the ENERGY lab

PROJECT FACTS

Carbon Storage – CO_2 Use and Re-use

Chemical Fixation of CO_2 to Acrylates Using Low-Valent Molybdenum Sources

Background

The Department of Energy's (DOE) Carbon Storage Program encompasses five Technology Areas: (1) Geologic Storage and Simulation and Risk Assessment (GSRA), (2) Monitoring, Verification, Accounting and Assessment (MVAA), (3) Carbon Dioxide (CO_2) Use and Re-Use, (4) Regional Carbon Sequestration Partnerships (RCSP), and (5) Focus Areas for Sequestration Science. The first three Technology Areas comprise the Core Research and Development (R&D), which includes studies ranging from applied laboratory to pilot-scale research focused on developing new technologies and systems for greenhouse gas (GHG) mitigation through carbon storage. This project is part of the Core R&D CO_2 Use and Re-use Technology Area and focuses on developing pathways and novel approaches for reducing CO_2 emissions in areas where geologic storage may not be an optimal solution. Carbon dioxide use and re-use applications could generate significant benefits through the capture or conversion of CO_2 to useful products such as fuels, chemicals, or plastics. Revenue generated from these applications could offset a portion of the CO_2 capture cost. The program's R&D strategy includes adapting and applying existing technologies that can be utilized in the next five years, while concurrently developing innovative and advanced technologies that will be deployed in the decade beyond.

The area of CO_2 use and re-use for carbon storage is relatively new and less well-known compared to other storage approaches, such as geologic storage. Many challenges exist for achieving successful CO_2 use and re-use, including the development of technologies capable of economically fixing CO_2 in stable products for indirect storage. More exploratory technological investigations are needed to discover new applications and reactions. Each CO_2 use and re-use technology approach has a specific application, advantages over others, and challenges that are the focus of existing and future research. Technologies being developed will work towards meeting carbon storage programmatic goals and these technologies may provide coal-based electric power generating facilities and other industrial CO_2 emitters additional tools to manage CO_2 emissions. This project's research is using CO_2 in a process that produces acrylic acid or other acrylate compounds.

Project Description

Researchers at Brown University are assessing the viability of CO_2 reduction with ethylene using low-valent molybdenum as a catalyst to produce acrylic acid or valuable acrylate compounds. The potential environmental and economic advantages of producing acrylates from CO_2 and ethylene have spurred substantial research into catalysts to promote this transformation. Over the past twenty-plus years, a select number of

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PARTNERS

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PROJECT DURATION

Start Date	End Date
10/1/2010	9/30/2013

COST

Total Project Value
$776,688

DOE/Non-DOE Share
$617,155/ $159,533

Award Number

DE-FE0004498

transition metal complexes have shown the ability to couple CO_2 and ethylene, with molybdenum complexes, demonstrating particular promise by forming acrylate hydride complexes. Such acrylate complexes are enticing, as they appear to offer the prospect of closure of the (hypothesized) catalytic cycle for acrylic acid synthesis.

A catalytic cycle is a series of chemical reactions involving a catalyst that, at the end of the cycle, is returned to its initial state rather than being consumed in the reaction process; with cycle closure, the catalyst may be re-used repeatedly. In the case of these acrylate hydride complexes, researchers believe that such a cycle is achievable for CO_2/ethylene coupling, lacking only reductive formation of an oxygen-hydrogen (O-H) bond for closure. The outcome of the catalyzed process, besides catalyst restoration, should be the desired end product. A major challenge in this research area is that the elimination of free acrylic acid has yet to be observed for any complex capable of uniting CO_2 and ethylene.

Given the time span of research in this field, the absence of acrylic acid extrusion raises legitimate questions about the validity of this approach, despite computational evidence suggesting that the process has a slight thermodynamic favorability. This project outlines a systematic evaluation of factors and mechanisms which may impact the kinetics of reductive O-H elimination from acrylate hydride complexes en route to providing a definitive assessment of the potential for acrylic acid production.

Goals/Objectives

The goal of the work is to provide core research and development necessary for establishing whether low-valent molybdenum catalysts will enable viability of CO_2 as a reactant in the production of acrylate compounds. This project is an interdisciplinary laboratory study with three phases:

- ***Scope of CO_2 and ethylene coupling:*** This phase of research expands the range of molybdenum complexes capable of coupling CO_2 and ethylene by defining the available ligand (a molecule bonded to a central metal atom) architectures which facilitate acrylate formation. The approach for this effort includes synthesizing two sets of molybdenum complexes shown by computational analysis to provide promising reaction thermodynamics and compare the relative reactions in CO_2 and ethylene coupling of each using multiple spectroscopic methods.

- ***Reductive elimination of acrylate products:*** This phase is evaluating computational and experimental investigations to determine the catalytic parameters necessary to enhance reductive acrylate elimination. This approach utilizes molybdenum complexes developed in Phase I via comparative rate experiments and mechanistic probes to access the relative importance of multiple variables which determine the favorability of reductive acrylate elimination.

- ***Design and prepare an optimized molybdenum catalyst for a bench-scale reaction to test the feasibility of molybdenum catalyzed acrylate formation from CO_2:*** This approach correlates the structure and reactivity relationships in ligand supports for molybdenum, found to be most influential in the first two phases of the project (Figure 1). In addition, the research determines the ligand architecture that most appropriately fits those correlations, and then synthesizes complex(es) which provide the optimal opportunity for efficient catalytic acrylate formation.

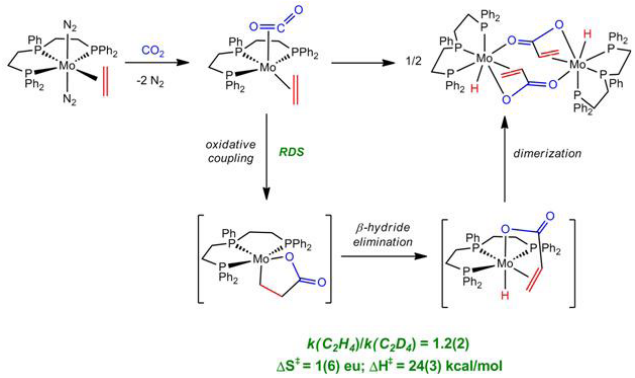

Figure 1: Process by which CO_2 is reduced with ethylene using low-valent molybdenum to produce acrylic acid or valuable acrylate compounds

Accomplishments

The following accomplishments have contributed to the goals of identifying a method to use CO_2 to generate and separate acrylate:

- Identified a molybdenum complex for CO_2 and ethylene coupling to acrylates.

- Identified that the molybdenum complex with a tridentate structural feature is best at enabling generation of acrylate using CO_2 as a reactant.

- Identified an indirect elimination method that separates the acrylate from the catalytic molybdenum structure.

Benefits

This research identifies critical factors in CO_2/ethylene coupling and catalyst design, specifically evaluating ligand attributes and reaction conditions which are critical to enabling acrylate elimination from the metal center. This project contributes to the understanding needed to optimize supporting platforms for molybdenum catalysts and should enable assessment of the viability of this production method. This technology contributes to the Carbon Storage Program's effort of developing cost-effective methods for CO_2 use and re-use, as a viable alternative to geologic storage. If the process is established, it will enable the utilization of significant quantities of CO_2 in acrylate production, economically reducing atmospheric levels of this important greenhouse gas.