CREATES: CO_2 REduction for grAphiTE Synthesis

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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

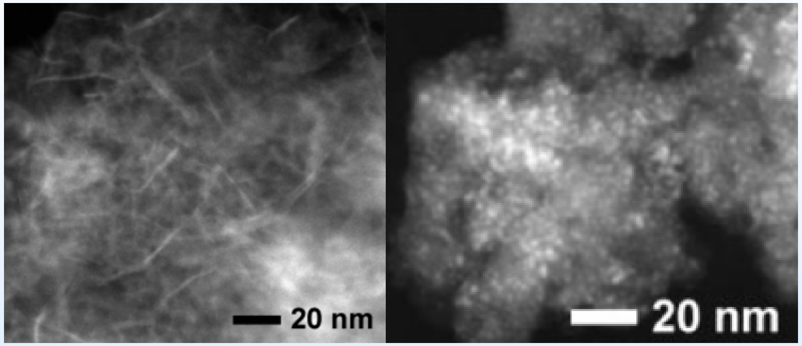
Project objectives are designed to exploit the strengths of the catalysts, and to evaluate catalyst performance and stability.

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



Calcined catalyst   Reduced catalyst

Metal silicate-based system

- Good CO_2 interaction
- Active at mild temperatures / ambient pressure
- Resistance to coking – carbon rejection
- Resistance to sintering
- Partial reduction yields isolated metal nanoparticles

Promoter addition

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

Richard, A. R.; Fan, M. ACS Catalysis 2017, 7 (9), 5679-5692.
Richard, A. R.; Fan, M. Fuel 2018, 222, 513-522.

Technology Background

Applied technology

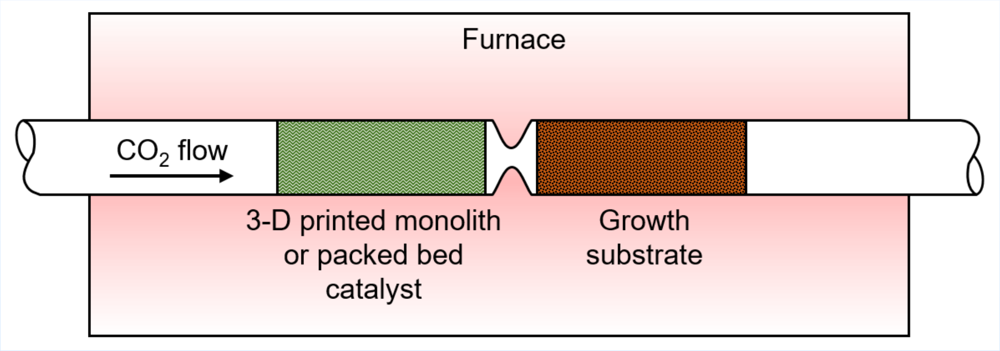
Aspect	Advantages
Catalyst metals	Catalytic activity with CO_2
Thermal treatment to form catalyst nanoparticles	Sintering resistance
Promoter	Increased activity
3D-printed morphology	High contact surface area and low pressure drop

Key challenges

Aspect	Challenges
Conversion	Rate must be sufficient for feasibility
Stability	Long catalyst life desired
Regeneration	Ability to repeatedly regenerate
Carbon growth	Growth on substrate / allotrope is graphite

Technology Background

Multi-stage reactor



- CO_2 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.

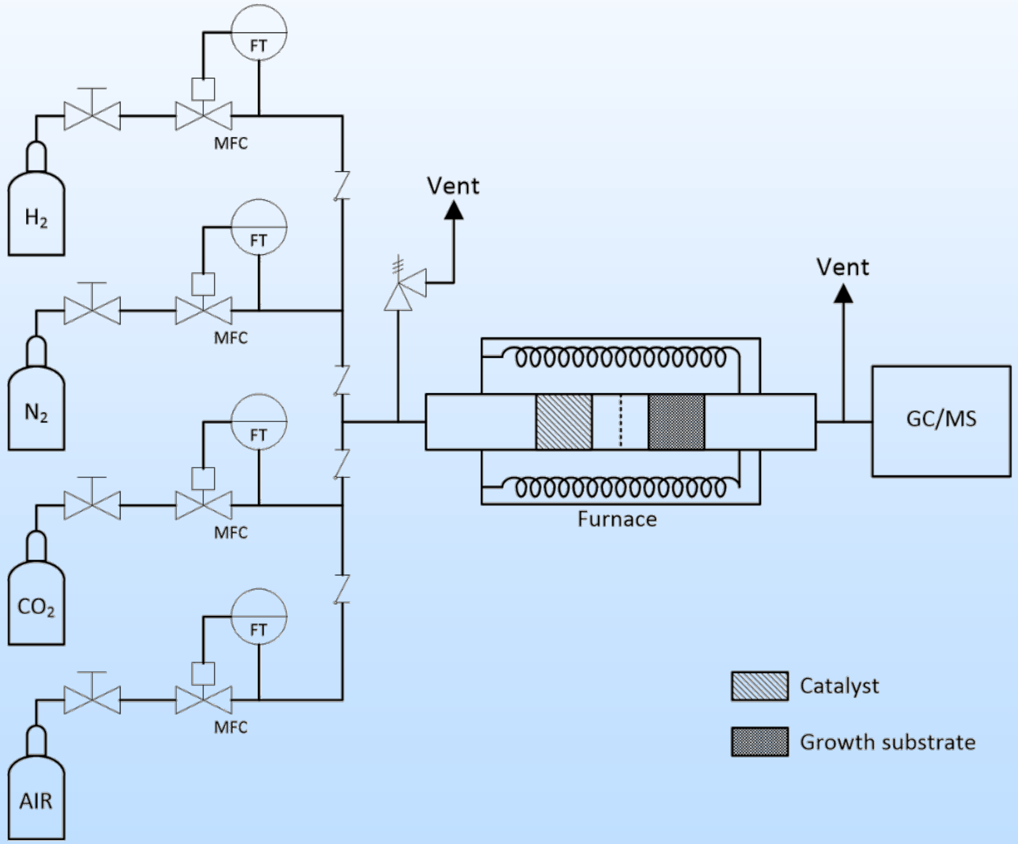
3D-printing: Monolith strong enough for handling, loading into reactor, and testing without significant attrition.

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

Cycling stability: Maintain >75% of the initial activity.

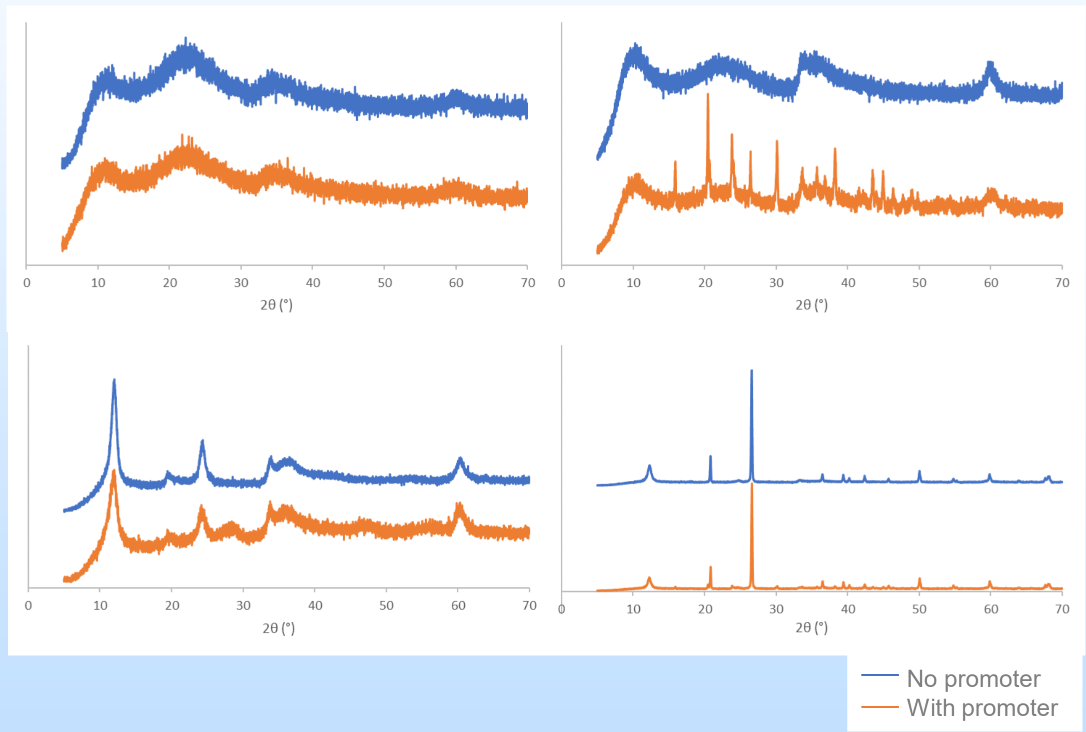
Progress and Current Status of Project

FBR testing setup



Progress and Current Status of Project

Synthesis



Progress and Current Status of Project

Performance

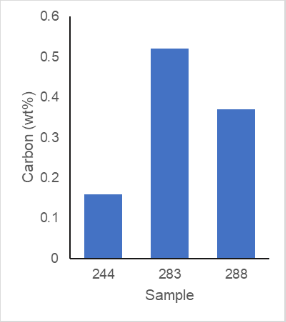
FBR testing with catalyst powder and sand

Catalyst reduced in situ

Reaction gas: Only CO_2

Temperature: 350–650 °C

Time: 1–55 h



Carbon formation in bed

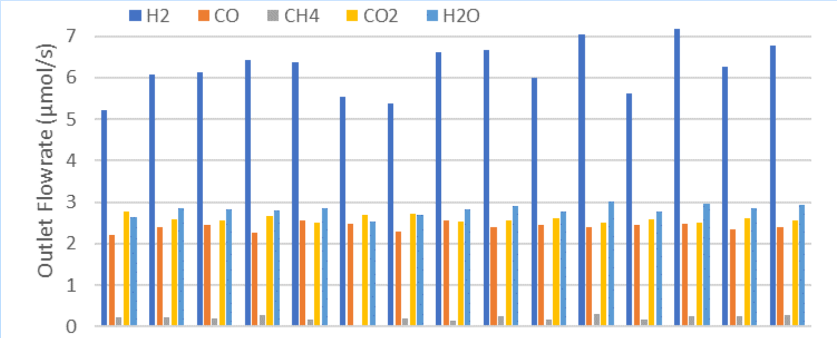
Formation rate: 0.03 wt%/h

Surface content: 0.52 wt%

Bosch Reaction:

$$CO_2 + 2\ H_2 \rightarrow C + 2\ H_2O$$

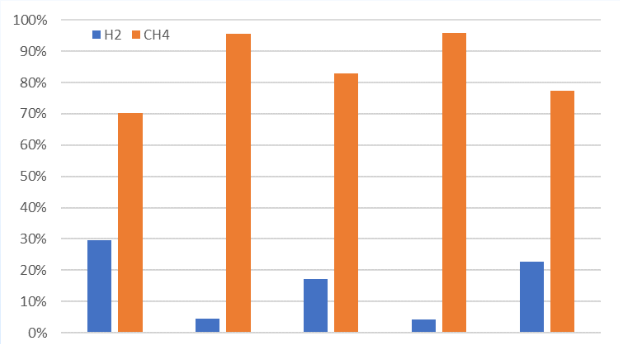
Moderate conversion and CO production



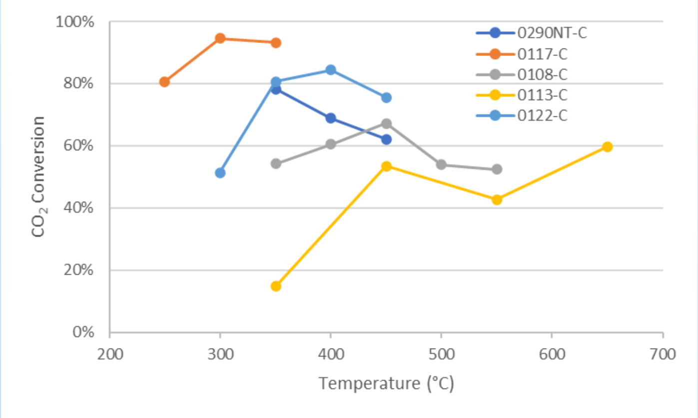
Progress and Current Status of Project

Performance

CH_4 decomposition: to confirm catalyst activity and system performance, methane decomposition was performed



Good performance led to testing CO_2 decomposition via the Sabatier reaction



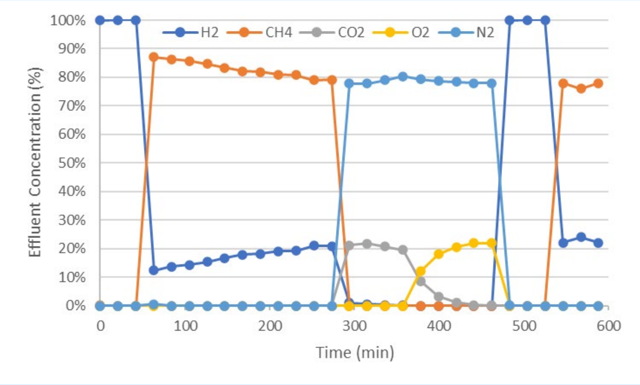
$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

- CH_4 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

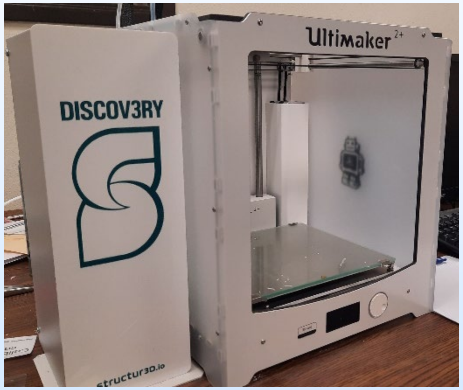
Extruded mixed support/catalyst

3D-printed:

- Printed substrate, coated
- Printed mixed support/catalyst

Progress and Current Status of Project

3D-printing



3D-printer paste extruder system

Ink development (paste for extrusion)

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

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

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

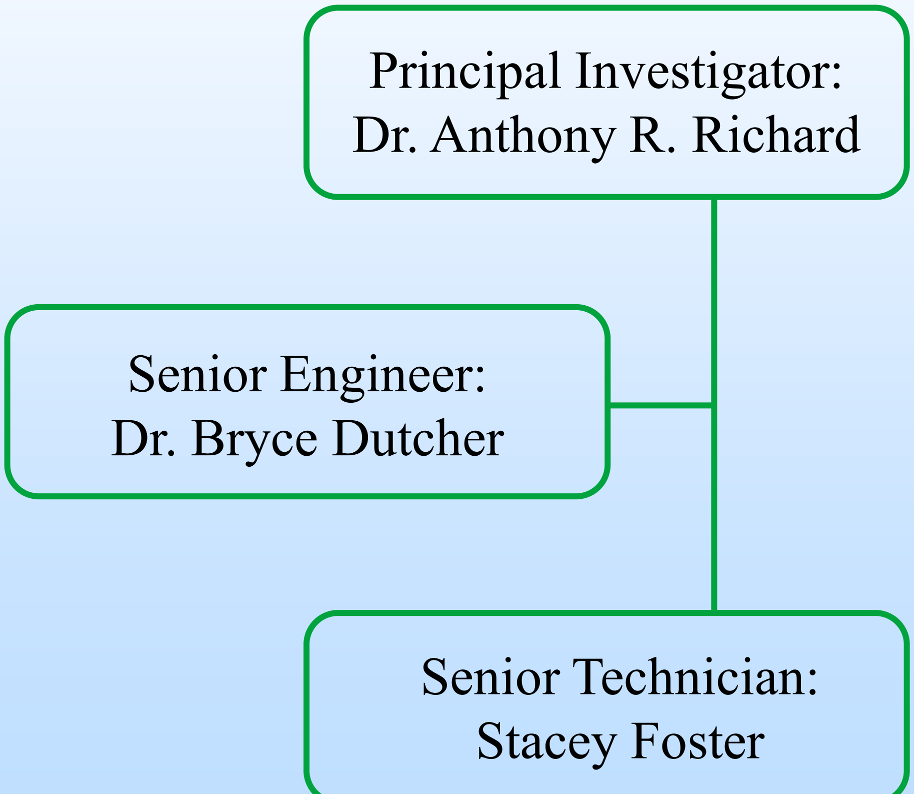
Questions?

Appendix

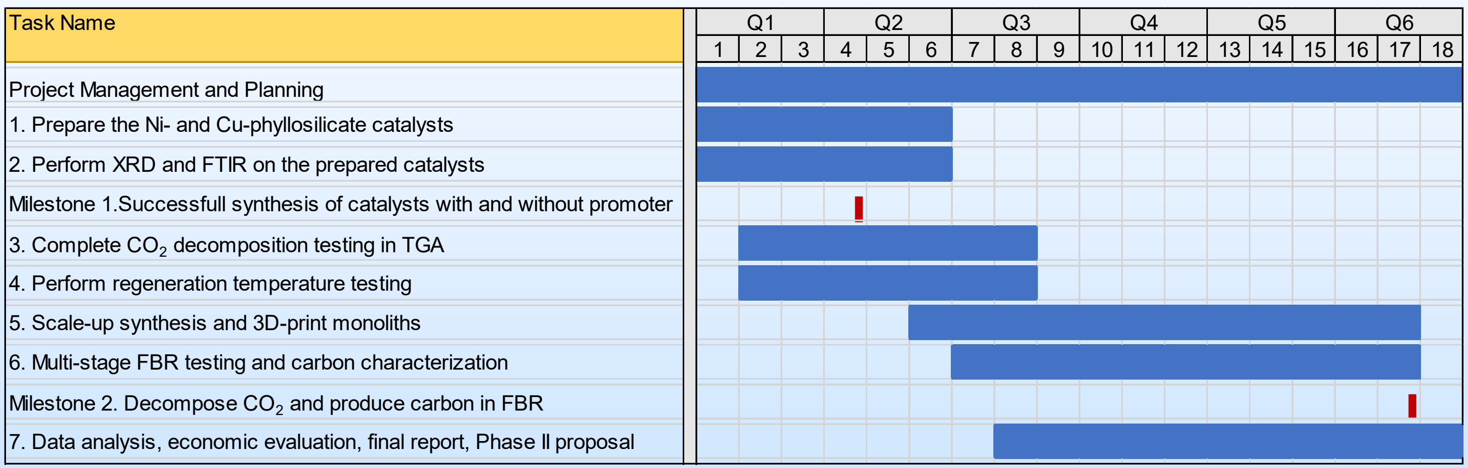
- These slides will not be discussed during the presentation but are mandatory.

Organization Chart

Project Team - Acadian Research & Development



Gantt Chart



Task Name
Q1
Q2
Q3
Q4
Q5
Q6
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Project Management and Planning
1. Prepare the Ni- and Cu-phyllosilicate catalysts
2. Perform XRD and FTIR on the prepared catalysts
Milestone 1.Successfull synthesis of catalysts with and without promoter
3. Complete CO_2 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
Milestone 2. Decompose CO_2 and produce carbon in FBR
7. Data analysis, economic evaluation, final report, Phase II proposal