the ENERGY lab

PROJECT FACTS

Carbon Sequestration

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

Background

In an effort to reduce carbon dioxide (CO_2) emissions from various industrial and power generation processes to the atmosphere, the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) is currently funding research intended to advance current state-of-the-art technologies that address the use of CO_2 in a variety of different economic and industrial processes.

Carbon dioxide utilization efforts focus on pathways and novel approaches for reducing CO_2 emissions by developing beneficial uses for CO_2 that will mitigate emissions in areas where geologic storage may not be the optimal solution. Utilization is an important component in carbon sequestration and some of the applicable approaches are conversion of CO_2 into useful chemicals and polycarbonate plastics; storage of CO_2 in solid materials having economic value; indirect storage of CO_2, and other breakthrough concepts.

Critical challenges identified in the utilization focus area include the cost- effective use of CO_2 as a feedstock for chemical synthesis or its integration into pre-existing products. The efficiency (CO_2 integration reaction rate and the amount of CO_2 sequestered in a product) and energy use (the amount of energy required to utilize CO_2 in existing products) of these utilization processes also represent a critical challenge. This project will provide core research and development necessary for producing low-valent molybdenum catalysts to establish CO_2 as a reactant in the production of acrylate (an organic chemical) 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 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.

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PARTNERS

Draper Laboratory

PROJECT DURATION

Start Date
10/1/2010

End Date
9/30/2012

COST

Total Project Value
$524,615

DOE/Non-DOE Share
$417,155 / $107,460

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 reused repeatedly. Researchers believe that such a cycle is achievable for CO_2/ethylene coupling, in the case of these acrylate hydride complexes, 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 product. Disappointingly, 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 those factors and mechanisms which may impact the kinetics of reductive O-H elimination from acrylate hydride complexes en route to providing definitive assessment of the potential for acrylic acid production in this manner.

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 will be an interdisciplinary laboratory study with three phases:

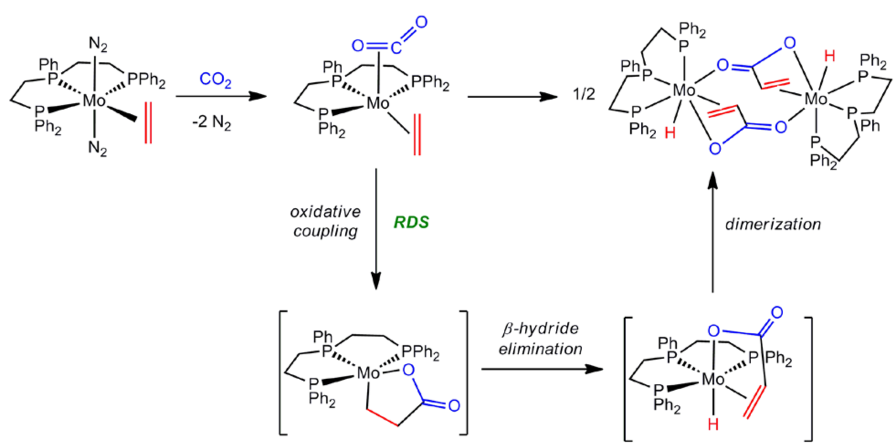
- Scope of CO_2 and ethylene coupling: This research will expand the range of molybdenum complexes capable of coupling CO_2 and ethylene by defining the available ligand (a molecule bonded to a central metal atom) architectures which facilitate acrylate formation. The approach for this effort will synthesize 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 will evaluate computational and experimental investigations to determine the catalytic parameters necessary to enhance reductive acrylate elimination. This approach will utilize 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 will correlate the structure and reactivity relationships in ligand supports for molybdenum found to be most influential in Phases I and II. In addition, the research will determine the ligand architecture that best fits those correlations, and then synthesize complex(es) which provide the optimal opportunity for efficient catalytic acrylate formation.

Benefits

This research will identify the 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 will yield the understanding needed to optimize supporting platforms for molybdenum catalysts and should enable assessment of the viability of this production method. 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.



$k(C_2H_4)/k(C_2D_4) = 1.2(2)$
$\Delta S^{\ddagger} = 1(6)$ eu; $\Delta H^{\ddagger} = 24(3)$ kcal/mol

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