Isolated Single Metal Atoms Supported on Silica for One-Step Non-Oxidative Methane Upgrading to Hydrogen and Value-Added Hydrocarbons

Project Number (DE-FE0031877)

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U.S. Department of Energy

National Energy Technology Laboratory

2021 Carbon Management and Oil and Gas Research Project Review Meeting

August 2021

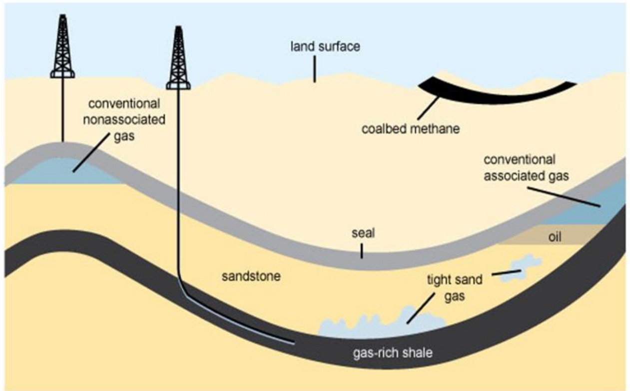
Presentation Outline

- Technical status
  - Project background & significance
- Accomplishments to date
  - Experimental & computational work update
- Lessons learned
- Synergy opportunities
- Project summary
- Appendix

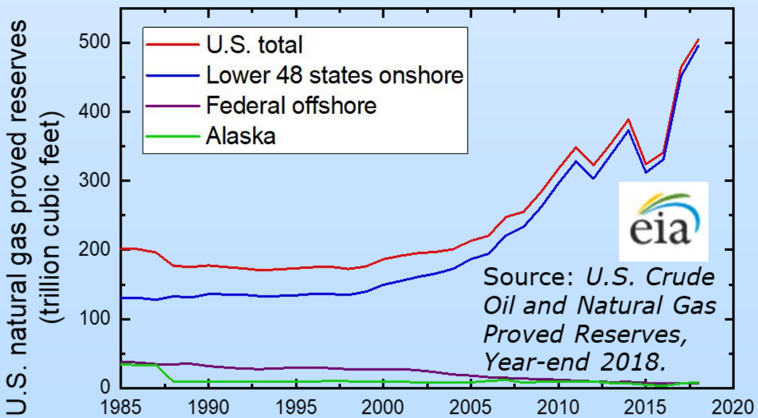
Technical Status - Methane (CH_4) abundance

CH_4 from fossil (natural gas) reserves

Schematic geology of natural gas resources

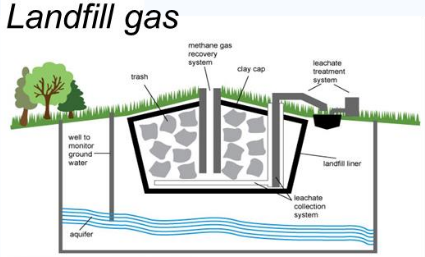


Source: Adapted from *United States Geological Survey factsheet 0113-01*



CH_4 from biomass sources

Landfill gas



Source: Adapted from *National Energy Education Project*

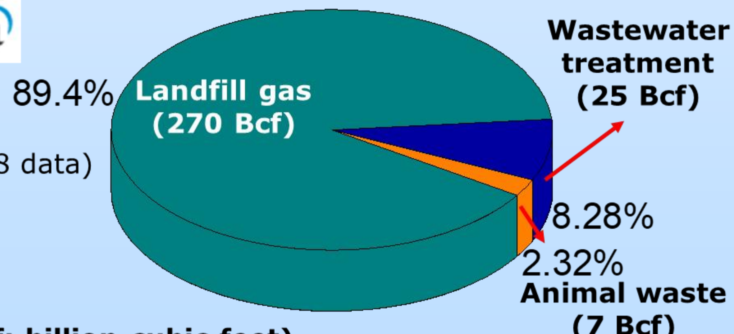
Biogas

Anaerobic digesters at the Lincoln, Nebraska **wastewater**-treatment

Biogas

Anaerobic digesters at a **dairy farm** (Michigan State University)

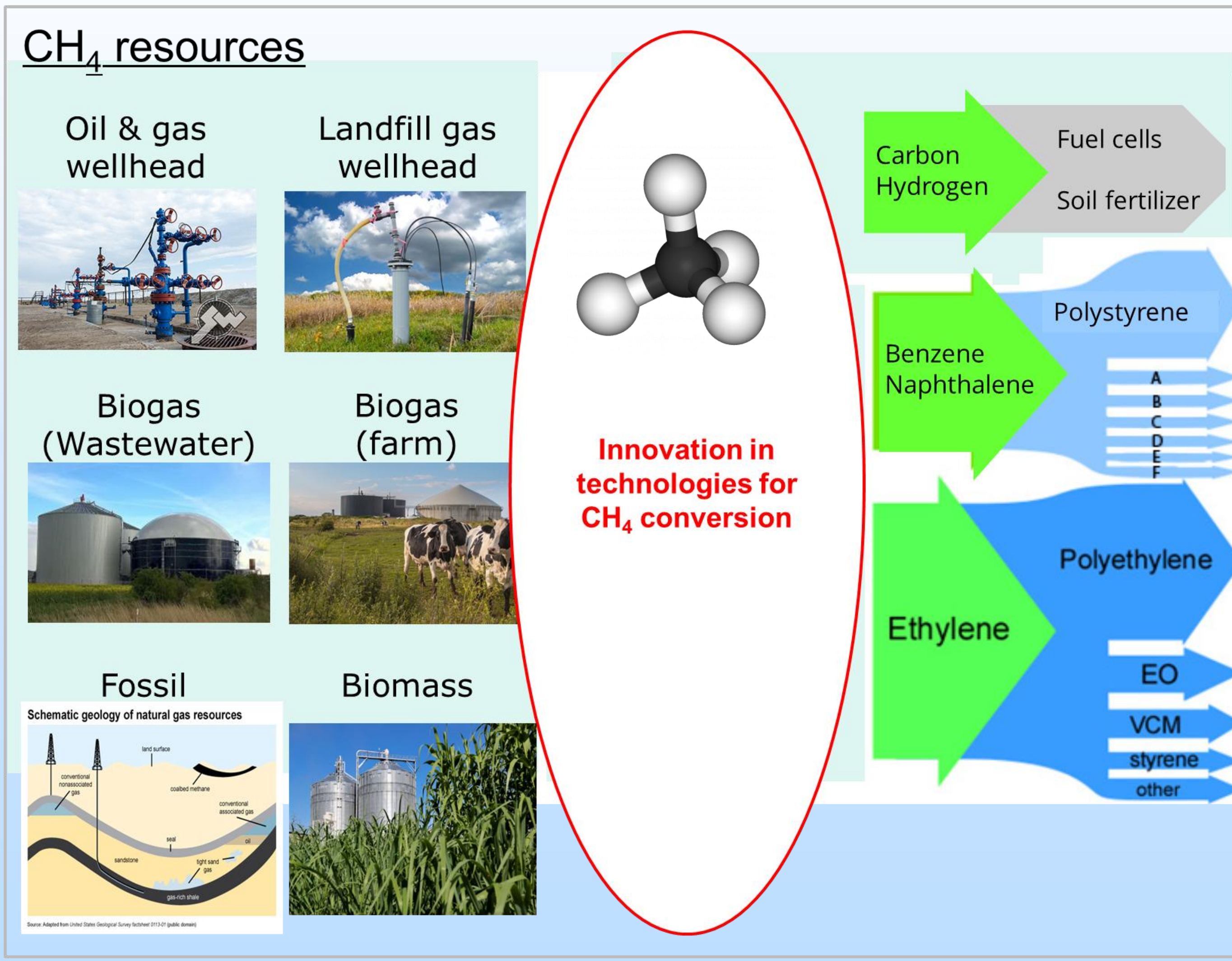
(2018 data)



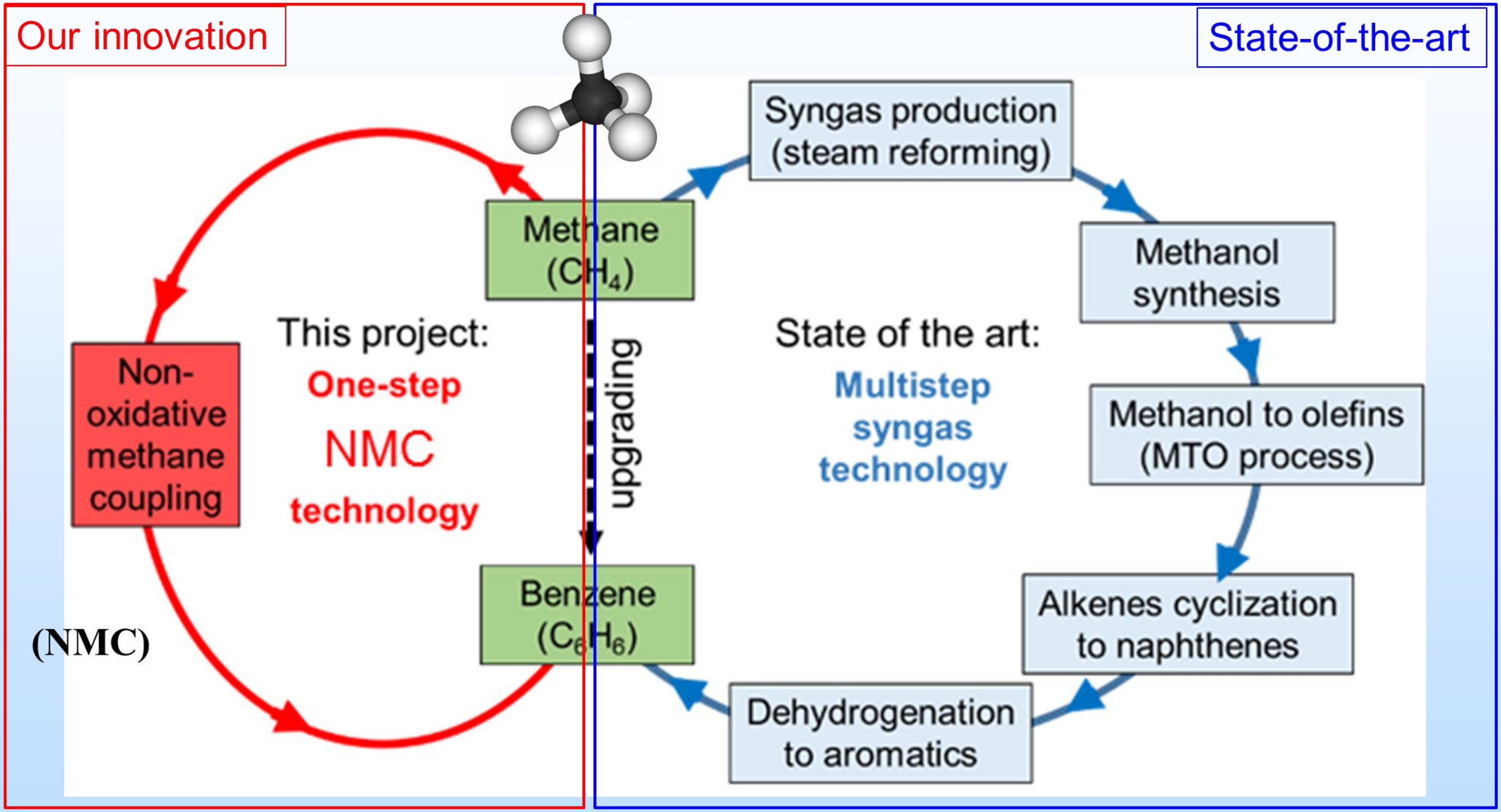
(Bcf: billion cubic feet)

Technical Status - CH_4 opportunities for fuel/chemical/material industry

A snapshot of the products from **CH_4 feedstock**

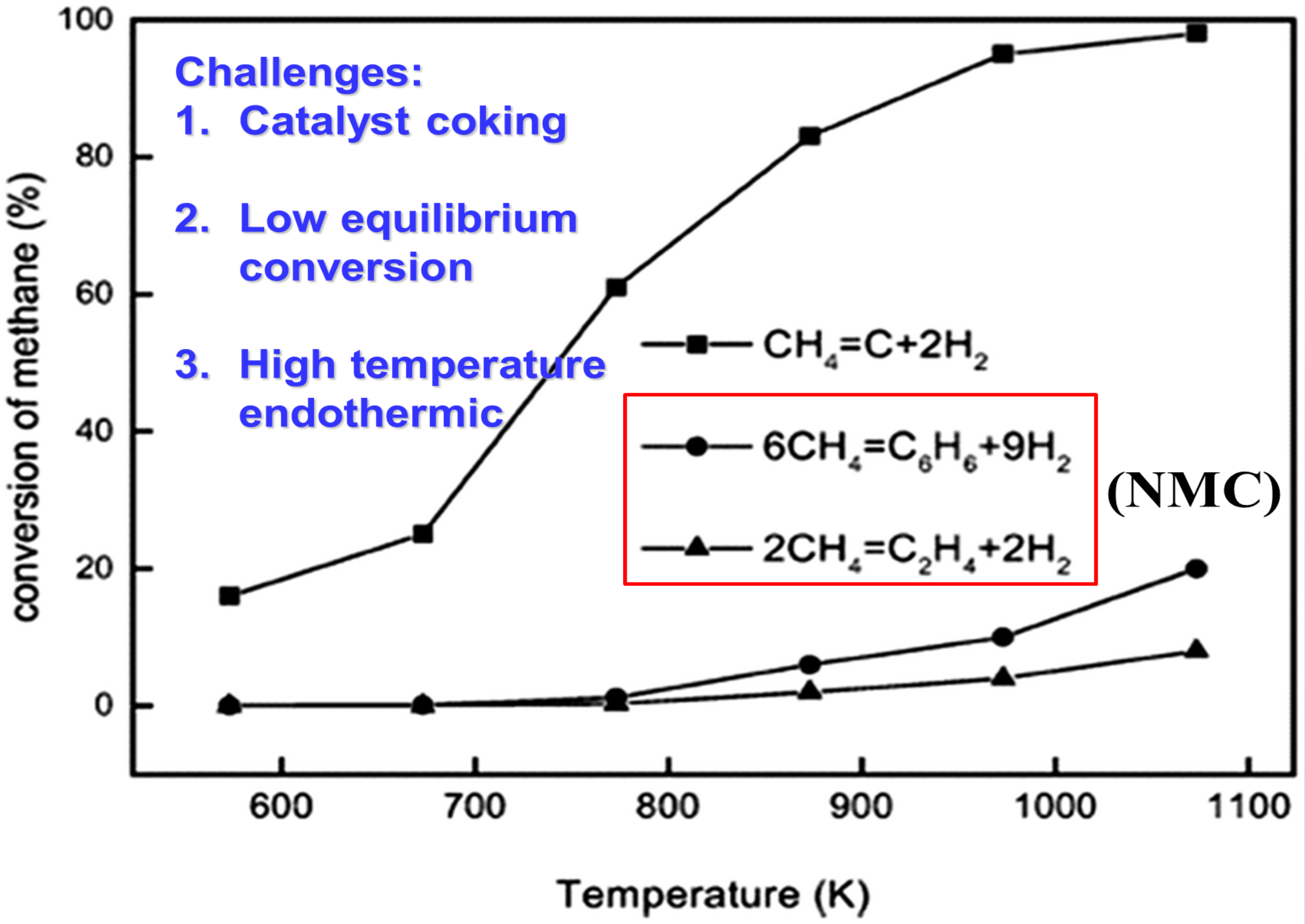


Technical Status - One-step NMC vs. multistep syngas



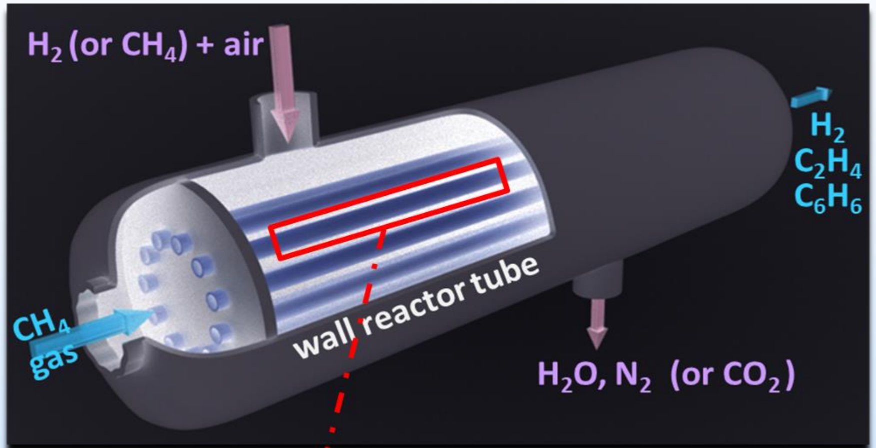
Methane upgrading via one-step NMC technology versus syngas approach in multistep technology

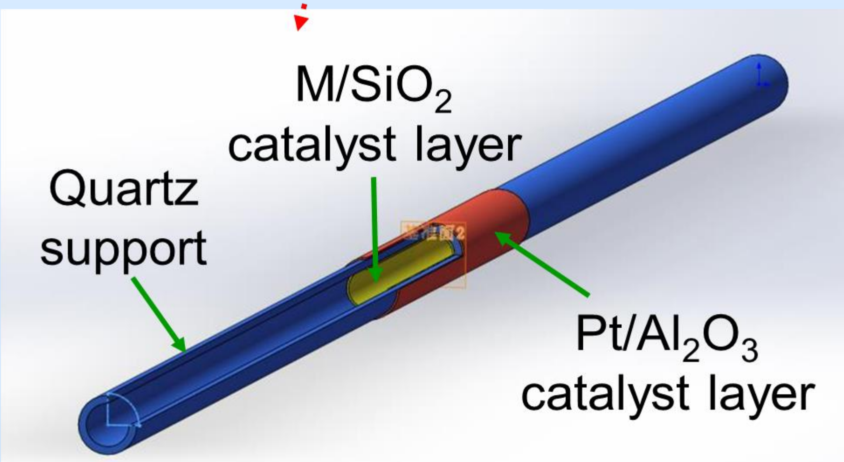
Technical Status - Scientific challenges in NMC



Technical Status - Our innovation #1: Autothermal catalytic wall reactor

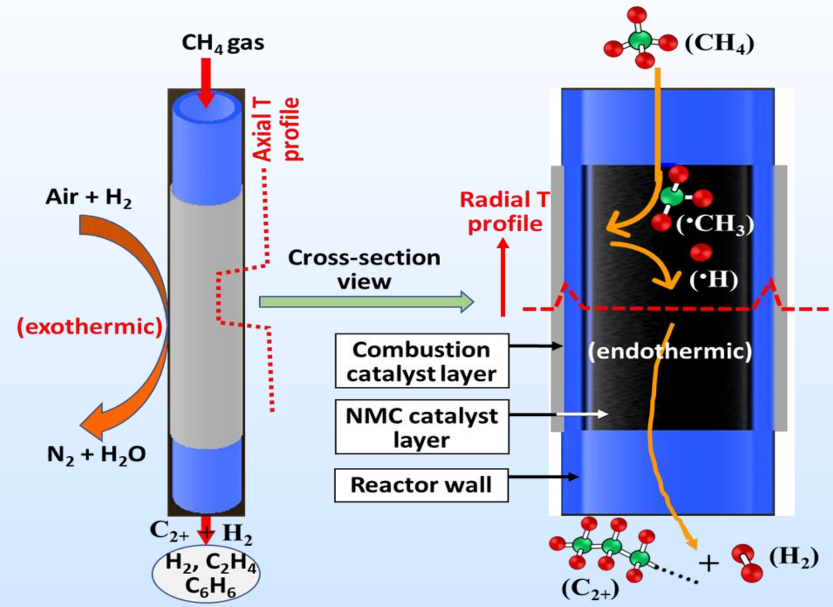
Autothermal catalytic wall reactor





Catalyst wall structure

Exo-/endothermic reaction coupling



Inner wall: endothermic (ΔHr^o = + 91.0 kJ/mol)

$$CH_4 = 3/52\ C_6H_6 + 5/104\ C_{10}H_8 + 9/104\ C_2H_4 + 19/13\ H_2$$

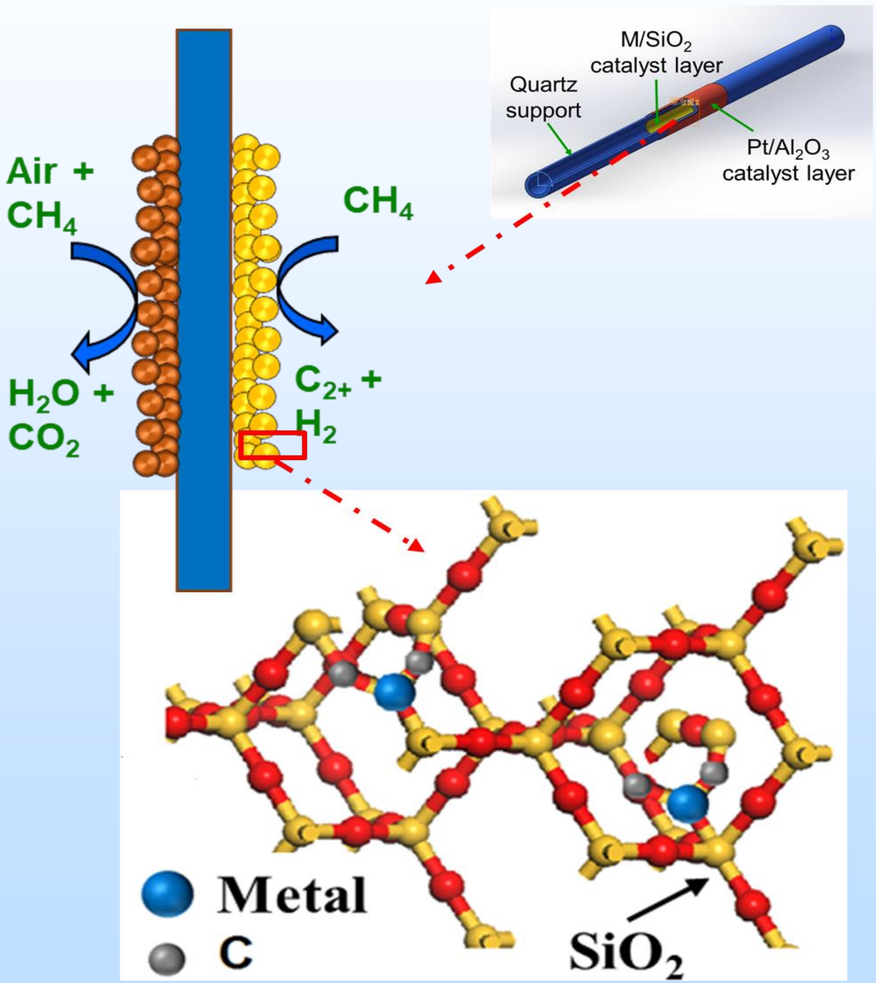
Outer wall: exothermic (ΔHr^o = - 802.6 kJ/mol)

$$CH_4 + 2O_2 = CO_2 + H_2O$$

- Integration of endo- and exothermic reactions to achieve autothermal operation
- Short contact time to inhibit secondary reactions to maximize C_2 selectivity

Technical Status - Our innovation #2: Single atom M/SiO_2 catalysts

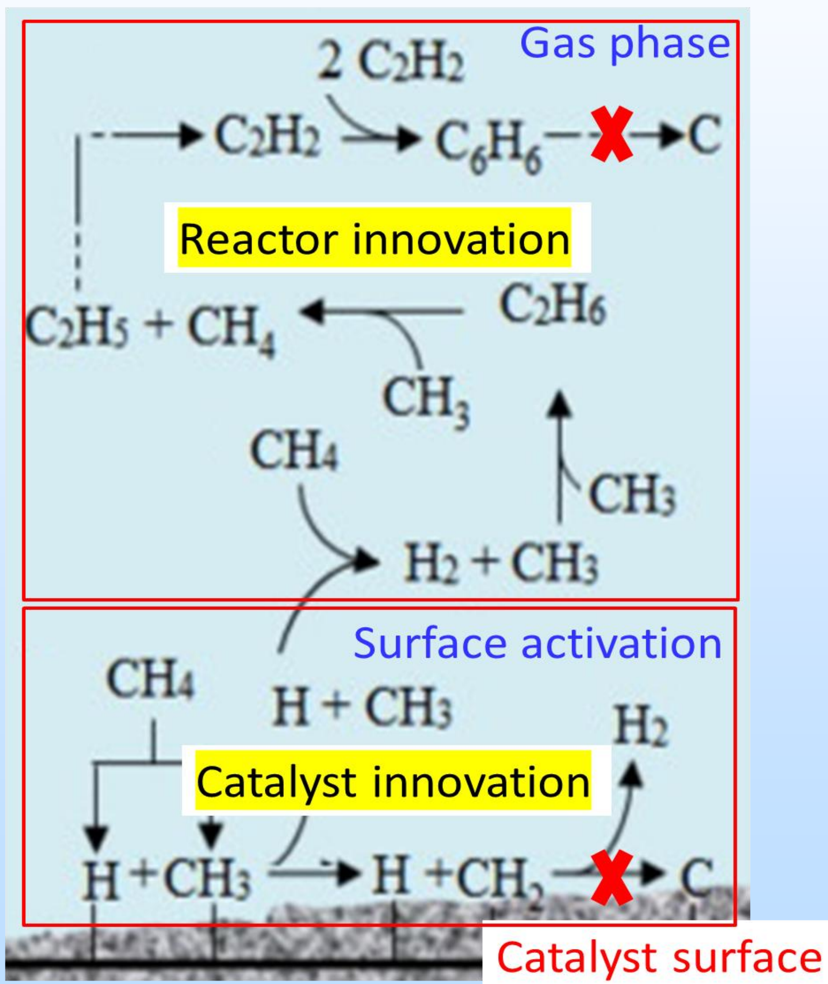
Single atom M/SiO_2 catalyst



Catalyst structure

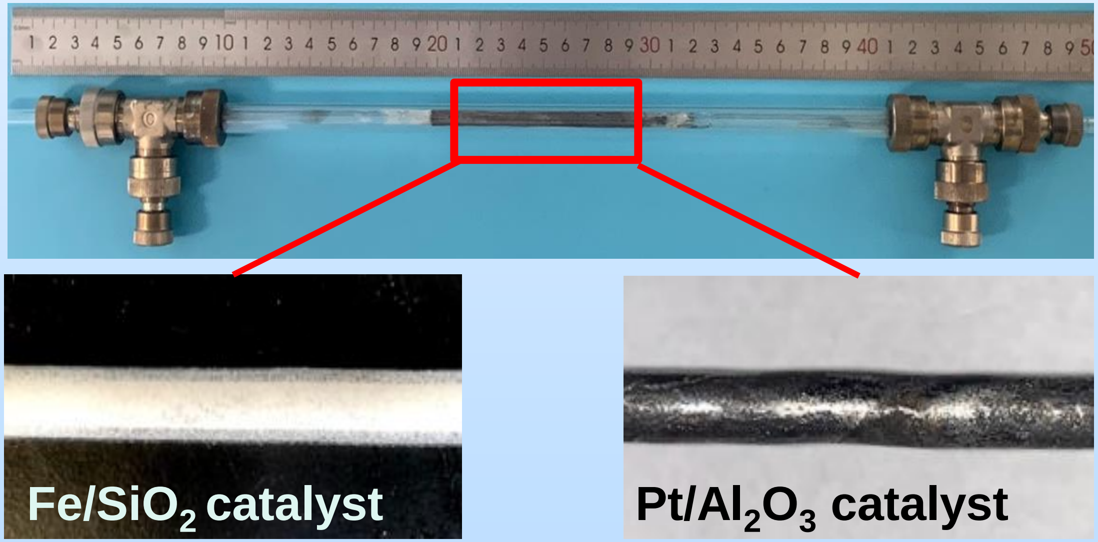
CH_4 activation mechanism (hypothetical)

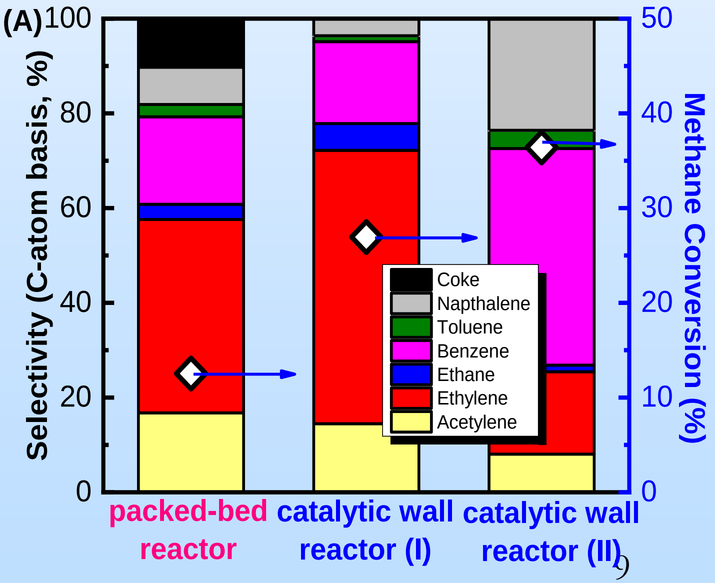
$$CH_4 = 3/52\ C_6H_6 + 5/104\ C_{10}H_8 + 9/104\ C_2H_4 + 19/13\ H_2$$



Accomplishments to Date - #1: Autothermal catalytic wall reactor development & test

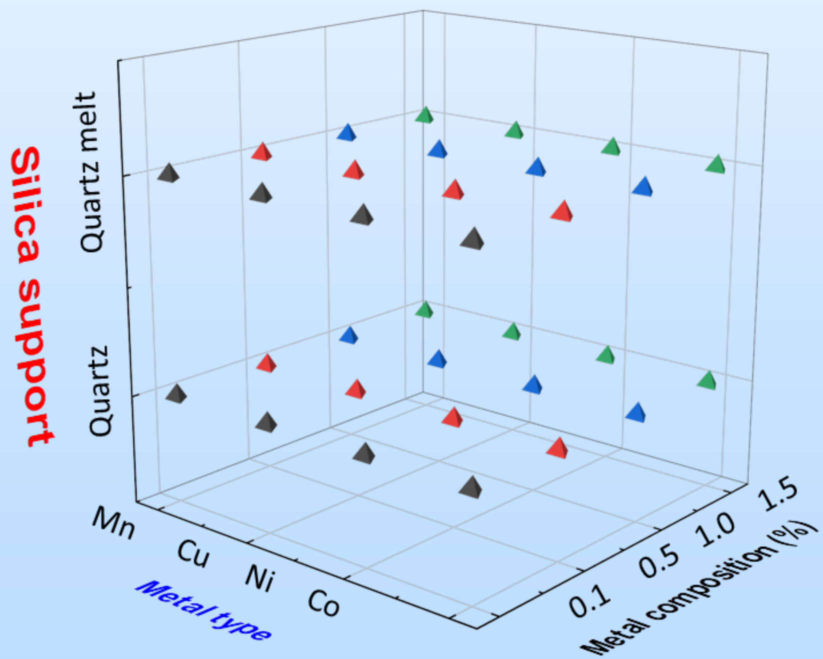
- Autothermal catalytic wall reactor was fabricated by flame fusing of Fe/SiO_2 catalyst for endothermic NMC and Pt/Al_2O_3 for methane combustion on inner and outer surfaces of reactor wall.
- NMC with high CH_4 conversion (37%), tunable and high ethylene or benzene selectivity (>99%) and negligible coke was achieved.

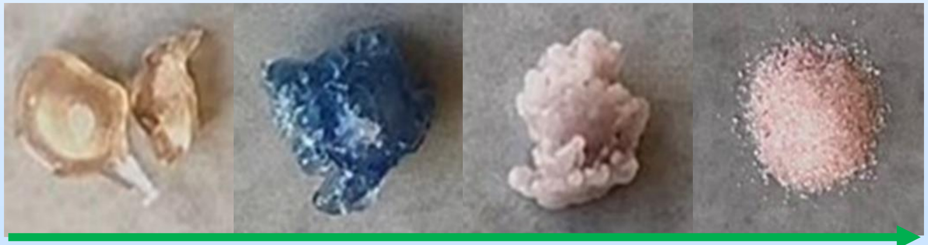




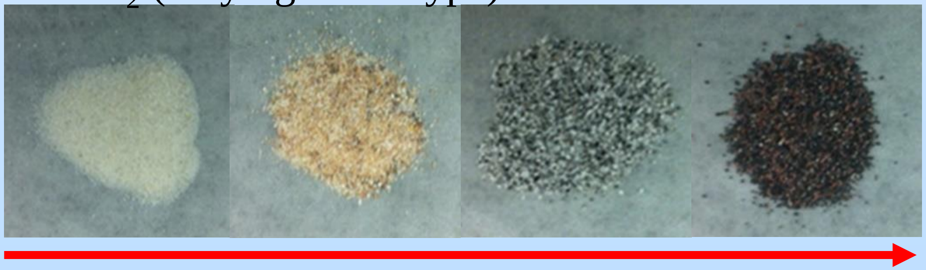
Accomplishments to Date - #2: Single atom M/SiO_2 catalyst synthesis & characterization

- Two catalyst synthesis approaches were established: furnace fusing and flame fusing to prepare M/SiO_2 catalyst.
- An array of M/SiO_2 catalysts have been prepared, in which metal type, silica crystalline phase and metal concentration were varied.
- Characterizations for synthesized catalysts are on-going.





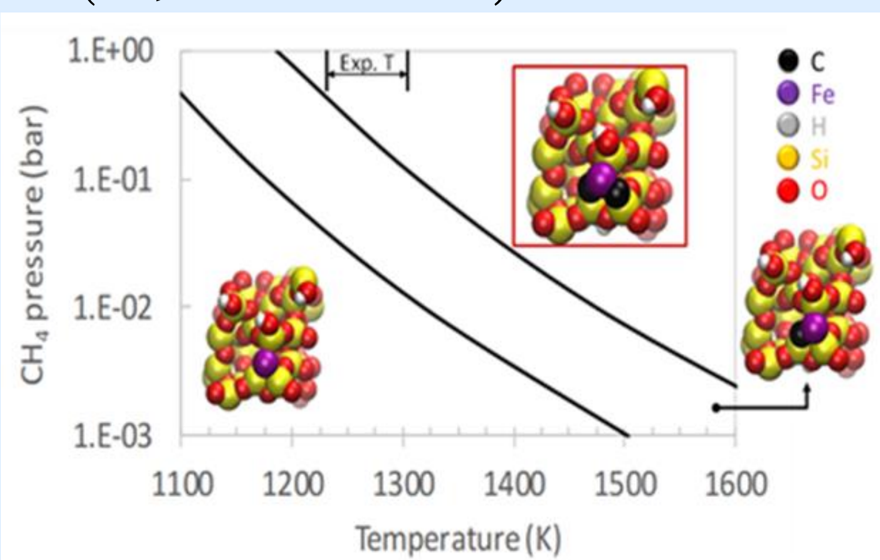
M/SiO_2 (varying metal type)

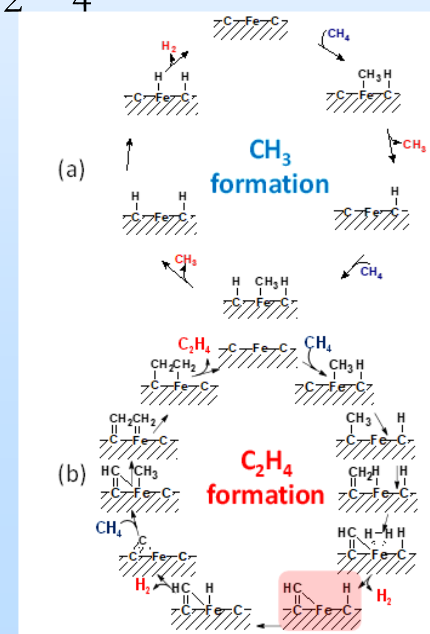


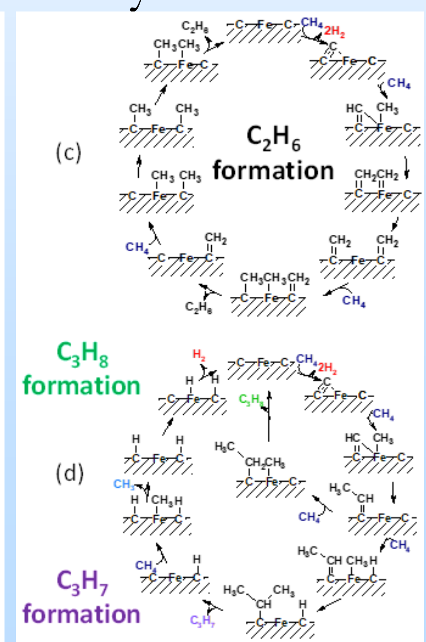
Fe/SiO_2 (increasing Fe concentration)

Accomplishments to Date - #3: M/SiO_2 catalyst activation mechanism

- Ab initio phase behavior of isolated iron atoms on amorphous silica was computed. At typical reaction temperatures and methane partial pressures, carburization of the catalyst occurs.
- The catalytic reaction network for C_1-C_3 species formation from methane over isolated FeC_2 was calculated. Gas-phase chemistry (10,000 reactions) was included. C_2H_4 forms on the catalyst.

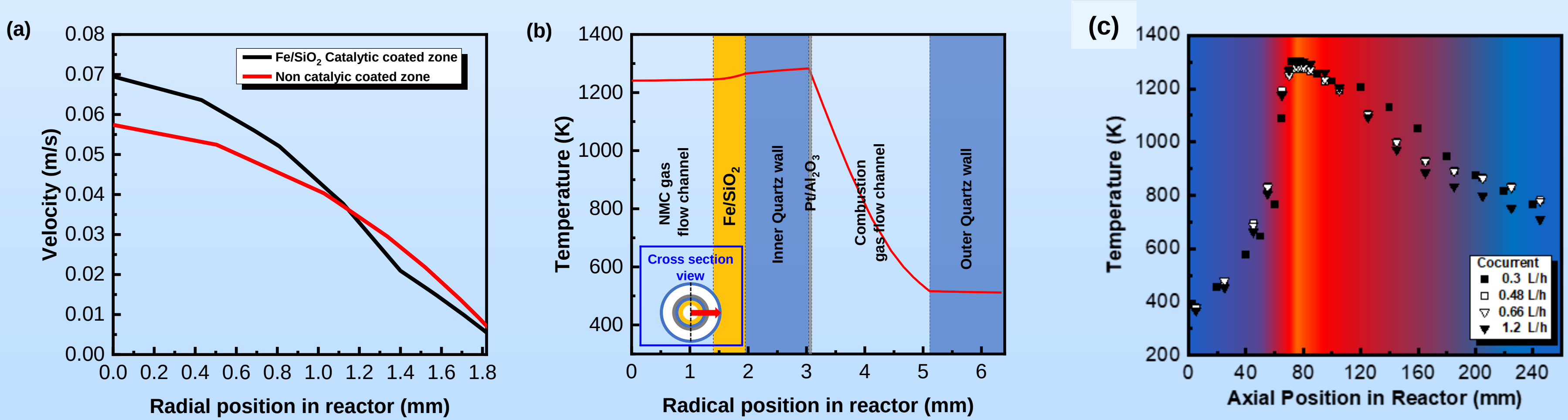






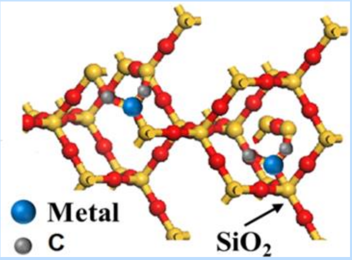
Accomplishments to Date - #4: Catalytic wall reactor process simulation

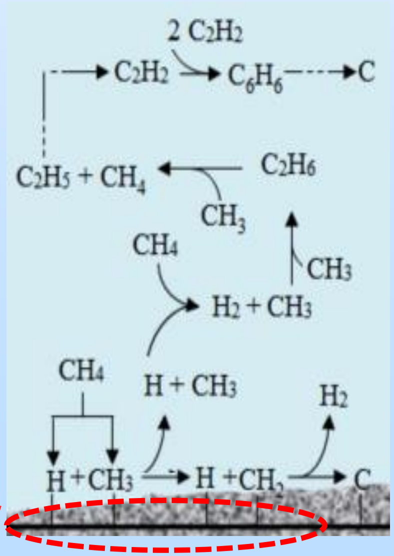
- COMSOL simulation in combination with measured experimental process parameters were used to understand the reactor temperature and species profiles along the radial and axial directions.
- Coupling of endo- and exo-thermic reactions across reactor wall promotes heat transfer across thermal boundary layers, while a sharp temperature profile is observed along the axial direction.



Lessons learned – Experimental challenges and changes to be made next time

- NMC reaction is tested at a medium-high temperature range, which experiences a mixed surface and gas phase reaction network. In order to precisely test catalyst properties, decoupling the surface and gas phase reactions is needed.
- In the next experiment, reactor design and fabrication will be studied to minimize the gas phase reaction.
- Correlations between catalyst physicochemical properties and NMC performance will be established.





Lessons learned – Computation challenges and changes to be made next time

- The degree of carbonization of the metal atom varies with the metal → repeat first-principles (DFT) calculations on every metal
- Spin cross coupling may occur on some systems → No periodic DFT calculations can handle this
- CFD simulations with detailed chemistry is impractical → Mechanism reduction is necessary

Synergy Opportunities

- In the “Natural Gas Infrastructure Upcycling” session, several projects on methane conversion in the absence of oxidants are being explored. The catalysts developed in our project could be integrated into those systems such as plasma and microwave assisted methane conversions.
- The catalyst and reactor systems as well as NMC performances obtained from this project could be input into the ceramic membrane reactor studies to further advance the methane conversion and product yields.
- More generally, in the “Oil and Gas session”, the NMC performance data could be integrated with upstream studies to explore technoeconomics of the NMC process for natural gas valorization.

Project Summary

- An array of M/SiO_2 catalysts with different metal and support compositions were prepared. The on-going research is studying their psychochemical and catalytic properties, and the correlations between both characteristics.
- Autothermal catalytic wall reactor was innovated, concurrently solving the challenges in NMC process, i.e., heat supply, coking, low methane conversion and hydrocarbon selectivity, etc.
- Computational efforts resolved the methane activation and the subsequent reaction steps on the single atom Fe/SiO_2 catalyst.
- Process simulations revealed the process features of the autothermal catalytic wall reactor under medium-high temperature conditions for NMC.
- In the next steps, advanced catalyst testing will be conducted to reveal the best catalyst formulations for NMC. Suppression of gas-phase reaction by advanced reaction design will be conducted.
- Mechanism reduction will be performed to enable CFD simulations and reactor optimization.

Appendix

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

Benefit to the Program

- Program goals being addressed: This research addresses the program's goals on "Early-stage development and evaluation of multifunctional catalysts for the conversion of methane to liquid petrochemicals (for example, but not limited to, methanol, ethanol, ethylene glycol, acetic acid, C_3 and C_4 analogs, C_{4+} olefins, and Benzene, Toluene, Xylene (BTX)) suitable for transportation and conversion into performance products." and "Research in this area will focus on process intensification (PI) methods at the nano- to micro-scale to design materials that facilitate high catalyst activity, product yield and selectivity, and mass and heat transfer rates; while also incorporating feed/product, fractionation, and purification." in Topic Area 2A: Multi-Functional Catalysts and will provide principles for Topic Area 2B on Process Intensification..
- Project benefits statement: The research project creates novel, resilient, inexpensive, active and selective catalyst materials for non-oxidative methane conversion (NMC) and integrate them in a novel catalytic wall reactor to achieve an efficient, scalable, and intensified NMC. The technology, when successfully demonstrated, will provide an improvement over current gas-to-liquids (GTL) processes via NMC of 200 percent concerning performance and 50 percent concerning cost. This technology contributes to the Fossil Energy Research and Development Program's effort of ensuring catalyst and modular equipment as well as process intensified design concepts for conversion of flare gas to high-value carbon products (Goal).

Project Overview

Goals and Objectives

- Overarching goal: Create novel, resilient, inexpensive, active and selective catalysts to concurrently conquer all these constraints and integrate them in an efficient, scalable, and intensified NMC reactor.
- Research objectives:

(1) Synthesize isolated single atoms of various metals in a silica matrix to prove universality of these catalysts in CH4 activation, provide data for catalyst optimization, and select the best one;

(2) Probe in situ and operando the surface and bulk structure of the 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 objectives.

Organization Chart

DOE
Program Officer

Project lead (UMD)
(Dr. Dongxia Liu)

Task lead
UMD (Dr. Dongxia Liu)
Experimental team

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

	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

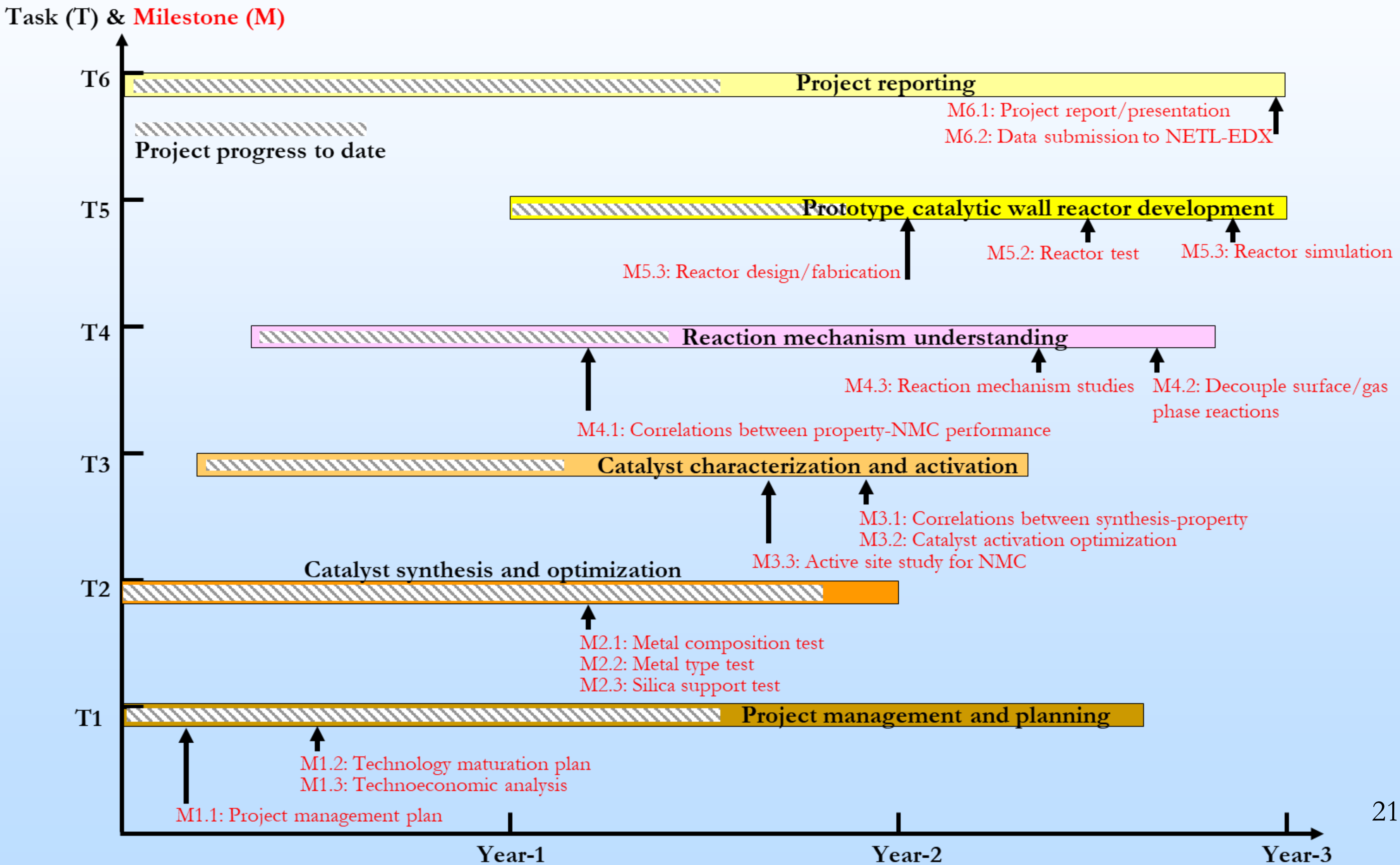
UMD
Graduate student

UD
Graduate student

UMD
Graduate student

UD
Postdoc fellow

Gantt Chart



Task (T) & Milestone (M)
T6
Project reporting
Project progress to date
M6.1: Project report/presentation
M6.2: Data submission to NETL-EDX
T5
Prototype catalytic wall reactor development
M5.3: Reactor design/fabrication
M5.2: Reactor test
M5.3: Reactor simulation
T4
Reaction mechanism understanding
M4.3: Reaction mechanism studies
M4.2: Decouple surface/gas phase reactions
M4.1: Correlations between property-NMC performance
T3
Catalyst characterization and activation
M3.1: Correlations between synthesis-property
M3.2: Catalyst activation optimization
M3.3: Active site study for NMC
T2
Catalyst synthesis and optimization
M2.1: Metal composition test
M2.2: Metal type test
M2.3: Silica support test
T1
Project management and planning
M1.2: Technology maturation plan
M1.3: Technoeconomic analysis
M1.1: Project management plan
Year-1
Year-2
Year-3

Bibliography

- Toraman, H. E., Alexopoulos K. , Oh, S. C., Cheng, S., Liu, D., and Vlachos, D. G., 2021, Ethylene Production by Direct Conversion of Methane over Isolated Single Active Centers. Chemical Engineering Journal, v. 420, article #: 130493, available at: https://www.sciencedirect.com/science/article/pii/S1385894721020799.

- Cheng, S., Malhotra A., Liu, Z., Albertus P., Tran, D., Vlachos, D. G., and Liu, D., 2021, Self-sustaining Nonoxidative Methane Coupling in Autothermal Millisecond Catalytic Wall Reactor, Manuscript to be submitted.

- Liu, Z., Schulman, E., Vlachos, D. G., and Liu, D., 2021, Optimizing Catalyst Support Structure and Composition for Direct Nonoxidative Methane Coupling, Manuscript under preparation.