Isolated Single Metal Atoms Supported on Silica for One-Step Non-Oxidative Methane Upgrading

DE-FE0031877

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National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
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Project Overview

- Funding

  DOE ($1.0 M) + Cost Share ($292,515)

- Overall Project Performance Dates

  March 20th, 2020 – March 19th, 2023

- Project Participants

  PI: Dongxia Liu, University of Maryland

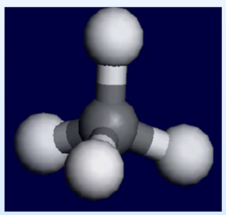
  Co-PI: Dionisios G. Vlachos, University of Delaware

- Overall Project Objective

  Create new, inexpensive, stable, active and selective catalysts to solve challenges in non-oxidative methane conversion (NMC) to produce hydrogen and higher hydrocarbons, and integrate catalysts in an efficient, scalable, and intensified NMC reactor.

Technology Background

- Different methane conversion pathways



Methane

Indirect

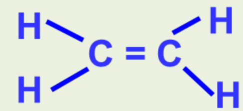
Syngas ($CO+H_2$)
- By steam reforming of methane
- By partial oxidation of methane
- By oxy-steam and/or CO_2 reforming of methane

Syngas → Methanol → Hydrocarbons

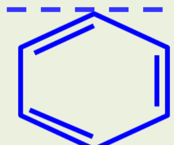
↳ Hydrocarbons or Oxygenates (by FT synthesis)

Direct

C_2 hydrocarbon
- By oxidative coupling of methane (OCM)
- By high temperature coupling of methane



Benzene
- By direct non-oxidative methane conversion (NMC)



Methanol/formaldehyde, carbon disulfide, methyl chloride, etc

↓

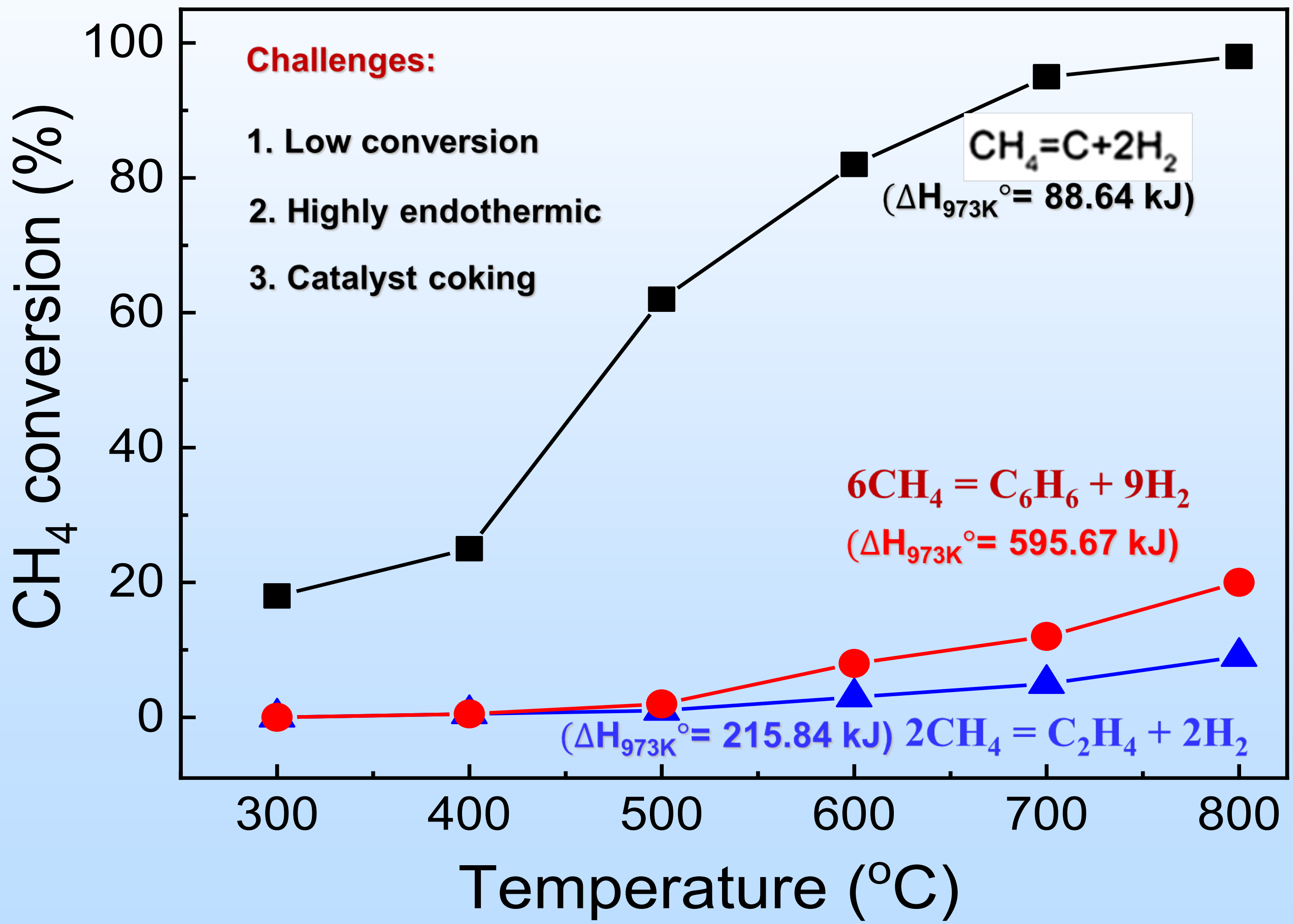
Hydrocarbons

Carbon and Hydrogen

Goodman, D. W., et al., *Catal. Rev. Sci. Eng.* **2003**, *45,* 151.

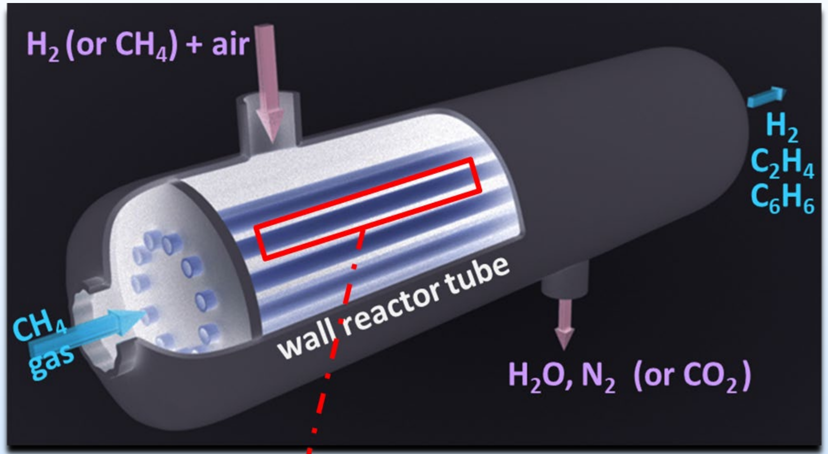
Technology Background

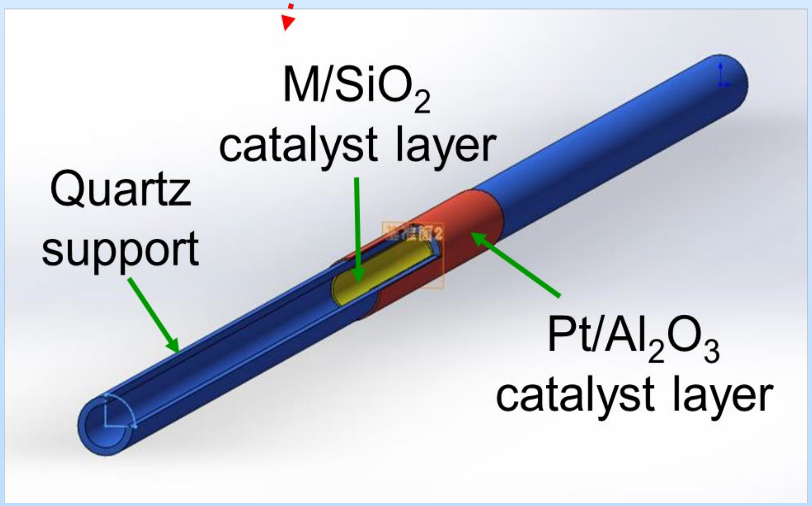
- Scientific challenges in NMC

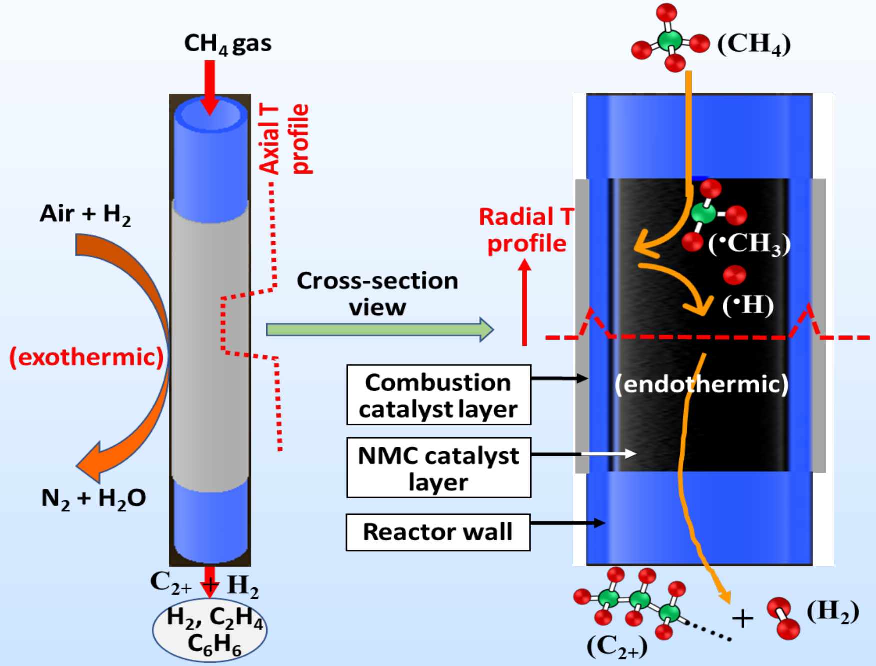


Technology Background

- Autothermal catalytic wall reactor: short contact time + sharp temperature profile



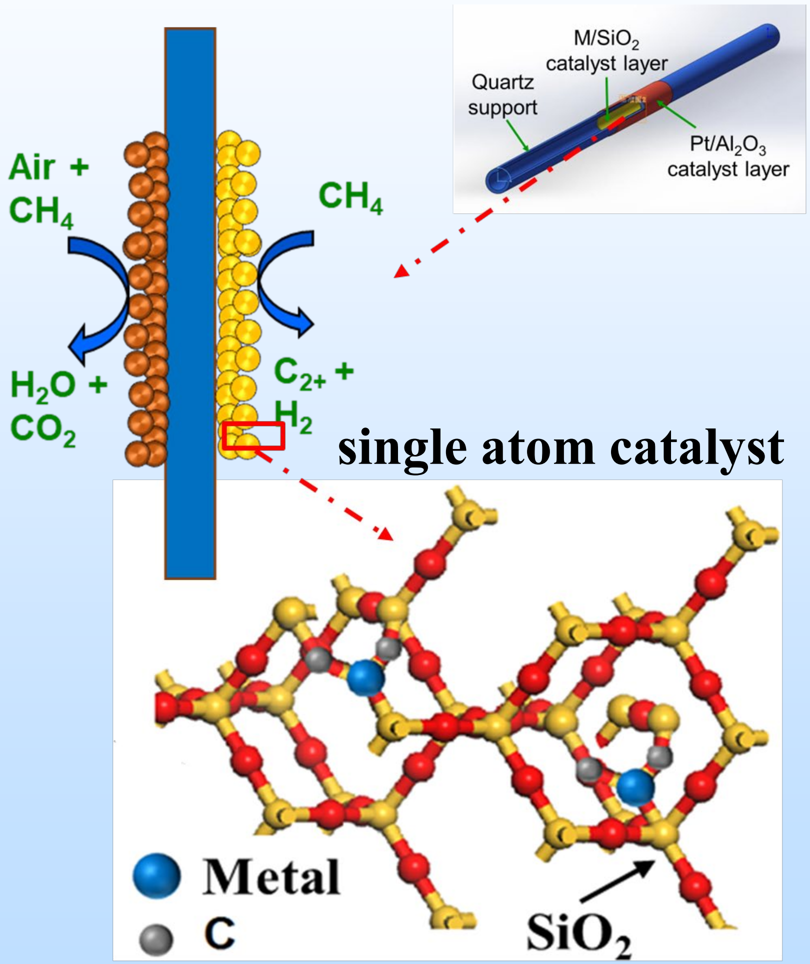




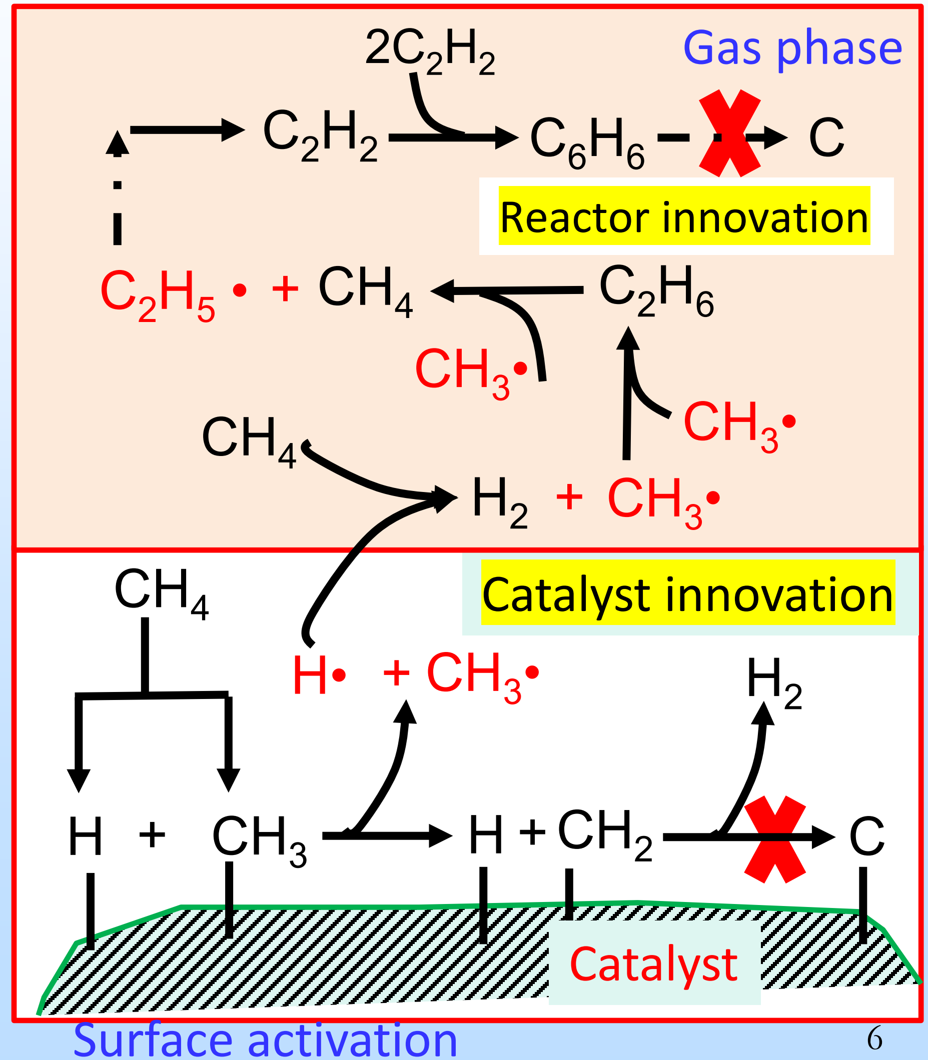
- Integration of endo- and exothermic reactions to achieve autothermal operation
- Temperature profile controlled by zoning oxidation catalyst on reactor outer surface
- Short contact time by placing NMC catalyst on reactor wall to inhibit secondary reactions

Technology Background

- Both catalyst and reactor innovation to achieve high NMC performance



Catalyst structure



Technical Approach/Project Scope

a. Experimental design (or project steps and work plan)

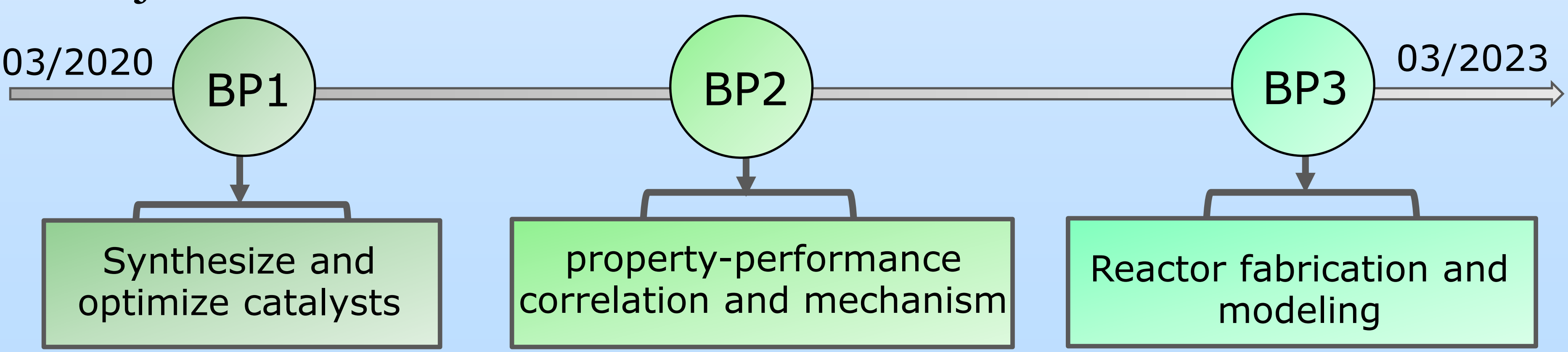
(1) synthesize isolated single atoms of various metals in a silica matrix to prove universality of these catalysts in CH_4 activation, provide data for catalyst optimization, and select the best one;

(2) probe in situ and operando the surface and bulk structure of NMC catalysts using a wide range of experimental and ab initio thermodynamic techniques;

(3) understand the reaction mechanism and kinetics by an integrated experimental and computational effort to quantify species and temperature, and use this information to create performance windows in an ideal reactor;

(4) demonstrate an efficient prototype reactor that integrates knowledge and data from the above steps for NMC.

b. Project schedule



Technical Approach/Project Scope

c. Project success criteria

(1) Make M/SiO_2 catalysts and obtain synthesis-structure-performance correlations;

(2) Attain surface and gas phase reaction mechanism and kinetics by an integrated experimental and computational effort to create performance windows in reactor operation;

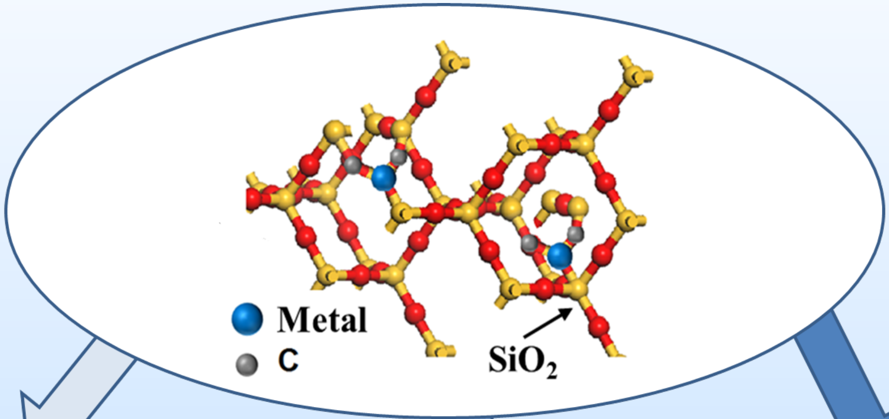
(3) Demonstrate an efficient prototype reactor. The proposed catalyst/reactor system attains single-pass CH_4 conversion and C_{2+} yields of >25%, with > 90% C_{2+} selectivity, lifetime of >1000 h, and a low cost of catalyst and reactor materials.

d. Project risks and mitigation strategies

Risk	**Mitigation strategy**
Poor chemical/physical stability of M/SiO_2 catalyst and microreactor	(1) Operate reaction at medium high temperature conditions; (2) Employ standard thermally stable support and metal catalyst materials in synthesis.
Measurement for real active sites in both catalyst surface and gas-phase reactions	Develop spatially resolved microprobe mass spectrometry equipment for in-situ measurement; Run co-feed experiments to probe NMC performance and reaction mechanisms.
Proper kinetic model for chemistry coupling both surface and gas phase reactions	Rely on first-principles models and use local computational resources and supercomputers to overcome this barrier.

Progress and Current Status of Project

1a. Prepared various silica supported single atom catalysts



Metal (M) type

Fe; Co; Ni; Cu; Mn; Pt

Metal (M) content

0.10wt%; 0.50wt%;
1.00wt%; 1.50wt%

SiO_2 Support

Silicalite-1;
Cristobalite;
vitreous SiO_2

Liu, D. et al., Catalysis Today, in press.

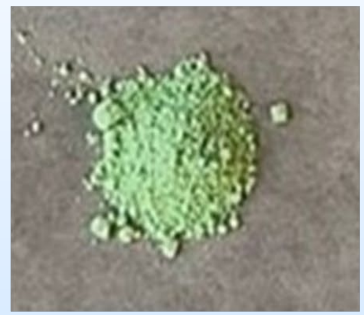
Progress and Current Status of Project

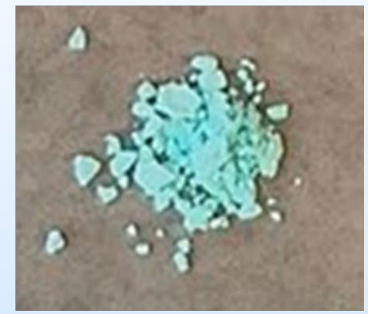
1a. Representative M/SiO_2 catalysts synthesized for NMC

Metal (M) precursors


Fe_2SiO_4


Co_2SiO_4


Ni_2SiO_4


$CuSiO_3$

M/SiO_2 catalysts with different metal type


Fe/SiO_2


Co/SiO_2

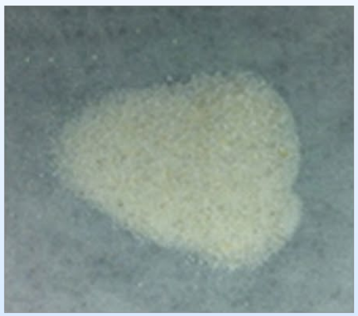

Ni/SiO_2


Cu/SiO_2

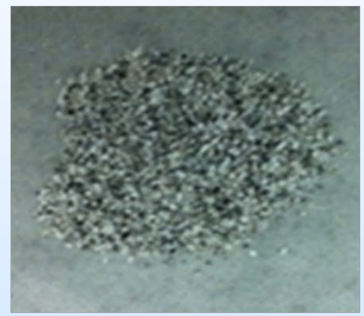
Progress and Current Status of Project

1a. Representative M/SiO_2 catalysts synthesized for NMC

Fe/SiO_2 catalyst with different Fe content

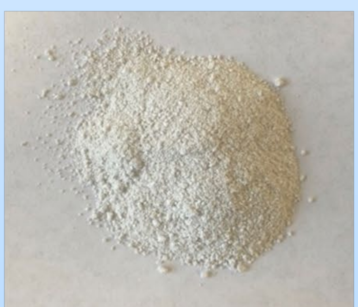

0.05wt%


0.1wt%


0.5wt%


1.50wt%

Fe/SiO_2 catalyst with different SiO_2 crystalline phase


silicalite-1

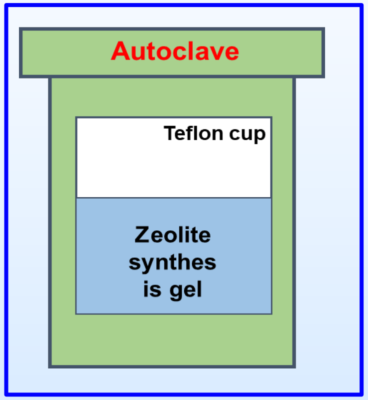

α-quartz

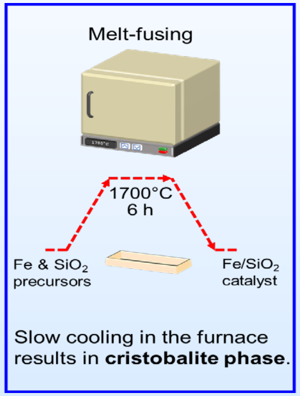

quartz-melt

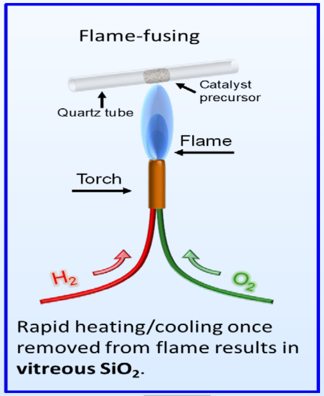

cristobalite

Progress and Current Status of Project

1b. Employed three different routes to synthesize catalysts



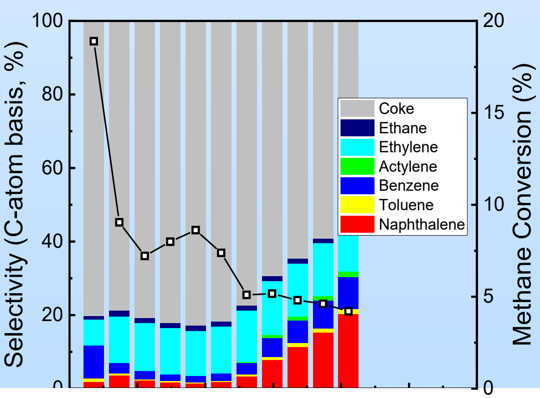


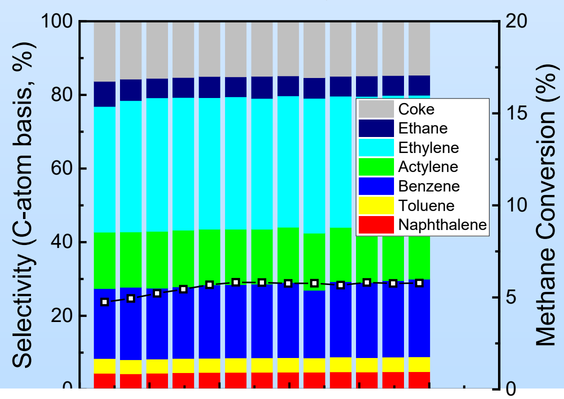


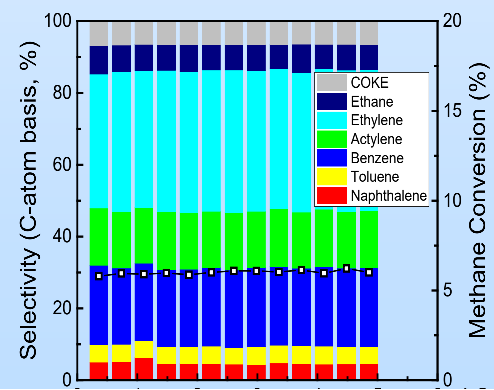
Fe/Silicalite-1

Fe/SiO_2–CRS (Cristobalite)

Fe/SiO_2-VS (Vitreous)

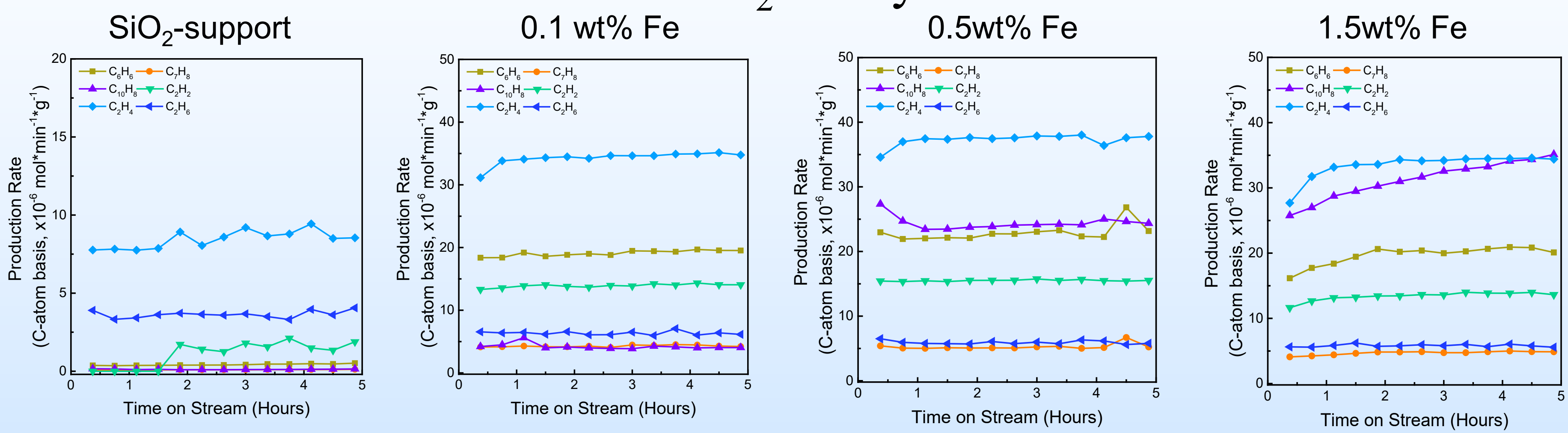




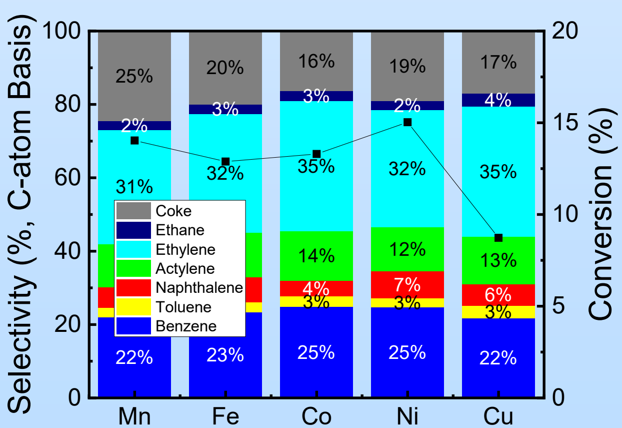


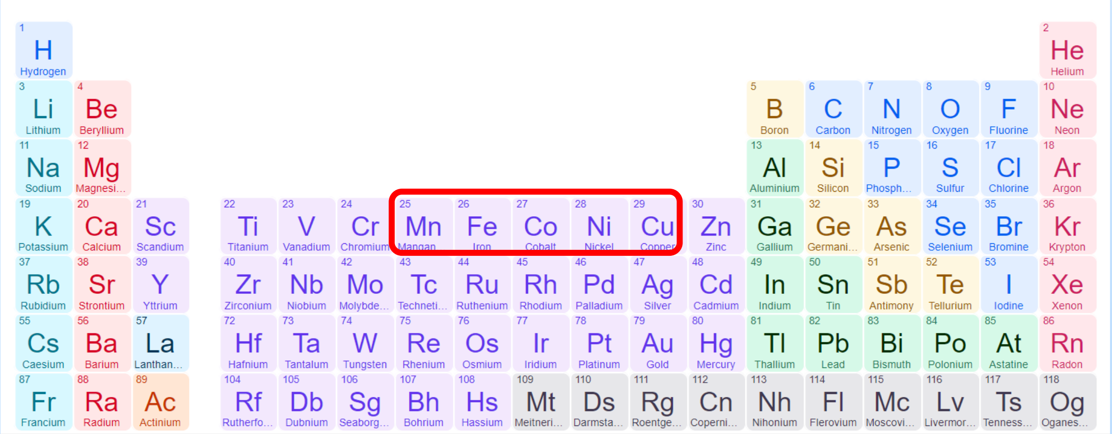
Progress and Current Status of Project

1c. Effect of metal conc. in M/SiO_2 catalysts on NMC



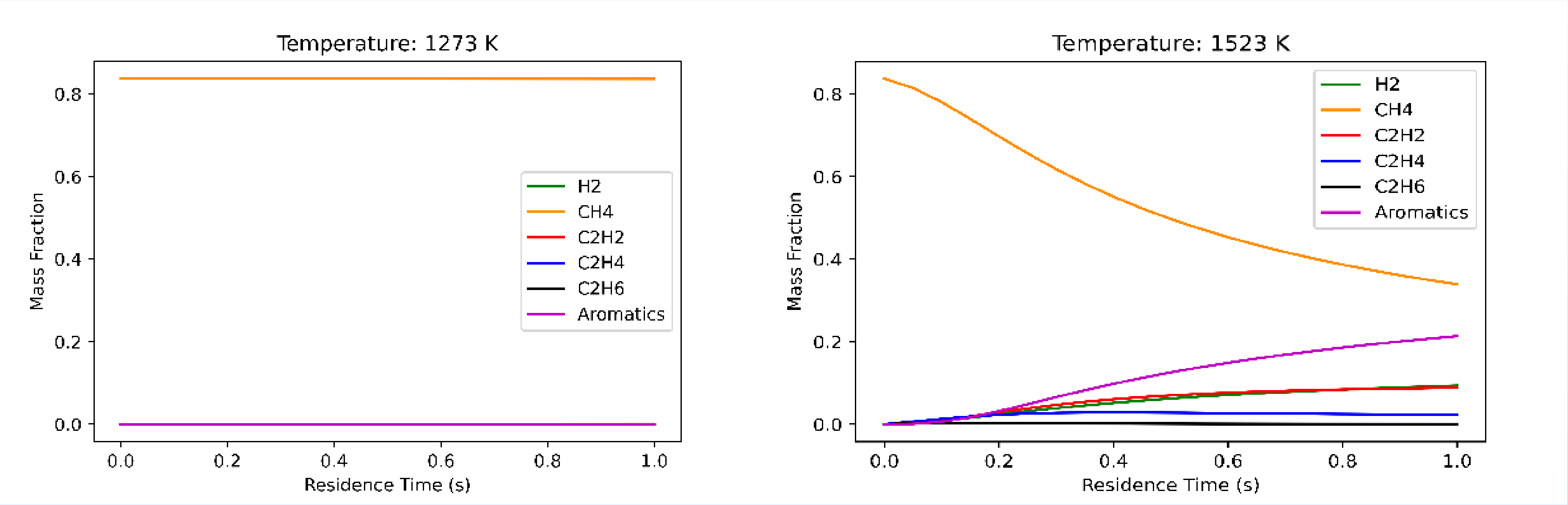
1d. Effect of metal type in M/SiO_2 catalysts on NMC





Progress and Current Status of Project

1e. Simulated conversion with only gas-phase chemistry (90% CH_4+10% inert)



(1) CH_4 does not readily couple in the gas phase at typical reactor temperatures;

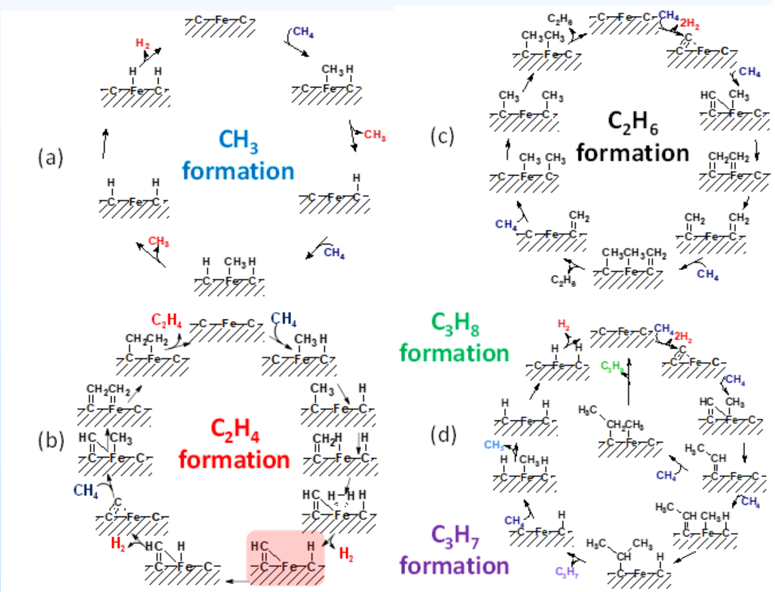
(2) >1473 K is required for a direct conversion of methane, form aromatics and acetylene with little ethylene;

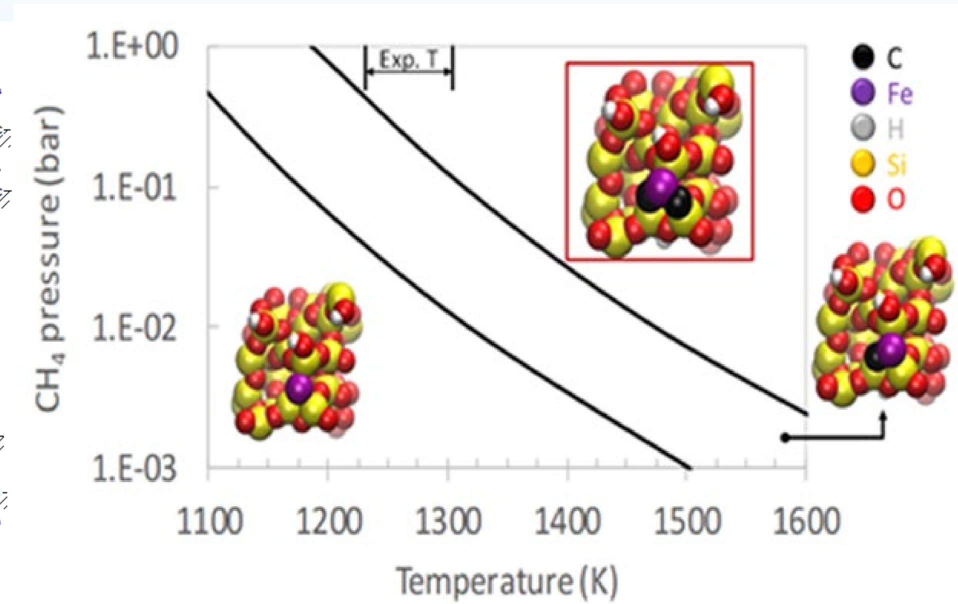
(3) High temperature requirement for methane coupling in the gas phase suggests that methane coupling occurs primarily on the surface to form ethylene.

(4) Ethylene formed on the surface readily reacts further in the gas phase to form compounds like aromatics. This agrees with the expectation that gas phase chemistry is detrimental to ethylene selectivity.

Progress and Current Status of Project

1f. Simulation of CH_4 activation mechanism on Fe/SiO_2 catalyst





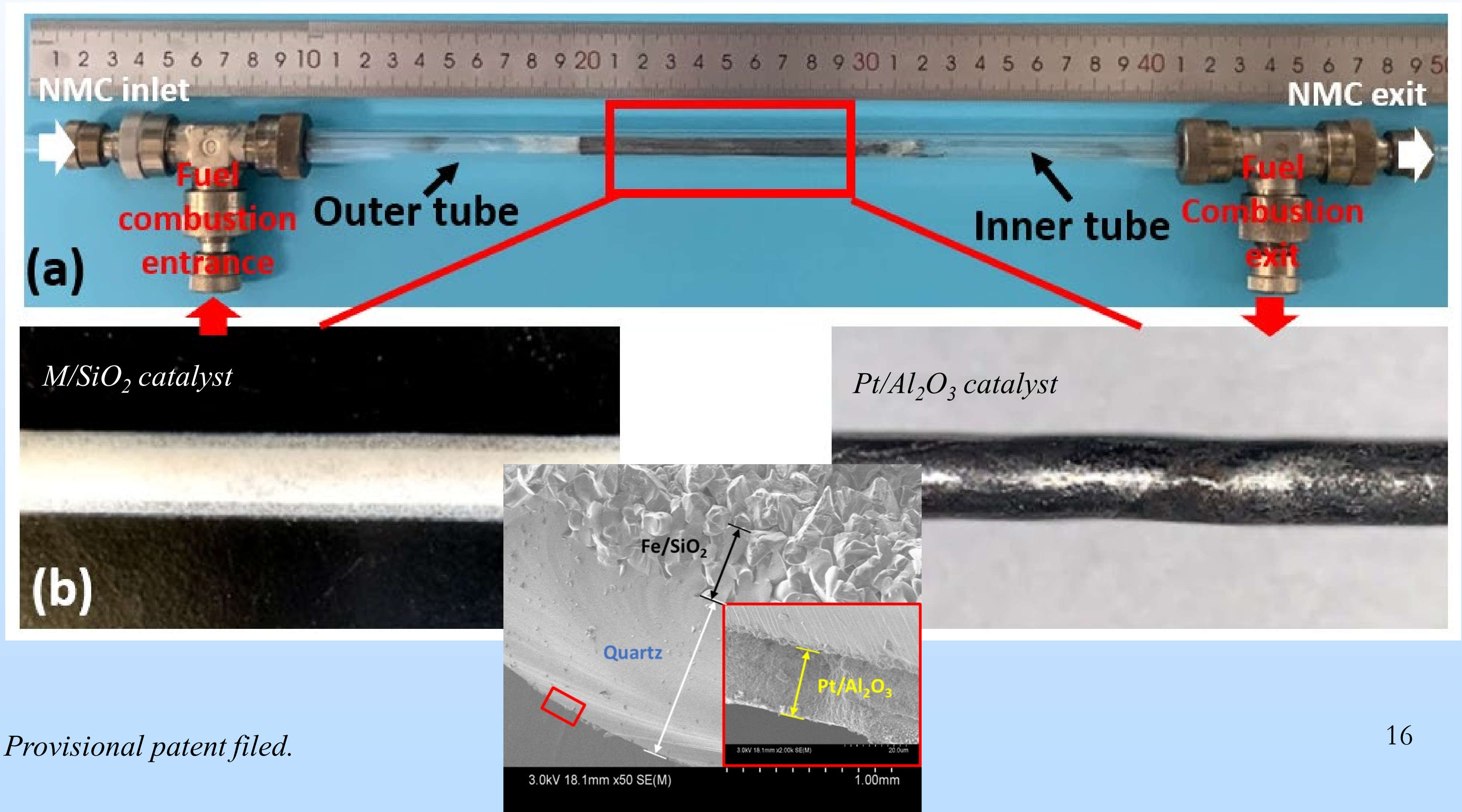
(1) Ab initio phase behaviour of isolated iron atoms on amorphous silica. Thermodynamic analysis is done for $FeO_3/SiO_2 + xCH_4 \leftrightarrow FeC_{x-3}/SiO_2 + 3CO + 2xH_2$ with x = 3, 4, 5, 6, $P_{H2} = 10^{-3}$ bar, and $P_{CO} = 10^{-8}$ bar. At typical reaction temperatures and methane partial pressures, carburization of the catalyst occurs.

(2) Catalytic reaction network for C1-C3 species formation from methane over isolated iron carbide species. The steps leading to the formation of coked iron carbide active site are common in all C2-C3 species formation cycles and are shown for ethylene only.

Angew. Chem. Int. Ed., 2021.

Progress and Current Status of Project

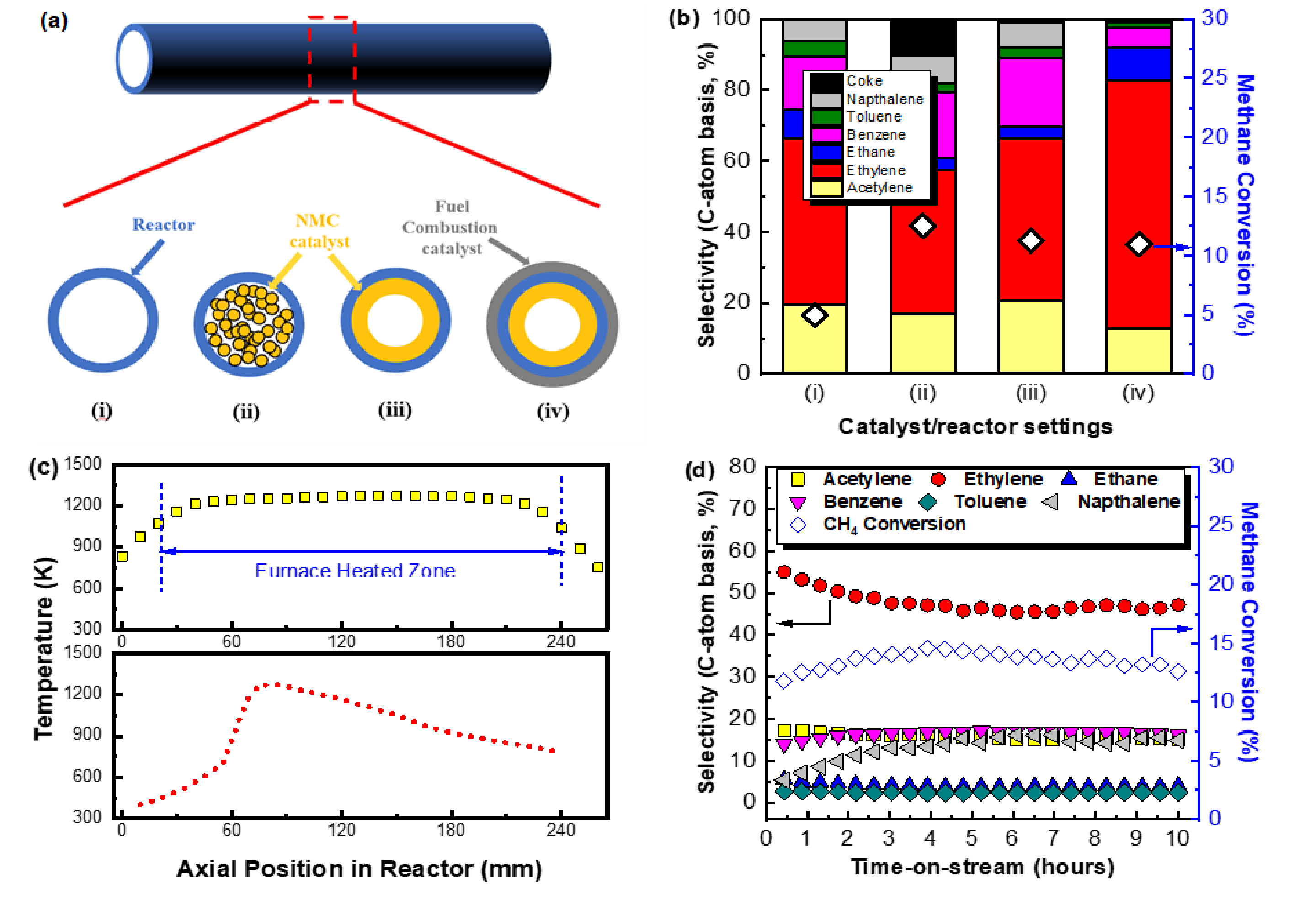
2a. Design/fabrication of catalytic wall reactor



Provisional patent filed.

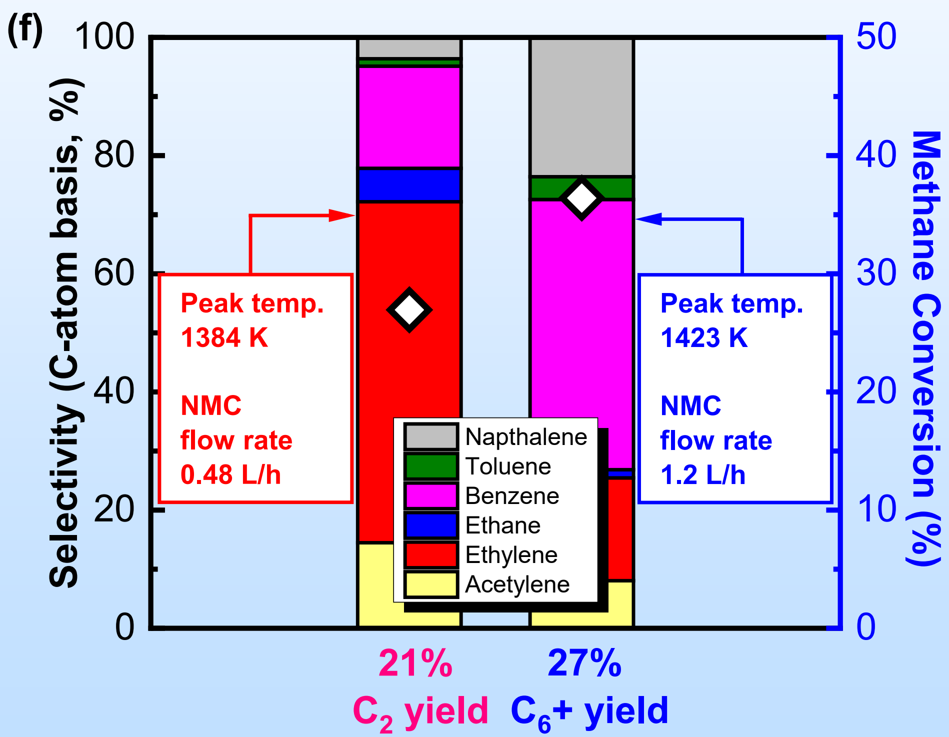
Progress and Current Status of Project

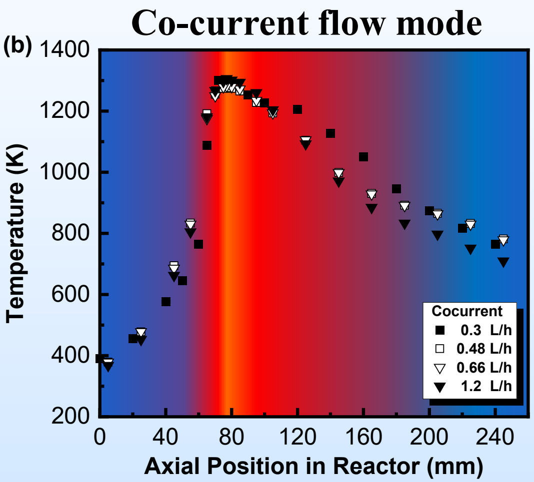
2b. Effect of catalyst layout in reactor on NMC

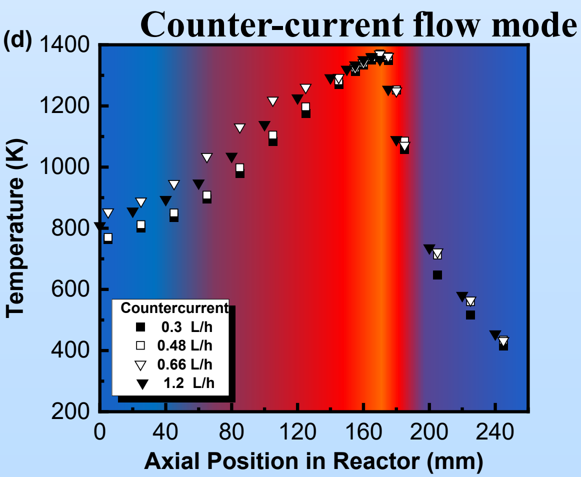


Progress and Current Status of Project

2c. Maximized NMC performance in autothermal catalytic wall reactor



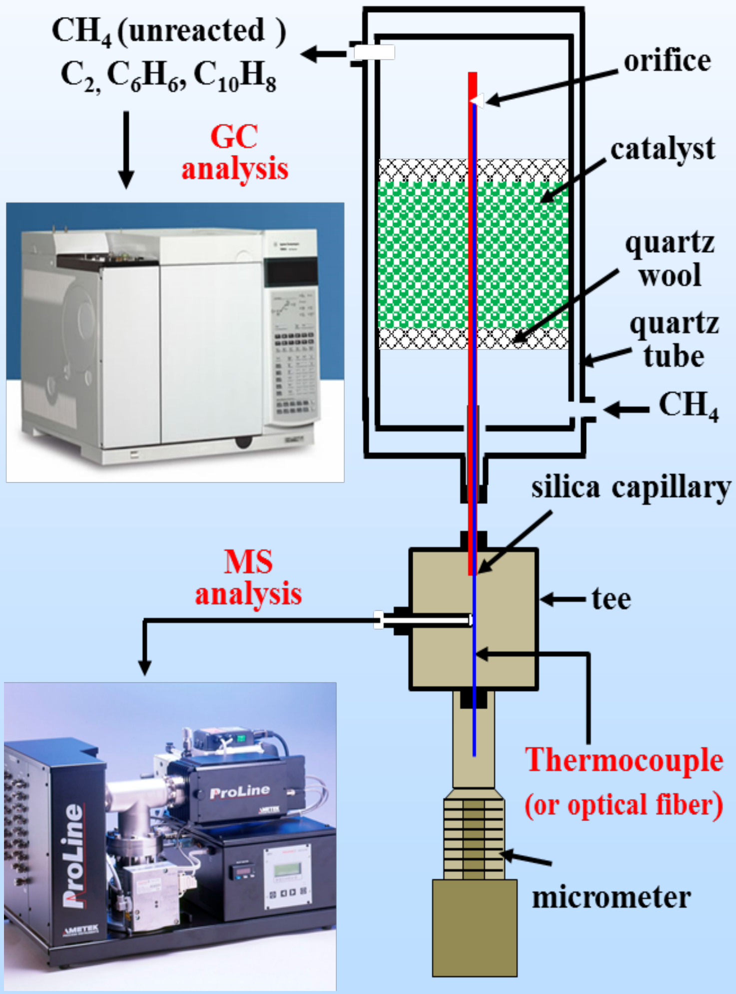




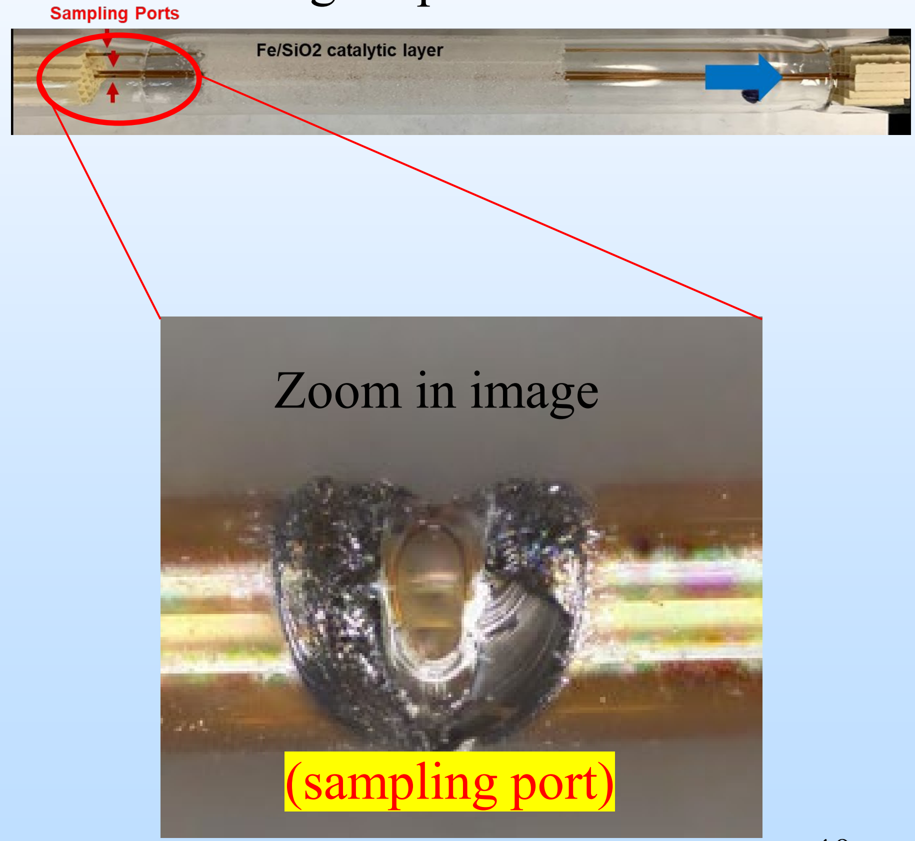
Tune process conditions towards target products

Progress and Current Status of Project

2d. Design/fabricate spatial/temporal measurement equipment

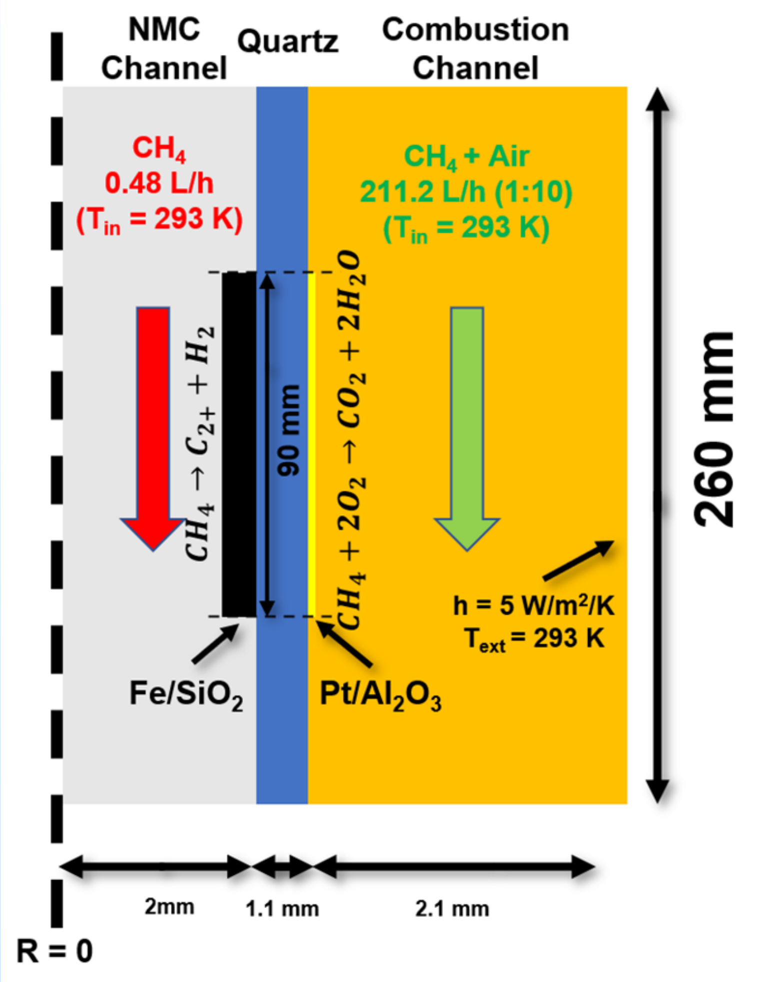


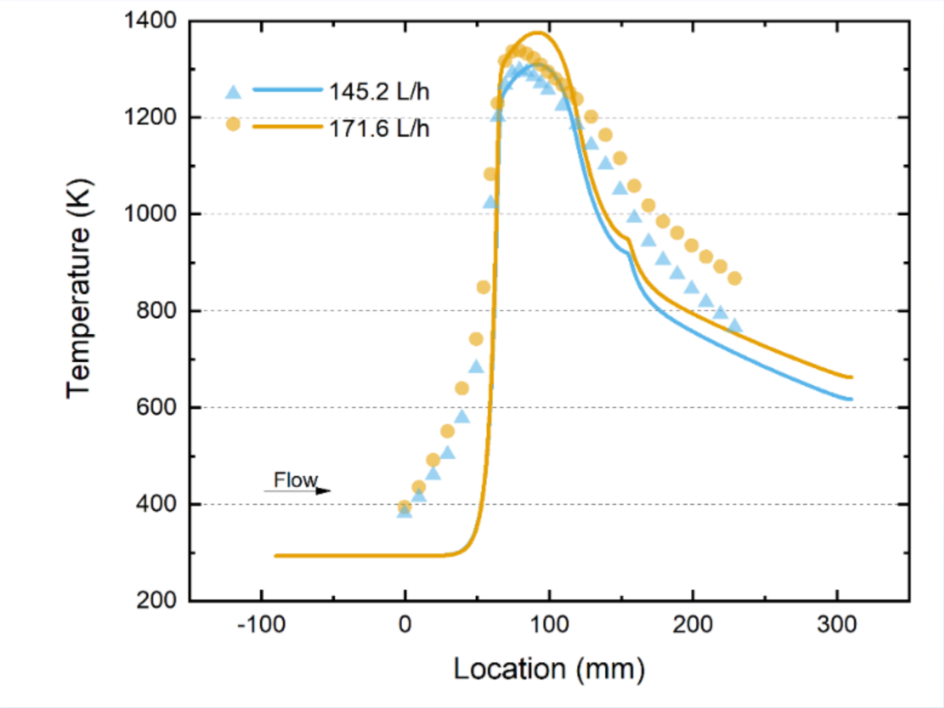
Digital photo



Progress and Current Status of Project

2e. 2D-axisymmetric steady-state COMSOL simulation





High flow rate → high peak temperature

Model and experiment fits each other

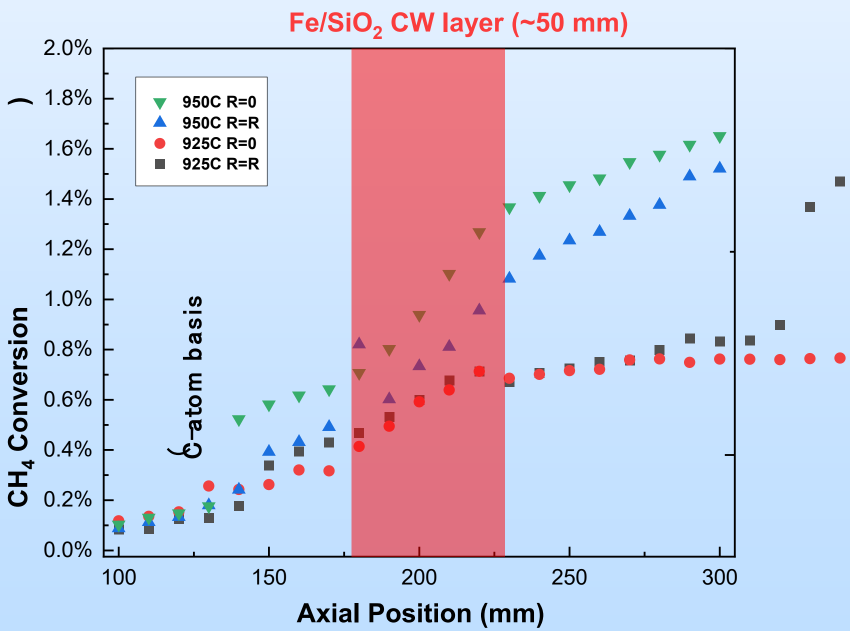
Plans for future testing/development/ commercialization

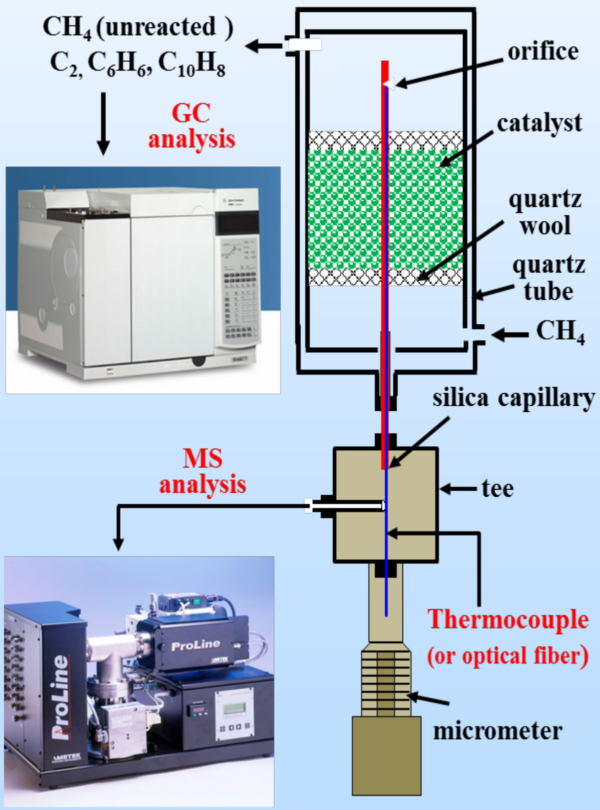
a. In this project

(1) continue to measure spatial/temporal species concentrations;

(2) develop coupled surface and gas phase mechanism for NMC optimization;

(3) long-term test for reactor.



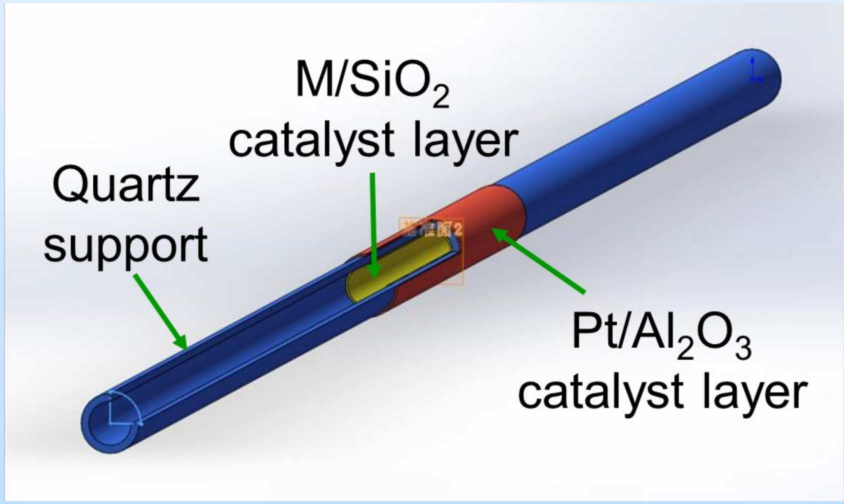


Plans for future testing/development/ commercialization

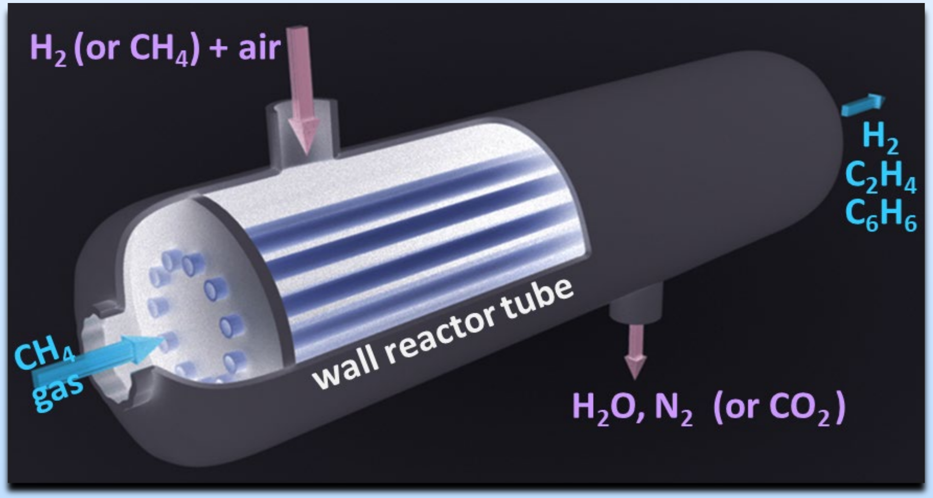
b. After this project

Scale up the catalytic reactor design/fabrication and catalyst for high TRL-level research for NMC

Singe reactor tube



Reactor bundle



Outreach and Workforce Development Efforts or Achievements

- Outreach: Hosted undergraduate students in ENES240, the intro to science, technology, ethics, and policy (STEP) every semester

  Students' feedback: There was just so much "magic" happening there... I'm glad I went... It was good to see so many projects' people were working on and the kind of inspirations they drew on to get there. In my extremely humble opinion, science is as much about finding out what doesn't work as finding out what does. The students encouraged each other to keep going and try new methods. The prof even stated that it was best to just go through a couple failures as quickly as possible to get used to it and the idea of persisting notwithstanding."

- Workforce Development: Trained 3 undergraduate and 3 graduate students, and 1 postdoc fellow; integrate research findings into courses that the PIs teach to educate broad student body in STEM field.

Summary Slide

a. Single atom M/SiO_2 catalysts with variable metal type, metal concentration and support are synthesized by high temperature synthesis routes;

b. NMC performance depends on metal type, concentration and silica support properties. Among all studied catalysts, Co/SiO_2 and Fe/SiO_2 are the most promising ones for scale up;

c. NMC over M/SiO_2 catalyst involves surface activation of C-H bond in CH_4, and gas phase chemistry to produce larger C_xH_y products. Suppression of gas phase chemistry is needed to improve ethylene selectivity;

d. Reactor engineering is a strategy to control gas phase reaction to tailor product selectivity. Innovations in both catalyst and reactor engineering are needed to maximize NMC performance.

Appendix

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

Organization Chart

DOE
Program Officer

Catalysis Consortium of
CCEI at Delaware

Task lead
UMD (Dr. Dongxia Liu)
Experimental team

Project lead (UMD)
(Dr. Dongxia Liu)

Task lead
UD (Dr. Dion G. Vlachos)
Computational team

UMD
Graduate student

UMD
Postdoc fellow

UD
Graduate student

UD
Graduate student

	Task(T.)/Subtask(S.T.)
T.1.0	**Project Management and Planning**
S.T.1.1	Project management plan
S.T.1.2	Technology maturation plan
S.T.1.3	Techno-economic analysis
T.2.0	**Catalyst Synthesis and Optimization**
S.T.2.1	Synthesize and optimize metal composition in catalysts
S.T.2.2	Synthesize and optimize metal type in catalysts
S.T.2.3	Tailor silica support properties in catalysts
T.3.0	**Catalyst Characterization and Activation**
S.T.3.1	Measure physicochemical properties of catalysts
S.T.3.2	Study catalyst activation (i.e. active sites) in NMC
S.T.3.3	Predict catalyst active sites by first-principle computation
T.4.0	**Reaction Mechanism Understanding**
S.T.4.1	Measure catalytic performance of M/SiO_2 catalysts
S.T.4.2	Measure surface and gas phase reaction kinetics
S.T.4.3	Multiscale computation for reaction kinetics/mechanisms
T.5.0	**Prototype Catalytic Wall Reactor Development**
S.T.5.1	Fabricate catalytic wall reactor for NMC
S.T.5.2	Factorial testing for reactor performance in NMC
S.T.5.3	Process modelling and computation for NMC reactors
T.6.0	**Project Reporting**
S.T.6.1	Attend project meetings and submit reports
S.T.6.2	Submit project data to NETL-EDX

Gantt Chart

	Task(T.)/Subtask(S.T.)/Milestone(M.)	Assigned resources	Y1				Y2				Y3			
			Q1-Q4				Q1-Q4				Q1-Q4			
T.1.0	**Project Management and Planning**	UMD-UD												
T.2.0	**Catalyst Synthesis and Optimization**	UMD												
M.2.1	*Completion of tests for metal compositions in catalyst*	UMD												
M.2.2	*Completion of tests for metal types in catalyst*	UMD												
M.2.3	*Completion of tests for silica supports in catalyst*	UMD												
T.3.0	**Catalyst Characterization and Activation**	UMD-UD												
M.3.1	*Completion of synthesis-property correlations in catalysts*	UMD												
M.3.2	*Optimization of conditions for catalyst activation*	UMD-UD												
M.3.3	*Completion of studies for active sites for NMC*	UD												
T.4.0	**Reaction Mechanism Understanding**	UMD-UD												
M.4.1	*Completion of studies for catalyst property-performance correlations*	UMD												
M.4.2	*Completion of studies for decoupling of surface and gas-phase reaction contributions*	UMD-UD												
M.4.3	*Completion of studies for reaction mechanisms of catalysts*	UD												
T.5.0	**Prototype Catalytic Wall Reactor Development**	UMD-UD												
M.5.1	*Completion of development for protocol for design/fabrication of catalytic wall reactor*	UMD												
M.5.2	*Completion of tests for operation variable effects on NMC*	UMD-UD												
M.5.3	*Completion of simulation for reactor operation for NMC*	UD												
T.6.0	**Project Reporting**	UMD-UD												
M.6.1	*Completion of presentations and reports*	UMD-UD												
M.6.2	*Complete data submitted to NETL-EDX*	UMD-UD												