired by our recent discovery that, in molten salt media with alkali cations, CO_3^{2-} deprotonates extremely weak acids including H_2 and un-activated C–H bonds, generating hydride (H^-) and carbanion (C^-) intermediates that undergo H–C and C–C bond-forming reactions with CO_2. The research utilizes a highly synergistic collaboration between experimental studies in the Kanan lab and theory in the Martinez lab to elucidate the chemical principles of carbonate-catalyzed CO_2 hydrogenations and use these insights to optimize reactions.

In the past eight months, we have made substantial progress towards the project goal by 1) discovering reaction conditions for efficient and selective CO_3^{2-}-promoted CO_2 hydrogenation to oxalate, the first target product, and 2) demonstrating that our *ab initio* molecular dynamics simulator, the *nanoreactor*, readily uncovers CO_3^{2-}-promoted

reaction pathways relevant to the target catalytic cycles. These milestones provide the foundation for ongoing work aimed at developing CO_3^{2-}-based hydrogenation catalysts that produce the remaining target C_2 products.

Introduction

The technologies to extract and process fossil fuels have provided abundant energy and the feedstocks for synthetic chemistry for the past century. While these achievements have transformed society, the enormous rate of fossil fuel consumption that has accompanied these changes is not sustainable because of the accumulation of CO_2 in the atmosphere. Despite the growing awareness of the risk factors of the rising CO_2 levels, high demand for fuels and chemicals will remain for the foreseeable future because modern society has been built on these pillars.[1] One way to address this paradox is to develop an alternative, sustainable production of fuels and chemicals. In principle, it is possible to synthesize these compounds from CO_2, H_2O and renewable energy. In practice, such syntheses using existing technologies are far too inefficient and expensive to be viable. If it were possible, however, to "recycle" CO_2 into fuels and chemicals in a way that is competitive with fossil fuel–based production, these processes would be rapidly adopted and scaled because of their dual economic and environmental benefits. We view this prospect as the ultimate synthetic chemistry challenge for sustainability.

This project is pursuing a radically new approach to CO_2 hydrogenation chemistry ($CO_2 + H_2 \rightarrow$ fuels and chemicals). CO_2 hydrogenation reactions have been known for over a century, but the available methods are only useful for the production of C_1 compounds (e.g. methane, CO, methanol) that are either themselves fossil fuels or very easily produced from these sources.[2-4] As such, CO_2 hydrogenation has not been a competitive method for fuel and chemical production. The ability to hydrogenate CO_2 to produce multi-carbon (C_{2+}) compounds could fundamentally change this picture. Compared to C_1 compounds, C_{2+} compounds are generally more difficult to produce from fossil fuel sources, more valuable, and have more applications. All of the available CO_2 hydrogenation catalysts are comprised of transition metals or metal oxides. Selectively hydrogenating CO_2 to a multi-carbon product is enormously challenging because it requires finding a surface that activates CO_2 and H_2 and mediates C–C bond formation in a controlled manner. While there has been some recent progress in the development of Fe carbide catalysts that hydrogenate CO_2 into light olefins,[5, 6] catalysts that suppress methane formation and selectively produce one or a few high-value products remain elusive.
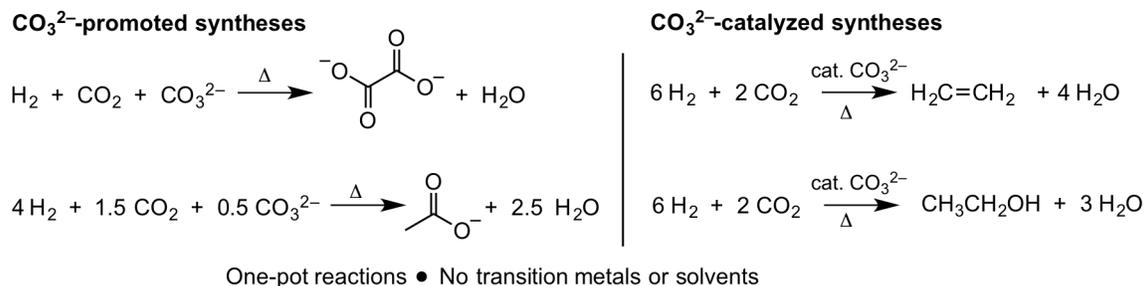

Figure 1: Target CO_2 hydrogenation reactions

Our approach is to use simple acid–base reactions to create a catalytic cycle in which CO_2 is selectively hydrogenated to a high-value C_{2+} compound. We have recently discovered that intermediate temperature (200 °C–350 °C) molten salts containing alkali cations enable CO_3^{2-} to deprotonate extremely weak acids including H_2 and un-activated C–H bonds, generating hydride (H^-) and carbanion (C^-) intermediates that undergo H–C and C–C bond-forming reactions with CO_2 and other carbon-centered electrophiles.[7] Our research aims to identify CO_3^{2-}-containing salt mixtures and reaction conditions that utilize these reactions to efficiently hydrogenate CO_2. Specific targets include are CO_3^{2-}-promoted CO_2 hydrogenations to oxalate and acetate (these reactions consume CO_3^{2-}) and CO_3^{2-}-catalyzed CO_2 hydrogenations to ethylene and ethanol (**Figure 1**). Our research combines experimental studies in the Kanan lab with *ab initio* molecular dynamics simulations in the Martinez lab.

Background

Carbonate-promoted C–H carboxylation

Carbonate-catalyzed CO_2 hydrogenation requires that CO_3^{2-} deprotonate extremely weak acids. Researchers have shown that CO_3^{2-} can deprotonate C–H bonds with pKa values up to 27 in polar aprotic organic solvents at elevated temperature.[8, 9] This level of basicity is insufficient to activate H_2 (pKa= 35)[10] and the C–H bonds necessary for producing the target C_2 compounds. We recently showed that intermediate temperature (200 °C–350 °C) molten salts with alkali cations greatly change the acid–base properties of molecules. In these media, CO_3^{2-} deprotonates very weakly acidic C–H bonds (pKa >40) to form reactive carbon-centered nucleophiles (C^-). The C^- nucleophiles react readily with CO_2 to form carboxylates ($C-CO_2^-$) (**Figure 2**).[7] This carboxylation
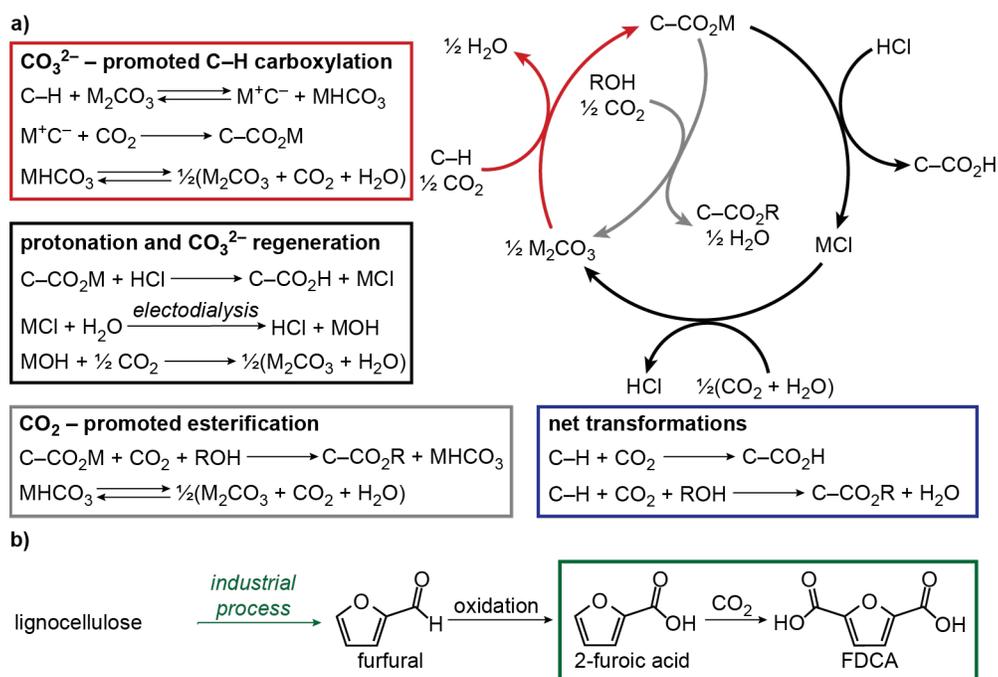

Figure 2: CO_3^{2-}-promoted C–H carboxylation and application to FDCA synthesis.

reaction can be combined with electrodialysis[11] or esterification processes[12] that generate an acid or ester product and re-generate the carbonate salt. We have utilized this chemistry to carboxylate aryl C–H bonds of multiple substrates, including furan-2-carboxylate and benzene. The carboxylation of furan-2-carboxylate generates furan-2,5-dicarboxylate, a monomer used to make polyester plastic.

Ab initio *molecular dynamics in the* nanoreactor

The *ab initio* nanoreactor is a recently developed technique to explore and predict complex reaction mechanisms.[13] Unlike traditional computational approaches, nanoreactor simulations can begin without knowledge of reaction products. The idea is to confine a number of molecules of interest (generally comprising a total of 100-300 atoms) in a sphere that is a few nanometers across. The interaction between atoms is described using electronic structure theory (such as density functional theory or DFT) that can model bond formation, rupture and rearrangement from first principles. Using DFT to describe the interaction between atoms, we then carry out molecular dynamics (i.e., we solve Newton's equations with forces derived from the DFT calculations—this is often known as *ab initio* molecular dynamics). The system is heated and the dynamics is followed in time. The temperature is typically chosen to be in the 1000–1500 K range in order to accelerate reactive events. This allows us to discover a number of reactions with simulation times on the order of hundreds of picoseconds. Other means of accelerating reactive events are also possible – for example, the use of a "virtual piston" that momentarily compresses the spherical container. The nanoreactor simulation is accompanied by an automated procedure that determines the molecular species present at any given point in time. This procedure identifies when reactions have occurred and accumulates a list of observed reactions. Due to the high temperature (and possibly pressure), the reaction path that is observed is unlikely to be representative of the most probable pathway under other conditions. Thus, we use the observed path as a starting point for computing a minimal energy path. This gives the transition state for the reaction (or transition states if the identified reaction has intermediates) and thus the information needed to compute the associated reaction rate (or rates). Importantly, we use a higher level of theory for this "refinement" step in order to obtain accurate rate information.

The most important aspect of the nanoreactor is that it *discovers* reaction mechanisms. Thus, it can be applied in cases where the reaction mechanism(s) is(are) unknown. Furthermore, the nanoreactor never assumes that a single mechanism is operative, and will discover multiple mechanisms if these are available. It is ideally suited to aid the development of CO_3^{2-}-catalyzed CO_2 hydrogenation because it is difficult to probe mechanisms in molten salt media by conventional methods and the desired catalytic cycles have many elementary steps with multiple branching points.

Results

In the first eight months of this project, our experimental studies have focused on CO_3^{2-}-promoted CO_2 hydrogenation to oxalate. As described below, we have discovered reaction conditions that produce oxalate in high yield from CO_3^{2-}, CO_2, and H_2. These results provide support for several key mechanistic hypotheses that underlie our strategy and inform our ongoing effort to find conditions that produce our other target C_2 compounds. In conjunction with the experiments, we have been testing and refining the

nanoreactor simulator by using it to investigate C–H carboxylation reactions. With a completely unbiased simulation, the nanoreactor recapitulated C–H carboxylation reactions that we have observed experimentally. With this validation, we are using the nanoreactor to find pathways to products beyond oxalate.

Progress

We have developed reaction conditions for selective CO_3^{2-}-promoted CO_2 hydrogenation to oxalate, the first target of our research program. This milestone validates our chemical strategy and provides a starting point for the remaining targets. We have also validated our computational approach by demonstrating that *ab initio* molecular dynamics simulations with the *nanoreactor* reveal C–H carboxylation pathways that are consistent with experimental results.

Future Plans

Future work will focus on accessing products beyond oxalate. We will further investigate the role of H_2O in controlling reactivity/selectivity, and examine the effects of using different carbonate salts and salt mixtures, adding other carboxylates to serve as molten solvents, and using inert supports to disperse the molten salts.

Publications and Patents

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