Conversion of CO_2 into Commercial Materials using Carbon Feedstocks

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Developing the Technologies and
Infrastructure for CCS

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Presentation Outline

- Project benefits and objectives
- Carbon reactivity studies
- Catalyst mechanism studies
- Catalyst development
- Test results
- Summary

Benefit to the Program

- Program goal: Reduce CO_2 emissions by developing beneficial uses that meet the DOE net cost metric of \$10/MT for captured CO_2 that will mitigate CO_2 emissions in areas where geological storage may not be an optimal solution
- Benefits statement: Development of a commercial process for converting CO_2 and a carbon source into a commodity chemical at a cost of < \$10 / MT of CO_2.

Accomplishments to Date

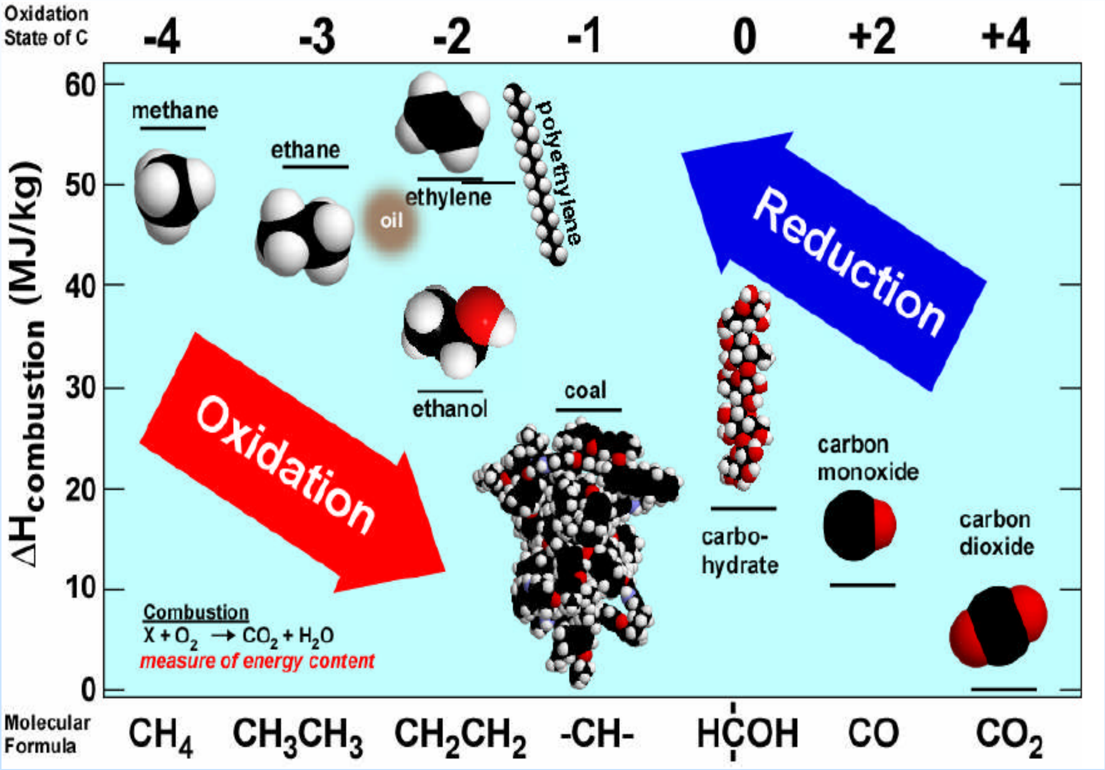
- CO_2 utilization with carbon feedstocks
  - Evaluated carbon reactivity for various carbon sources
  - Demonstrated significant increase in reactivity with catalysts
  - Develop transport reactor process maximizing carbon utilization and reactivity
  - Completed preliminary techno-economic analysis for production of CO, syngas, methanol, and methyl methacrylate
- Mechanistic studies of catalyst activity
  - Demonstrated oxygen extraction from CO_2
  - Demonstrated hydrocarbon oxidation with extracted oxygen
- Application of catalytic CO_2 oxidation of hydrocarbons for bulk chemical production
  - Modified catalyst formulation for lower temperature activity
  - Demonstrated production of
    - Syngas at 600°C
    - Alkanes and alkenes at 780°C

Project Overview:
Goals and Objectives

Overall goal: Develop a process that utilizes carbon as a reductant for CO_2 to produce CO at a net cost of less than \$10/MT

- Objectives:
  - Evaluate and identify the most reactive carbon sources for CO_2 gasification
  - Evaluate the potential to increase CO_2 gasification reactivity with catalysts
  - Demonstrate the economic feasibility of CO_2 gasification for the production of CO
  - Evaluate sensitivity of process economics to assist experimental program
  - Evaluate economic feasibility of producing commodity chemicals
  - Develop catalysts for direct production of methanol (or other commodity chemicals) from CO_2 and hydrocarbons

Challenges of CO_2 Utilization



CO_2 Properties

- Most fully oxidized form of carbon
- Extremely chemically stable

Challenges

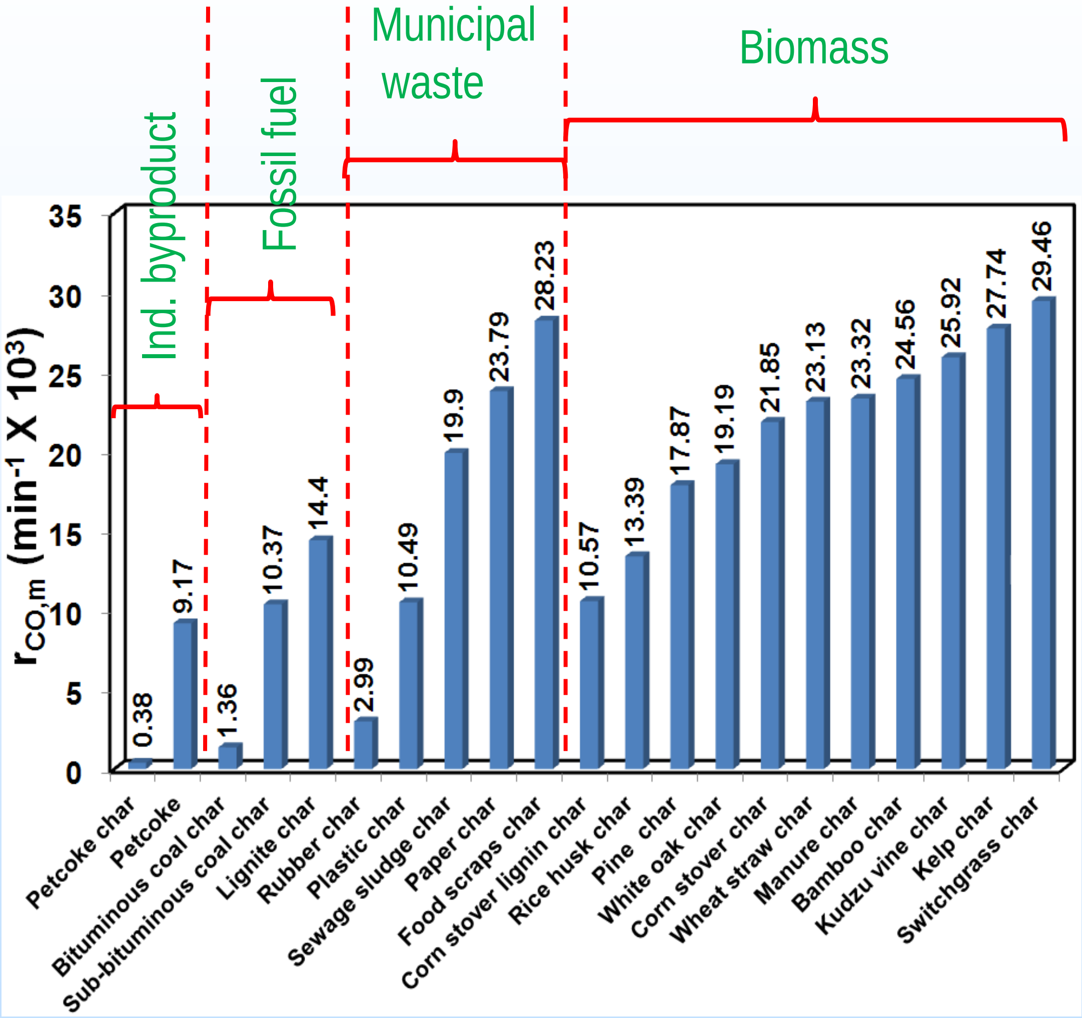
- CO_2 conversion requires abundant low cost reducing agents, energy (heat or electricity), and catalysts

Constraints

- Production of reducing agents, energy, and catalyst requires minimal CO_2 footprint

Banholzer, 2008

Carbon Reactivity Ranking



- Reactivity for different carbon sources ranges from about 0.0004 to 0.03 min^{-1} for CO production
- Petcoke char was the least reactivity
- Coal sources have intermediate reactivity
- Biomass and municipal waste has the largest range of carbon reactivity

$$r_{CO,m}\ (min^{-1} \times 10^3) = \frac{28 \times F_{CO,m}}{22.414 \times W_0}$$

$F_{co,m}$ = CO flow rate (SLPM)

W_0 = Initial sample mass (g)

Reaction conditions:

WHSV=2.36 hr^{-1}; T=800 ^oC; P=1 atm

Catalyst Screening Tests

Catalyst	Reactivity $r_{CO, m}$ ($min^{-1} \times 10^3$)
Cat-1	19.15
$K\text{-}Ca/Al_2O_3$	12.34
Cat-2	11.29
Cat-3	9.43
Cat-4	8.24
Cat-5	7.95
Cat-6	5.13
Cat-7	4.55
Cat-8	2.19
Cat-9	1.86
None	0.38

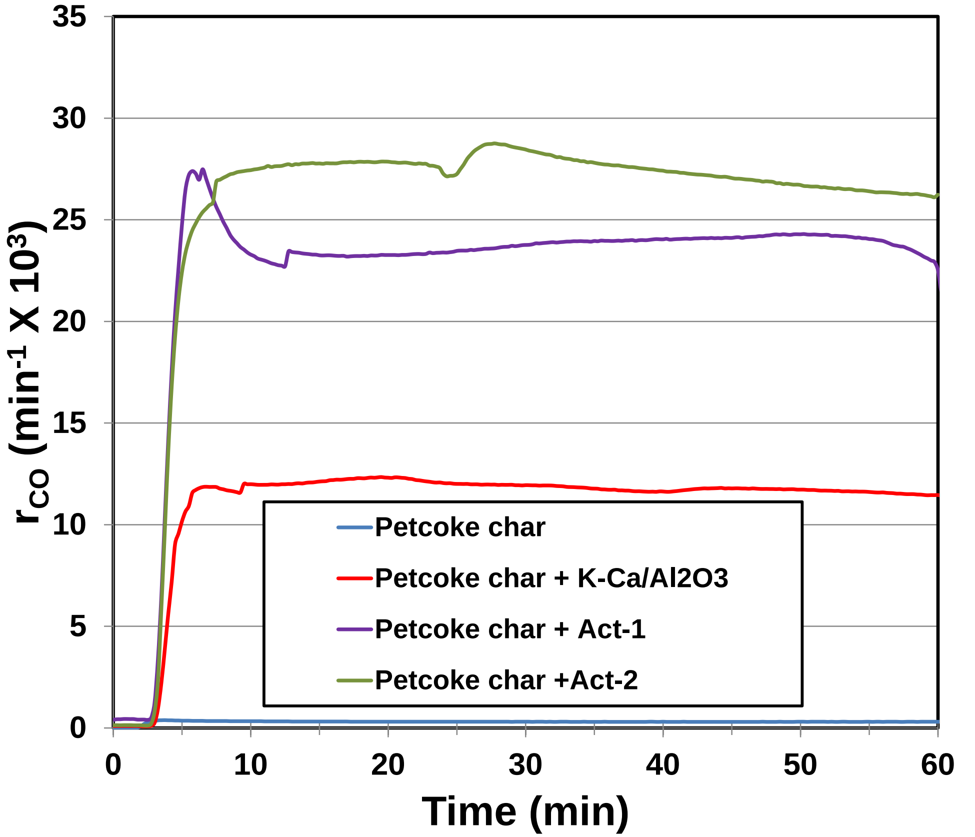
Reaction conditions:

Carbon source: Petcoke char; WHSV=2.36 hr^{-1}; T=800^{o}C; P- 1atm

- Petcoke char used because of its low reactivity
- $K\text{-}Ca/Al_2O_3$* (best performing catalyst in the literature)
- Demonstrated that catalytic effect improves performance of more reactive carbon sources

*J. Wang, et al., *Fuel*, 89 (2010) 310-317

Evaluation of Reaction Mechanism

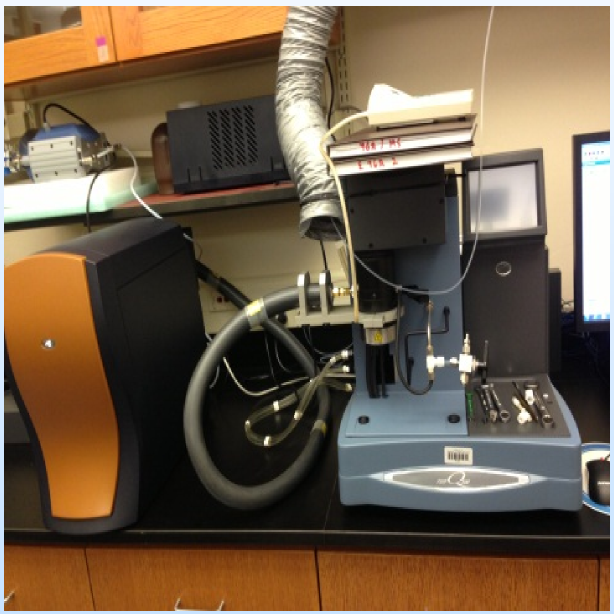


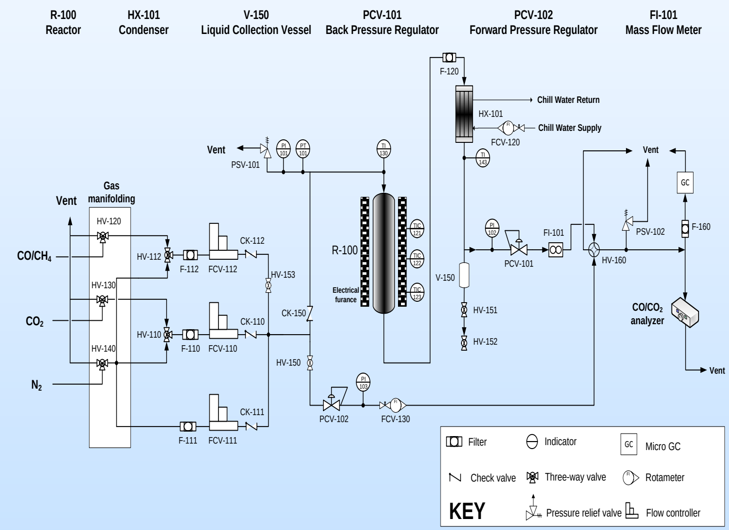
Reaction conditions:

Carbon source: Petcoke char; WHSV=2.36 hr^{-1}; T=800^{o}C; W_{cat}:W_{char}=1:1

- Completed parametric testing to investigate reaction mechanism
    - Catalyst formulations
    - Carbon sources
    - Reaction temperature
- Isotopically labeled CO_2 studies

Reactor Systems

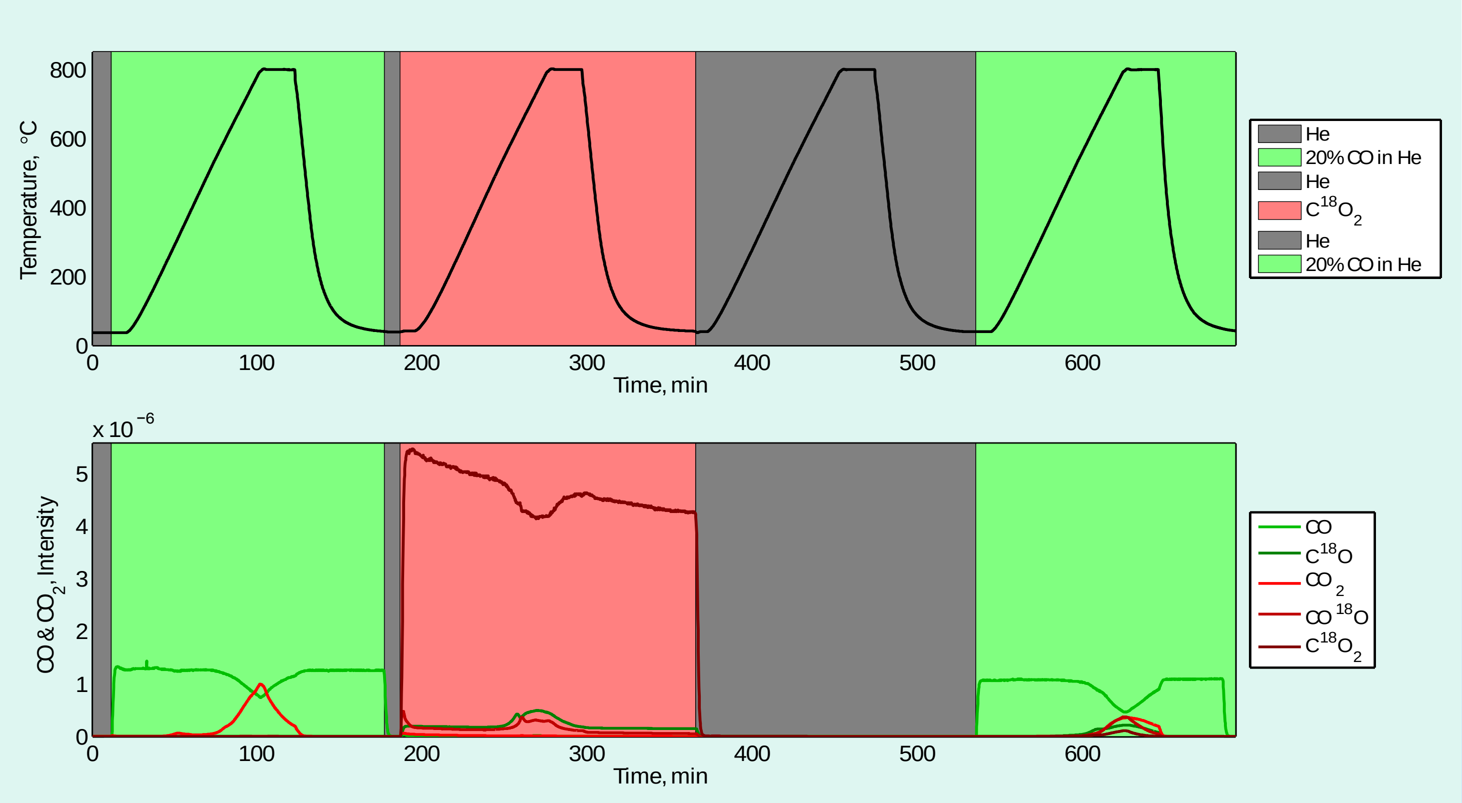




TGA-MS instrument used for analysis

Bench-scale Reactor

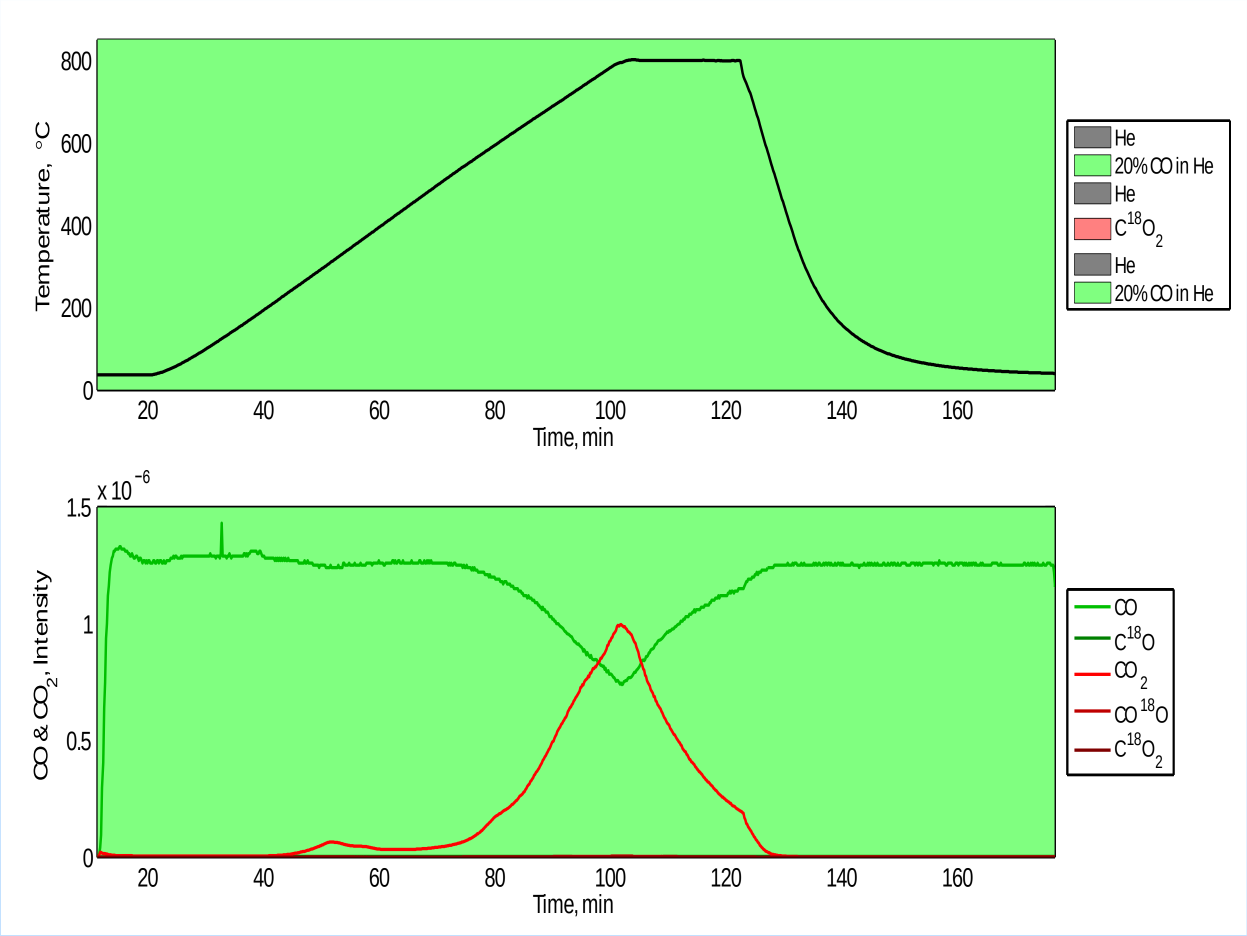
Isotopically-Labeled CO_2 Study



Testing Procedures

- For each test gas
  - Temperature ramp 30°C to 800°C
  - Isothermal soak at 800°C for 5 minutes
  - Cool to room temperature
- Test gases
  - CO (MW=28) [Green fill]
  - Isotopically labeled CO_2 (MW=48) [Red fill]
  - He (MW=4) [Grey fill]

Initial Reduction with CO

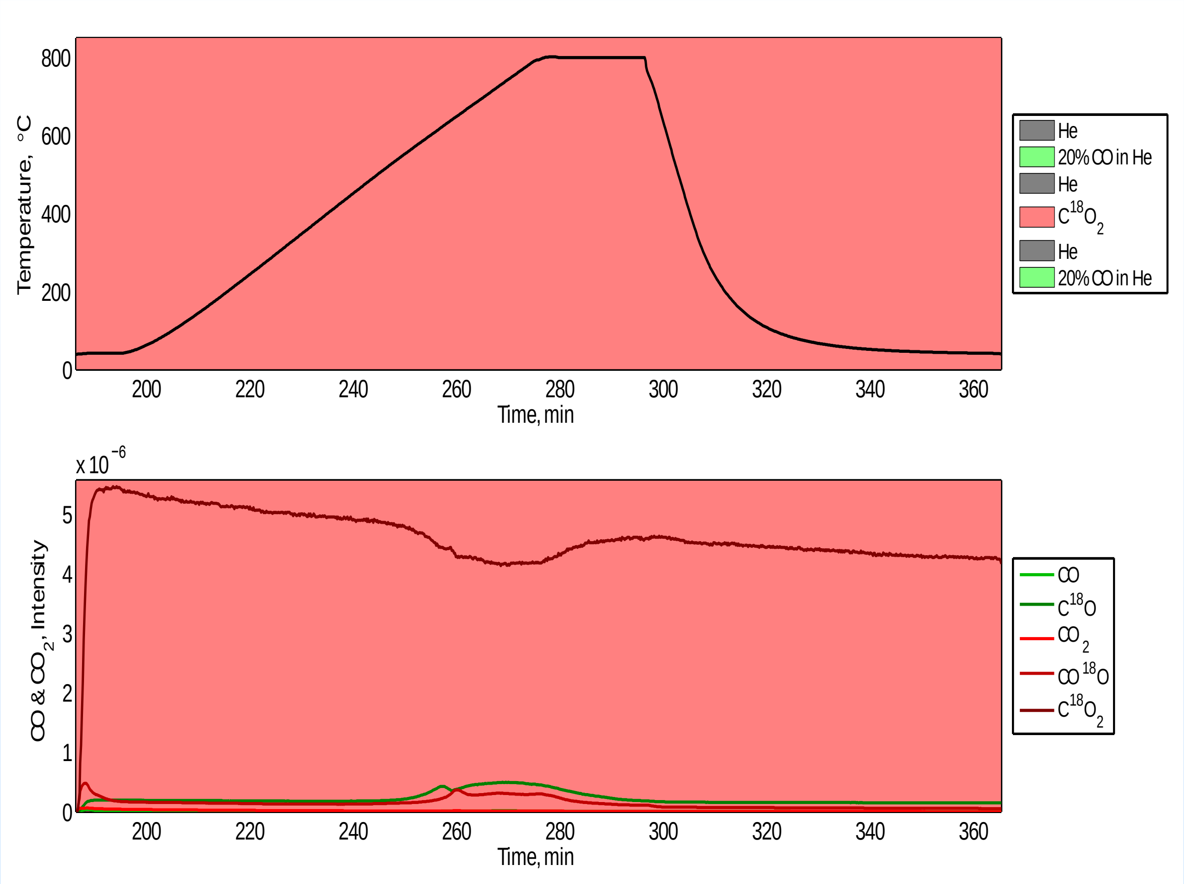


Expectation
- Catalyst reduction
  - Consumption of CO
  - Production of CO_2

Observations
- Consumption of CO
- Production of CO_2

Interpretation
- Catalyst is reduced

Oxidation in Isotopically-Labelled CO_2



Expectation

- Oxygen extraction by reduced catalyst
  - Decrease in $C^{18}O_2$
  - Increase in $C^{18}O$

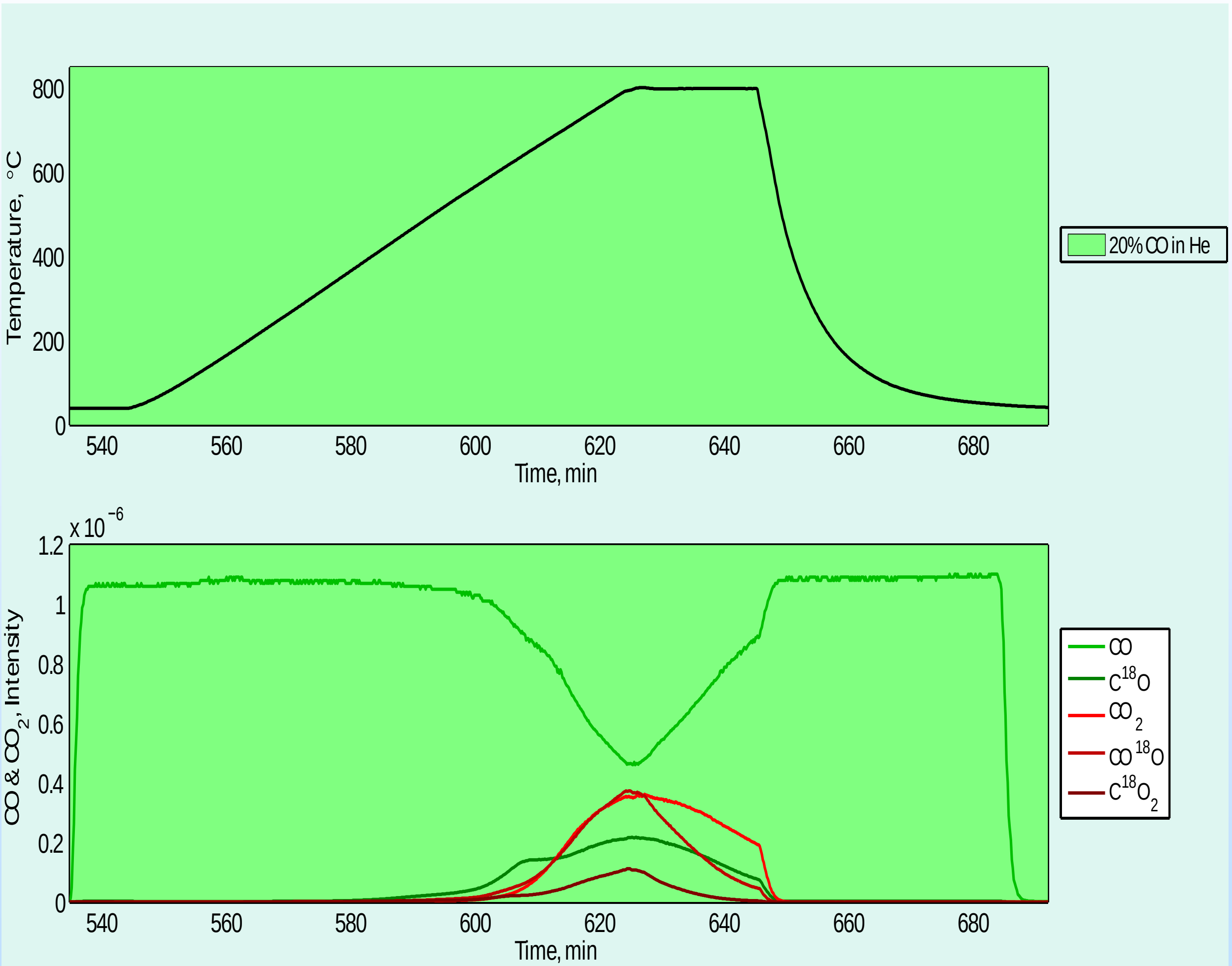
Observations

- Decrease in $C^{18}O_2$ (Expected)
- Increase on $C^{18}O$ (Expected)
- Increase in $CO^{18}O$ (Unexpected)

Interpretations

- Reduced catalyst does extract oxygen from CO_2
- High oxygen mobility on catalyst

Second Reduction in CO



Expectation

- Catalyst reduction
  - Decrease in CO
  - Increase in CO_2 (CO_2 and $CO^{18}O$)

Observations

- Decrease in CO (Expected)
- Increase in $CO^{18}O$ and CO_2 (Expected)
- Increase in $C^{18}O_2$ (Unexpected)
- Increase in CO^{18} (Unexpected)

Interpretations

- Extracted oxygen from CO_2 is available for oxidation reaction
- Any available oxygen on catalyst will participate in oxidation
- Activation energy barrier exists

Results from Isotopically-Labeled CO_2 Study

- Reduced catalyst does extract oxygen from CO_2
- All oxygen on catalyst surface are available for oxidation (including extracted oxygen)
- High mobility of oxygen on catalyst surface
- Activation energy barrier exists

Catalytic CO_2 oxidation of hydrocarbons is possible

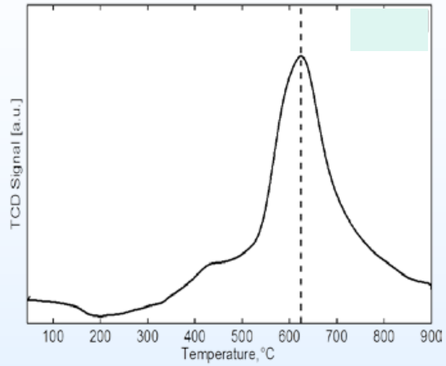
Challenges for practical/commercial application

- Lowering reaction temperature
  - Extraction for CO_2 extraction
  - Oxidation of hydrocarbon
- Maximizing activity
- Maximizing selectivity

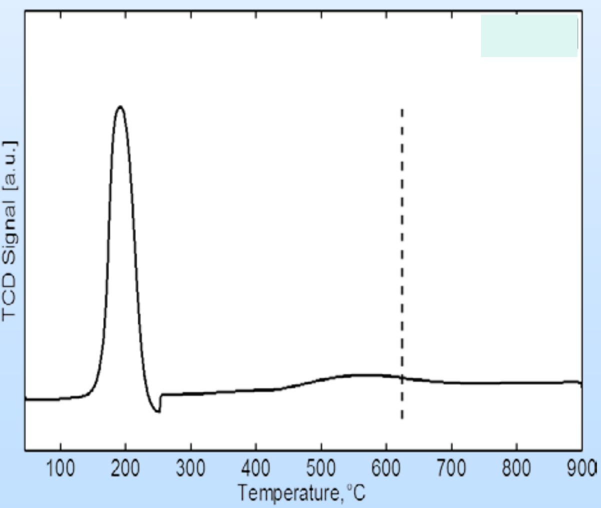
Potential Families of New Catalyst Formulations

Catalyst Family	Objective	Rationale
A	• Lower reaction temperature for hydrocarbon oxidation • Lower temperature for oxygen extraction from CO_2	Reported for oxidative methane coupling on other supports using air
B	• Lower reaction temperature for hydrocarbon oxidation	Reported for low temperature oxidations of VOCs, water, and nitrogen oxides
C	• Lower reaction temperature for hydrocarbon oxidation	$CuOZnOAl_2O_3$ used for industrial synthesis of methanol from syngas as well as carbon dioxide
D	• Lower reaction temperature for hydrocarbon oxidation • Lower temperature for oxygen extraction from CO_2	Reported for dry methane reforming on other supports and as co-catalysts with other metals than iron

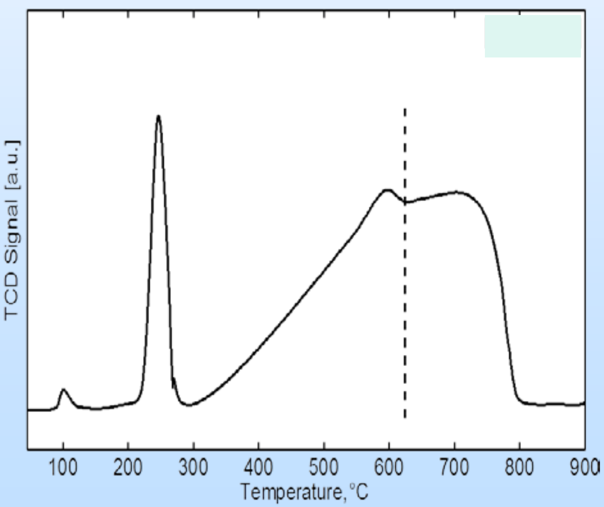
Lower Reduction Temperature



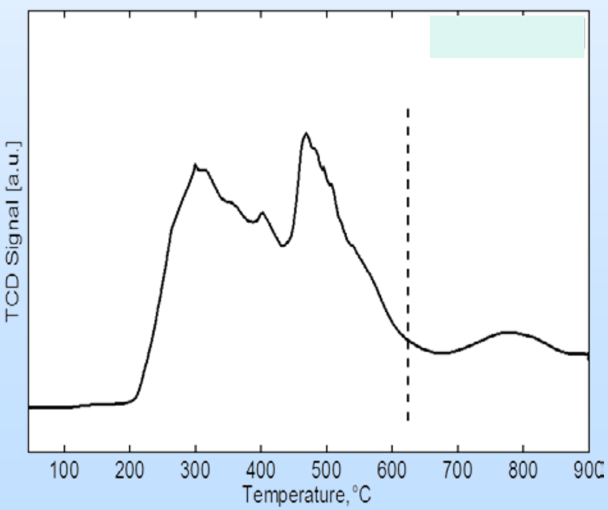
Original Catalyst



Catalyst C



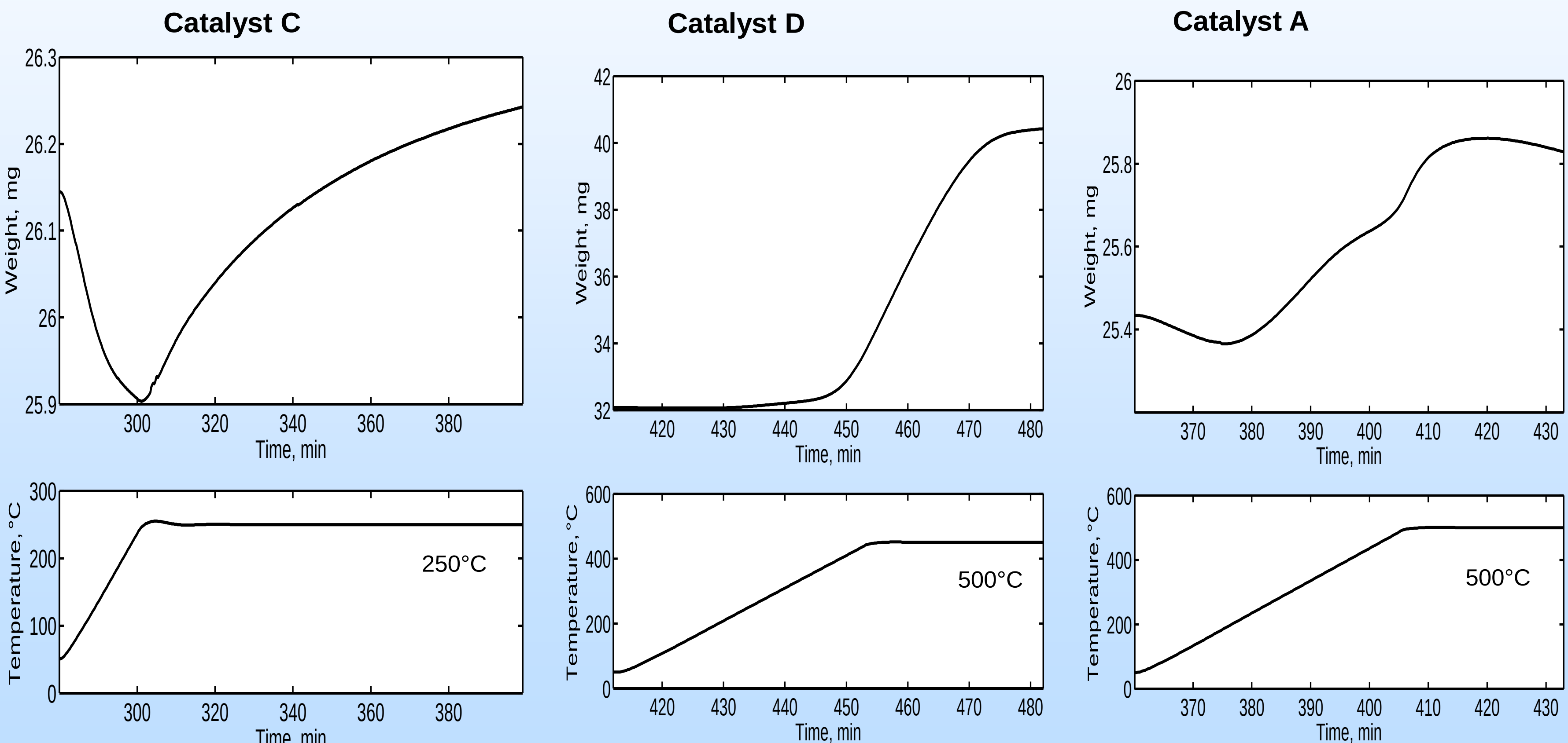
Catalyst D



Catalyst A

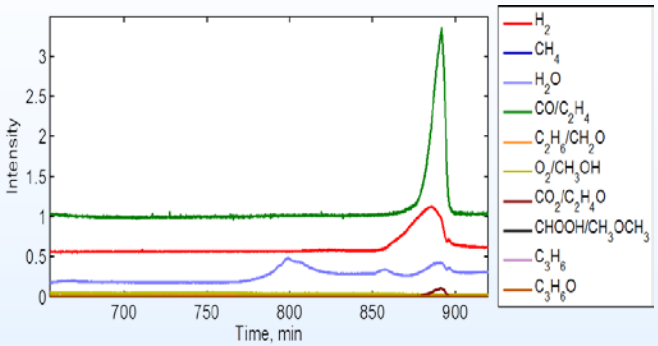
Lower Temperature Oxidation Extraction from CO_2

Original catalyst extracted oxygen from CO_2 at 800°C



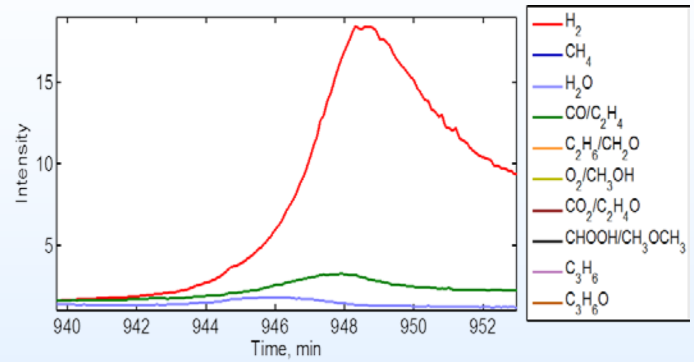
Production of Syngas from Methane and CO_2

TGA-MS



Catalyst D

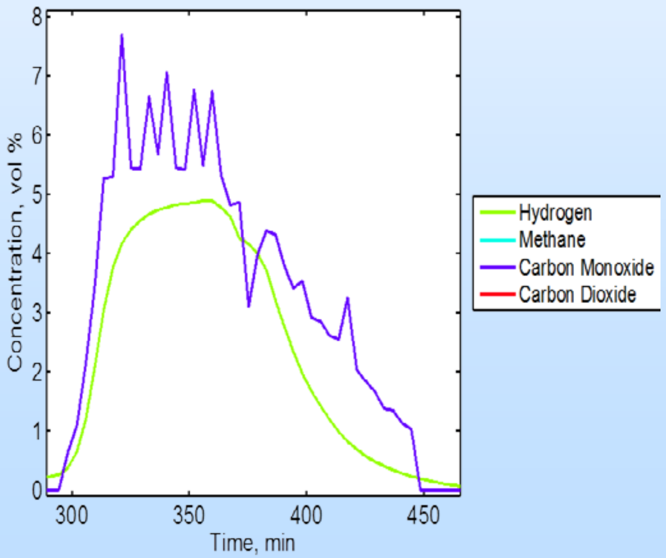
- 600°C



Catalyst C

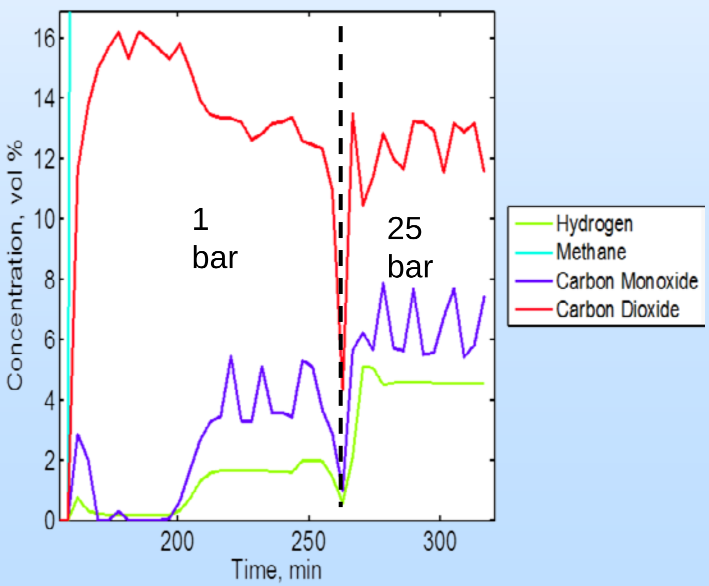
- Peak at 720°C

Bench-scale Reactor



Catalyst D

- 600°C
- 25 bar



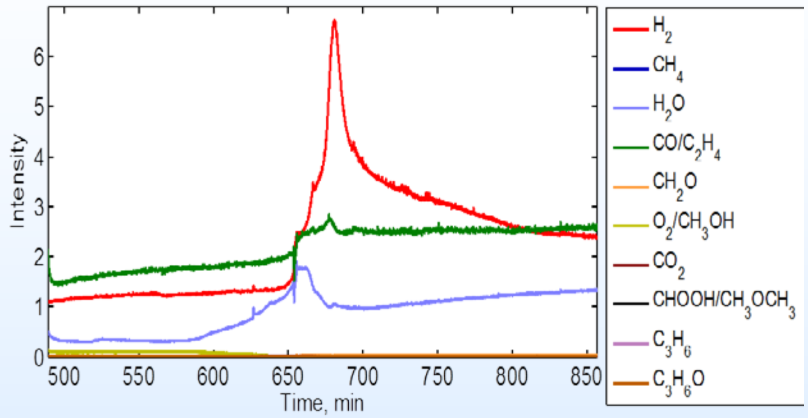
Catalyst D

- 600°C
- 1 25 bar

CO-rich syngas production from methane and CO_2 at 600°C

Production of Alkanes and Alkenes from Methane and CO_2

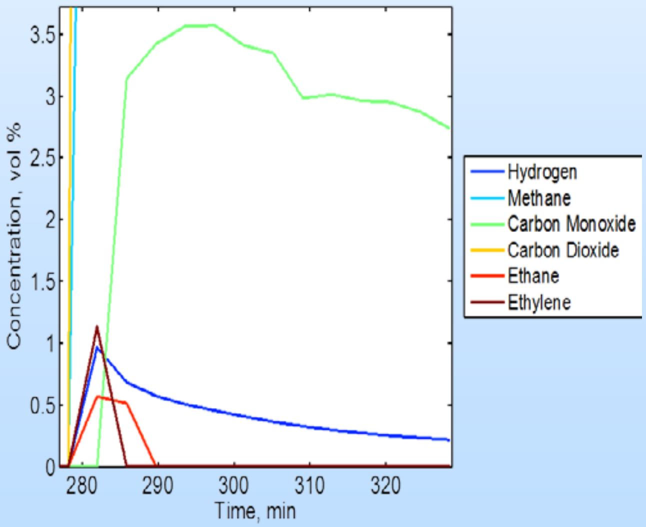
TGA-MS



Original Catalyst

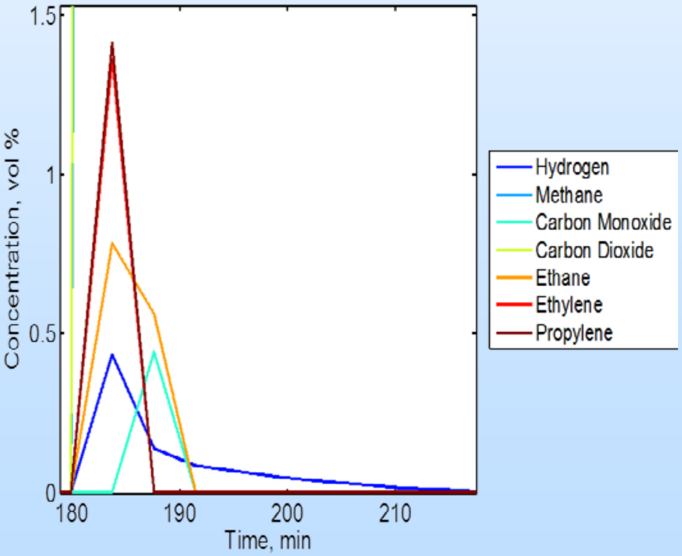
- 800°C

Bench-scale Reactor



Catalyst A

- 780°C



Catalyst A

- 780°C

Summary

– Demonstrated catalytic oxygen extraction from CO_2
– Demonstrated utilization of oxygen extracted from CO_2 for oxidation of hydrocarbons
– Developed catalysts with increased activity at lower temperatures
  - Oxygen extraction
  - Hydrocarbon reduction
– Initiated testing for direct conversion of CO_2 and hydrocarbons into commodity chemicals

Future Plans

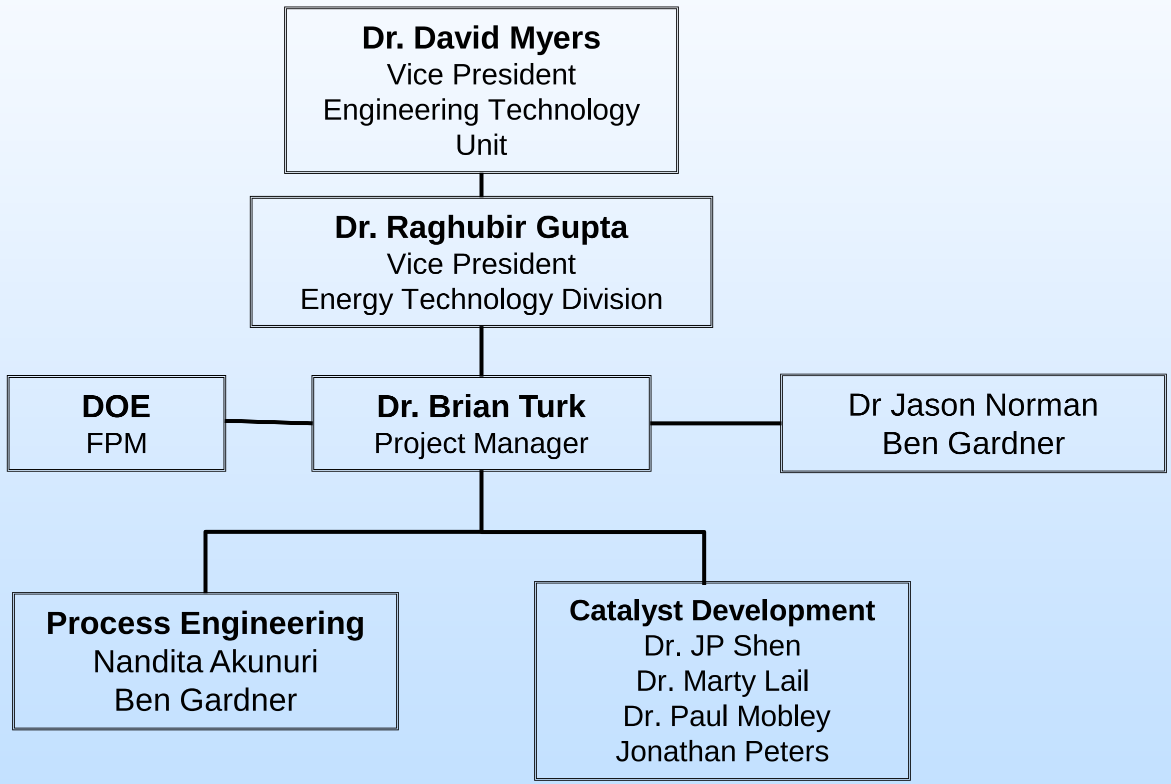
- Identify key commodity chemicals that can be produced with target catalyst families
- Optimize catalyst formulation for activity, conversion, and selectivity

Acknowledgments

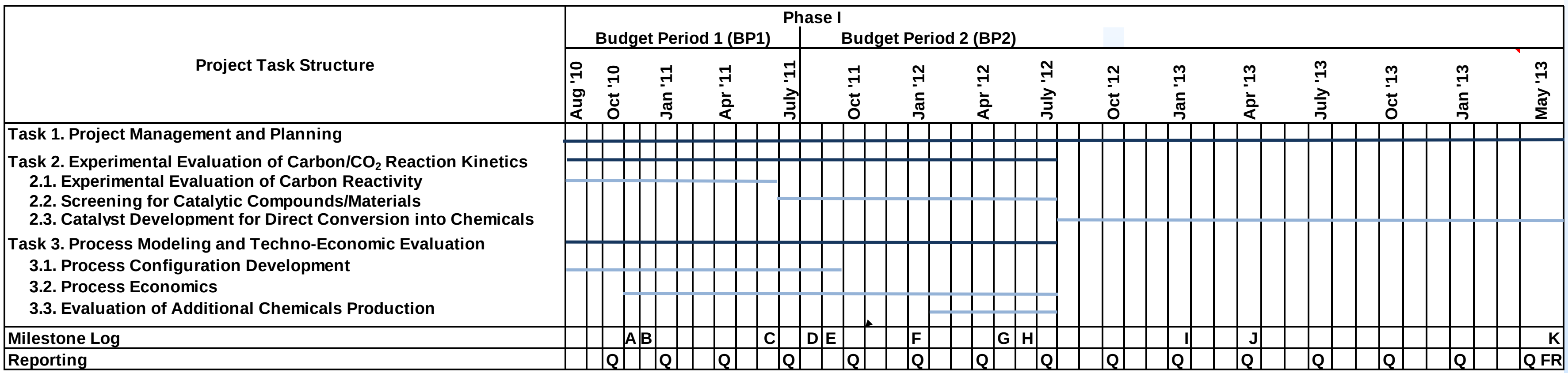
– Darin Damiani (DOE)
– Marty Lail
– Paul Mobley
– JP Shen
– Jason Norman

Appendix

Organization Chart



Gantt Chart



Q = Quarterly reports due one month after quarter's end; FR = Final report due three months after project's end.

Milestones: A. Updated Project Management Plan, B. Kickoff Meeting, C. Determination of carbon feedstock reactivity with CO2, D. Develop Aspen Plus simulation model for process configuration, E. Begin catalytic compound screening, F. Begin process economic evaluations, G. Determination of catalytic compound impact on carbon feedstock reactivity, H. Complete techno-economic studies, I Demonstration of catayltic oxygen extraction from CO2, J Evaluation of catalytic hydrocarbon reduction. K Evaluation of catalytic selective oxidation

Bibliography

- Jian-Ping Shen, Marty Lail, Paul D. Mobley, Jason S. Norman, and Brian Turk, Carbon Dioxide Utilization Mediated by an Iron Mixed-Metal Oxide, submitted to Nature in July 31, 2013.