CREATES: CO$_2$ REduction for grAphiTE Synthesis
DE-SC0020776

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021
Project Overview

Period of Performance:
Original: June 29, 2020 – June 25, 2021
No Cost Extension (COVID-19): December 31, 2021

Project Funding:
DOE $239,379
Cost Share $0

Project Participants:
Acadian Research & Development LLC
Project Overview

Project objectives are designed to exploit the strengths of the catalysts, and to evaluate catalyst performance and stability.

The five feasibility objectives of this Phase I SBIR project are:

a) Demonstrate successful synthesis of catalysts
b) Show that catalyst can reduce CO$_2$ to produce carbon
c) Demonstrate catalyst stability of greater than 30h and ability to regenerate
d) Demonstrate successful operation of the multi-stage reactor
e) Demonstrate that the dominant allotrope produced is graphite
Technology Background

Previous catalyst development: methanol synthesis from CO$_2$

- Good CO$_2$ interaction
- Active at mild temperatures / ambient pressure
- Resistance to coking – carbon rejection
- Resistance to sintering
- Partial reduction yields isolated metal nanoparticles

Metal silicate-based system

- Good promoter incorporation
- Improved methanol synthesis activity
- Stability not decreased by promoter

Promoter addition

# Technology Background

## Applied technology

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Advantages</th>
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<tbody>
<tr>
<td>Catalyst metals</td>
<td>Catalytic activity with CO₂</td>
</tr>
<tr>
<td>Thermal treatment to form catalyst nanoparticles</td>
<td>Sintering resistance</td>
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<tr>
<td>Promoter</td>
<td>Increased activity</td>
</tr>
<tr>
<td>3D-printed morphology</td>
<td>High contact surface area and low pressure drop</td>
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## Key challenges

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Challenges</th>
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<tbody>
<tr>
<td>Conversion</td>
<td>Rate must be sufficient for feasibility</td>
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<tr>
<td>Stability</td>
<td>Long catalyst life desired</td>
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<tr>
<td>Regeneration</td>
<td>Ability to repeatedly regenerate</td>
</tr>
<tr>
<td>Carbon growth</td>
<td>Growth on substrate / allotrope is graphite</td>
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</tbody>
</table>
Technology Background

Multi-stage reactor

- CO₂ is decomposed in the first stage
- Carbon is deposited on growth substrate in second stage
Technical Approach/Project Scope

Work plan

• Prepare the catalysts with and without promoter.
• Characterize catalysts via XRD, FTIR, SEM, Raman.
• Complete CO$_2$ testing in TGA.
• Examine regeneration performance.
• Scale-up catalyst synthesis for 3D printing.
• Testing in multi-stage FBR.

Milestones

1. Successfully synthesize catalysts with and without promoter
2. Decompose CO$_2$ and produce carbon in FBR
Technical Approach/Project Scope

Project success criteria:

**Synthesis:** Achieve intended catalyst structure as characterized by XRD and FTIR, and comparable to previous work and literature values.

**Performance:** Activity for at least 30 hours with final activity >70% of the initial (first 5 hours) activity.

**Regeneration:** Activity restored to at least 85% of initial activity.

**3D-printing:** Monolith strong enough for handling, loading into reactor, and testing without significant attrition.

**Carbon allotrope:** Graphite formation on growth substrate as determined by Raman.

**Cycling stability:** Maintain >75% of the initial activity.
Progress and Current Status of Project

FBR testing setup
Progress and Current Status of Project

Synthesis

[Images of synthesized materials with graphs showing data for 'No promoter' and 'With promoter']

Legend:
- Blue: No promoter
- Orange: With promoter
Progress and Current Status of Project

Performance

FBR testing with catalyst powder and sand
Catalyst reduced in situ
Reaction gas: Only CO₂
Temperature: 350–650 °C
Time: 1–55 h

Carbon formation in bed
Formation rate: 0.03 wt%/h
Surface content: 0.52 wt%

Bosch Reaction:
CO₂ + 2 H₂ → C + 2 H₂O
Moderate conversion and CO production
Progress and Current Status of Project

Performance

CH₄ decomposition: to confirm catalyst activity and system performance, methane decomposition was performed.

Good performance led to testing CO₂ decomposition via the Sabatier reaction:

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]

- CH₄ favored at low temperature
- CO appears above 500 °C
Progress and Current Status of Project

Regeneration

Before regeneration testing, catalyst was loaded with carbon via methane decomposition.

Catalyst regeneration in air at 450 °C showed equivalent or better performance after regeneration.
Progress and Current Status of Project

Catalyst geometry

- Extruded pellet support with catalyst coating
- Extruded mixed support/catalyst
- 3D-printed:
  - Printed substrate, coated
  - Printed mixed support/catalyst
Progress and Current Status of Project

3D-printing

Ink development (paste for extrusion)

Components:
• Binder
• Liquid
• Lubricant
• (Catalyst)

Requirements:
• Appropriate viscosity
• Layer adhesion
• Reasonable curing time/temperature

3D-printer paste extruder system
Plans for future testing/development/commercialization

This project:
Complete scheduled tasks
Identify best catalyst candidates

Next:
Scale-up production of catalysts
Scale-up of testing
Summary

• Pure CO$_2$ decomposition is possible at these reaction conditions, but the rate is slow.
• Bosch reaction shows moderate conversion.
• High methane decomposition performance inspired CO$_2$ conversion via Sabatier reaction.
• Graphite formation elusive.
• Successfully developed ink formulations for 3D-printing catalysts.
• Successfully grown catalyst on support surface.
Thank You

Questions?
Appendix

- These slides will not be discussed during the presentation but are mandatory.
Organization Chart

Project Team - Acadian Research & Development

Principal Investigator:  
Dr. Anthony R. Richard

Senior Engineer:  
Dr. Bryce Dutcher

Senior Technician:  
Stacey Foster
Project Management and Planning
1. Prepare the Ni- and Cu-phyllosilicate catalysts
2. Perform XRD and FTIR on the prepared catalysts
3. Complete CO₂ decomposition testing in TGA
4. Perform regeneration temperature testing
5. Scale-up synthesis and 3D-print monoliths
6. Multi-stage FBR testing and carbon characterization
7. Data analysis, economic evaluation, final report, Phase II proposal

Milestone 1. Successful synthesis of catalysts with and without promoter
Milestone 2. Decompose CO₂ and produce carbon in FBR