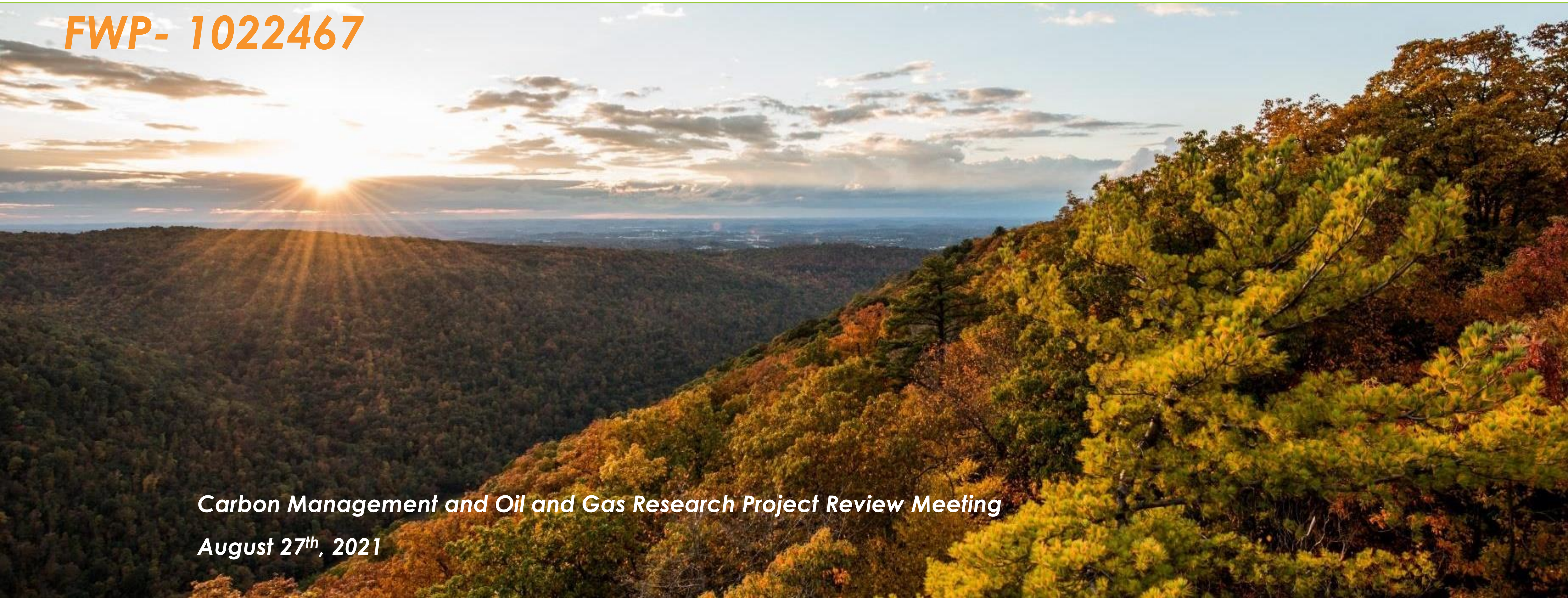
# Microwave Enhanced Flare Gas Conversion to Value-Added Chemicals

NATIONAL ENERGY TECHNOLOGY LABORATORY

Daniel J. Haynes, Pranjali Muley, Victor Abdelsayed, Hari Paudel

*FWP- 1022467*



*Carbon Management and Oil and Gas Research Project Review Meeting*

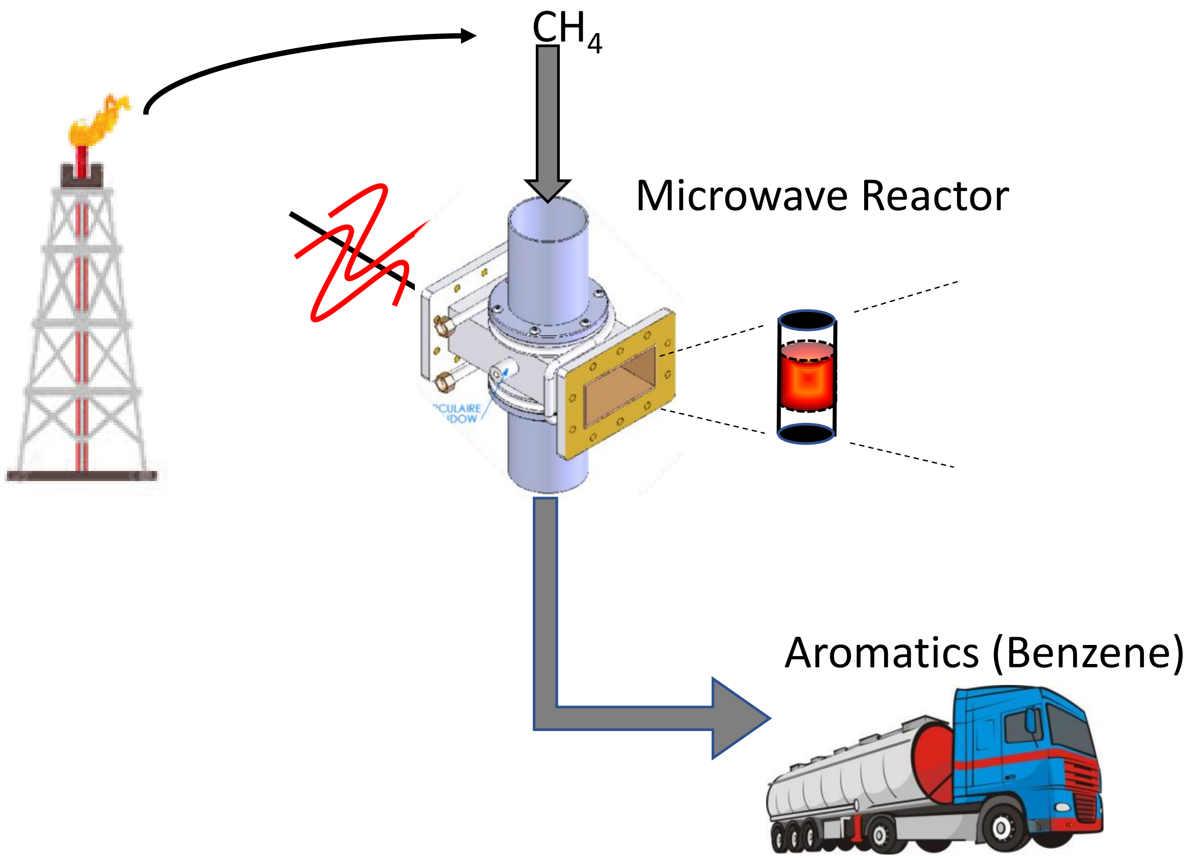
*August 27th, 2021*

# Outline

- Overview and Approach
- Timeline
- Background of MW Catalysis
- Technical Progress
- Accomplishments
- Summary/Future Work

# Project Overview

**Objective**-*Develop a modular, MW-based catalytic conversion system ready for field testing to produce BTX from distributed associated gas streams to mitigate gas flaring*



# Why Microwaves?

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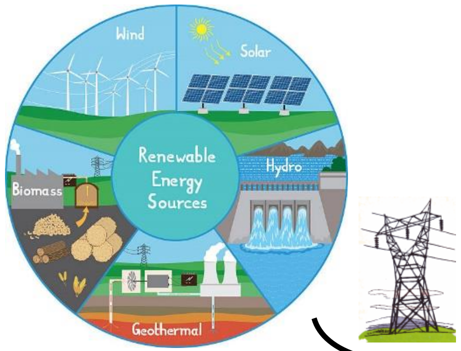
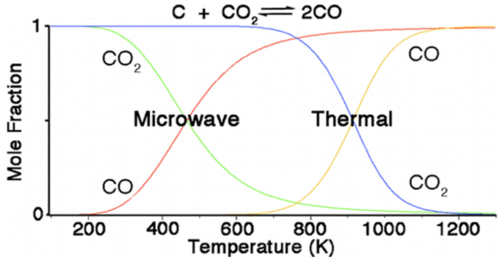
## Green Electrons

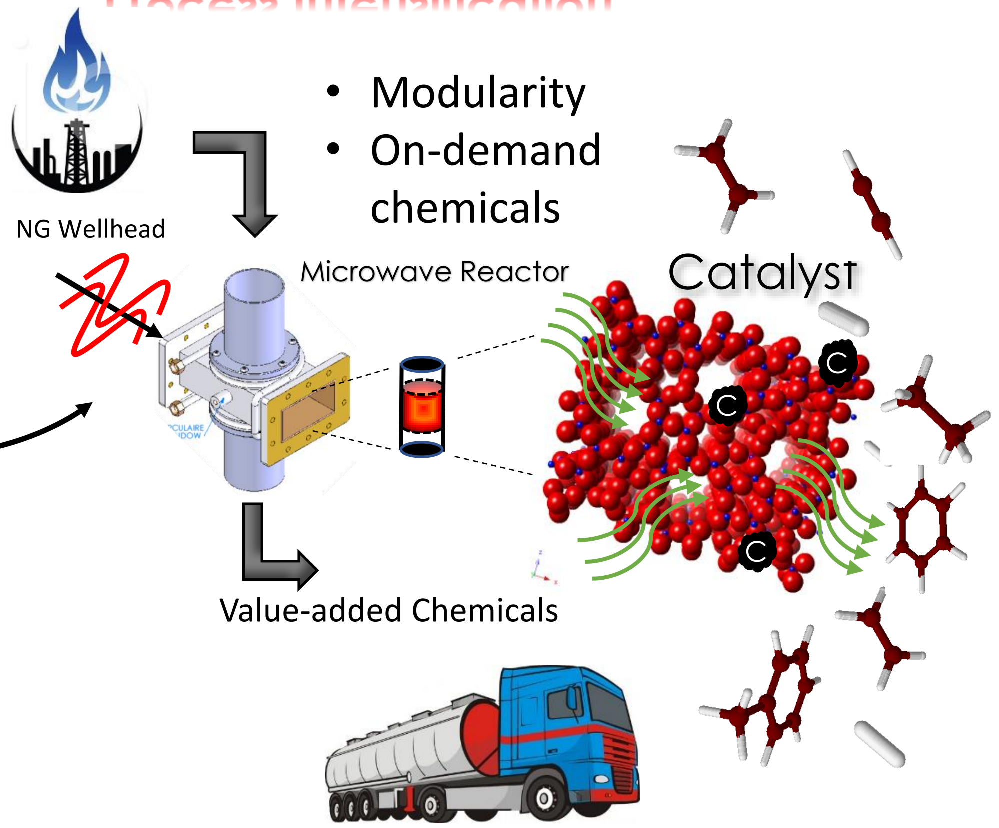



## Enhanced Rxn Rates and selectivities

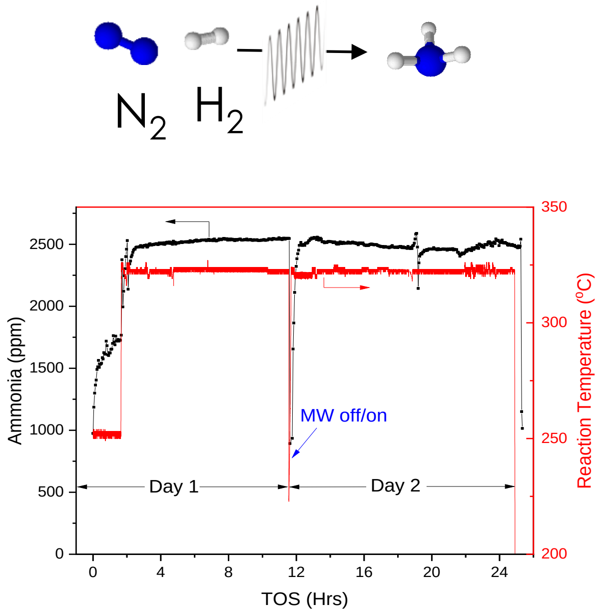



## Process Intensification

- Modularity
- On-demand chemicals



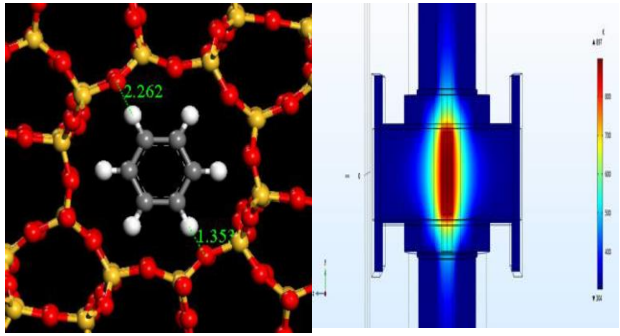

## Rapid Startup/Shutdown

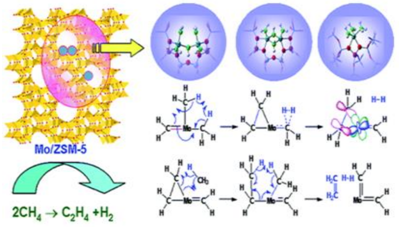


# Approach

## Develop MW-Active Catalyst from thermal state-of-the-art

- Evaluate Mo/ZSM5 MW interaction (EY 20)
  - MW heating /activation/reaction studies, parametric analysis
  - Construct COMSOL models of reactors (predict temp, MW field in reactor)
  - Develop and optimize DFT model for reaction studies
  - Comparison to traditional process
- Optimize MW Active Catalyst (EY 21)
  - Control MW field strength and temp. with heating aids (SiC), new support materials
  - Optimize MW coupling through compositional modifications
  - Mitigate carbon with promoters to control acidity and methane decomposition activity
  - High Level TEA- performance targets, preliminary process design




- Out Years- scaling studies
  - Demonstrate optimized catalyst performance long term (15h)
  - Finalize TEA/LCA
  - Scaling of catalyst synthesis and testing
  - Identify partners for reactor design construction
  - Fabrication of the reactor system and field demonstration

# Projected Timeline

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**TRL 3**

Intermediate Performance target (go/no-go) Q4EY21

**Demonstrate intermediate performance target:** MW catalyst demonstrates a higher yield of aromatics to conventionally heated process at a temperature of 700°C or below.

Performance optimization (go/no-go)

**25% hydrocarbon conversion, 80% benzene selectivity**

Q2 EY23

TRL 3

**TRL 4**

Scaling Catalyst Demonstrate Performance on 10x flows Q2 EY25

MW Reactor Design Concept

Q4 EY26

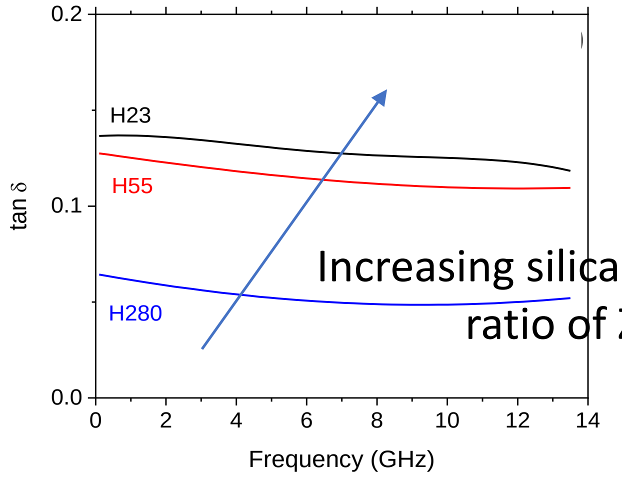
(Partnering Nuionic)

**TRL 5-6**

Fabrication of reactor and system EY28

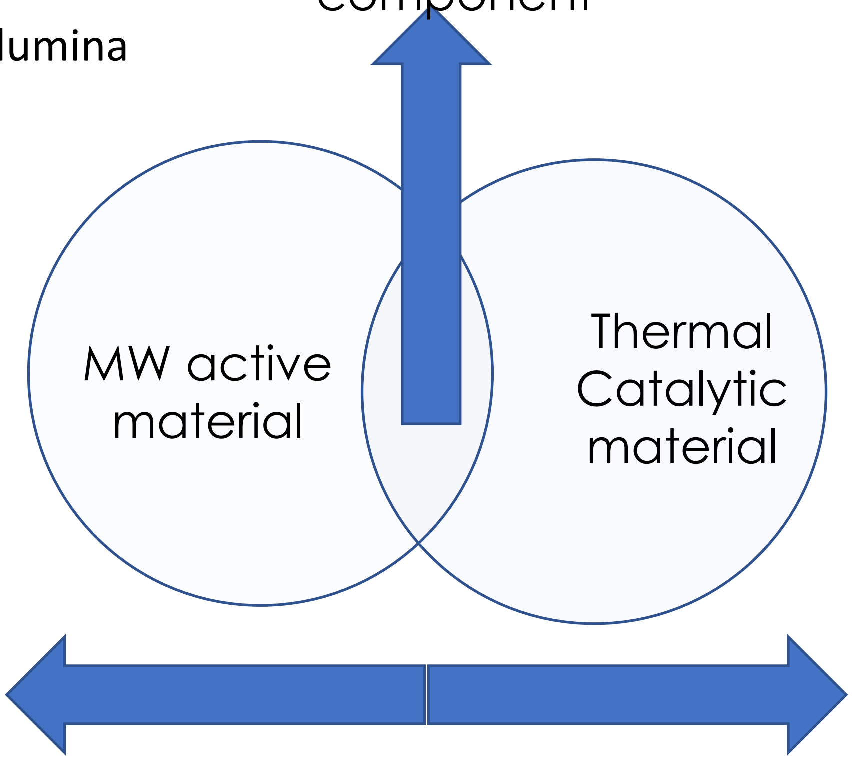
Demonstration pilot scale

# Background: Material selection criteria for MW catalysis




- Concentration of surface hydroxyl groups affects the MW absorption of zeolite

Catalyst has to be both microwave and catalytic active component




Hotspots and uncontrolled thermal runaways

No heating or requires high powers (deactivation)

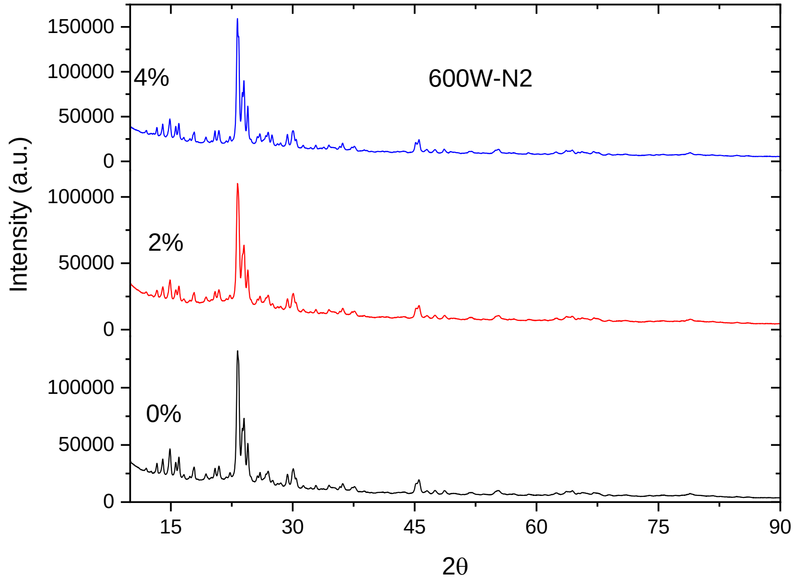
Dielectric constant
ZSM5-2.5
SiC-9.7

- ZSM-5 is a poor MW absorber
- Mo carbide is more lossy compared to ZSM-5 (helps with heating)

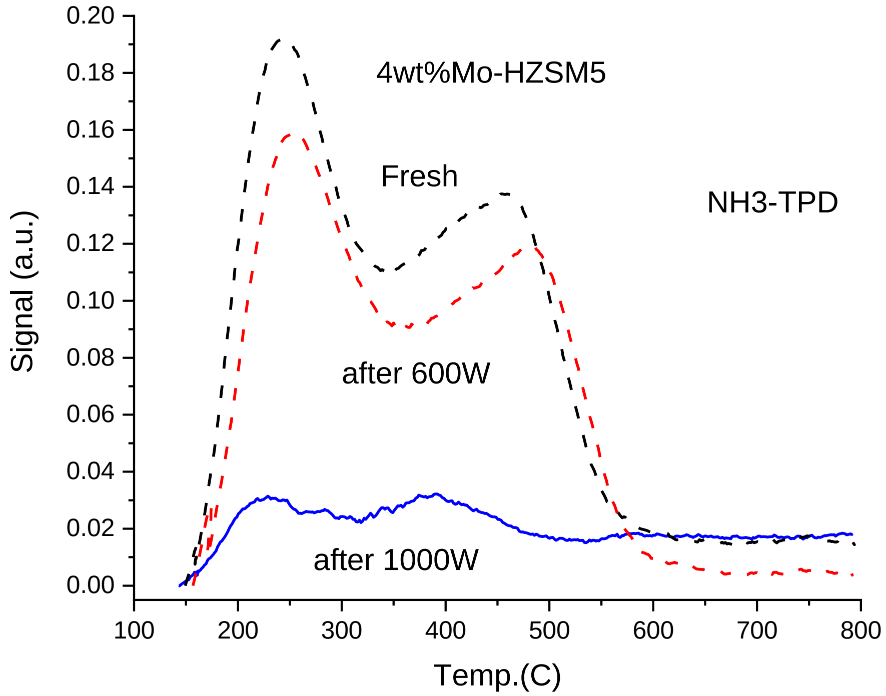
# Heating behavior of catalyst under inert N2 gas

- HZSM-5 structure can stand MW power of 600W under N2 at 200W it did not response to MW heating and at 1000W it breaks down mainly to SiO2.

- The acid properties slightly decrease at 600W under N2 compared to that under 1000W.



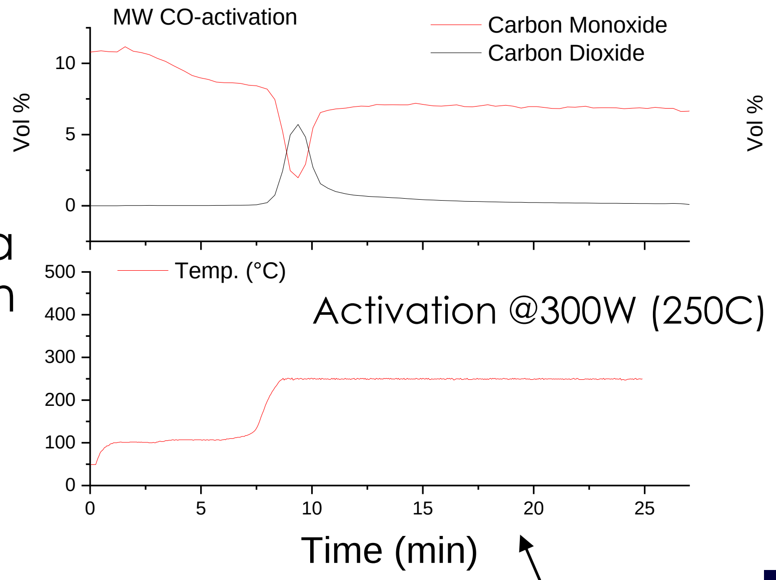

XRD of Mo/ZSM-5 with different loading after MW exposure at 600W

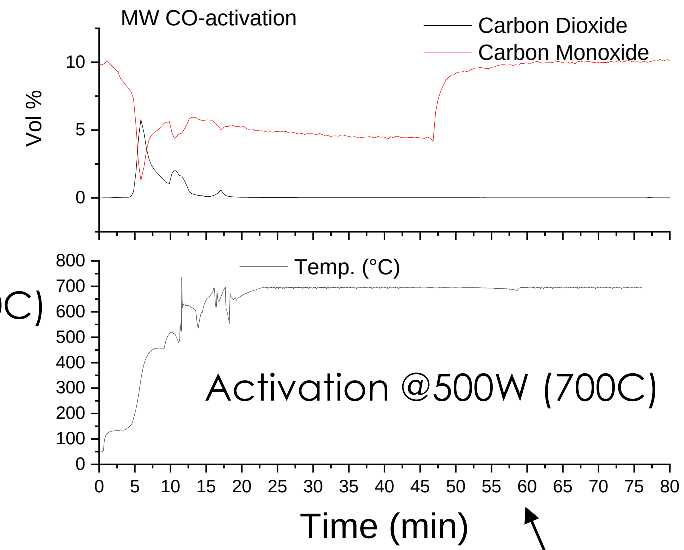


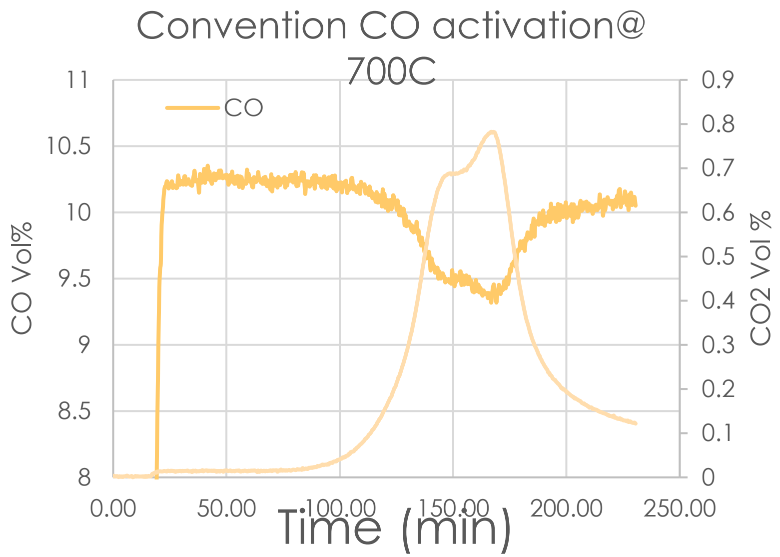

Acid properties of Mo/ZSM-5 (4wt% Mo) exposed to different MW powers (0, 600 and 1000W)

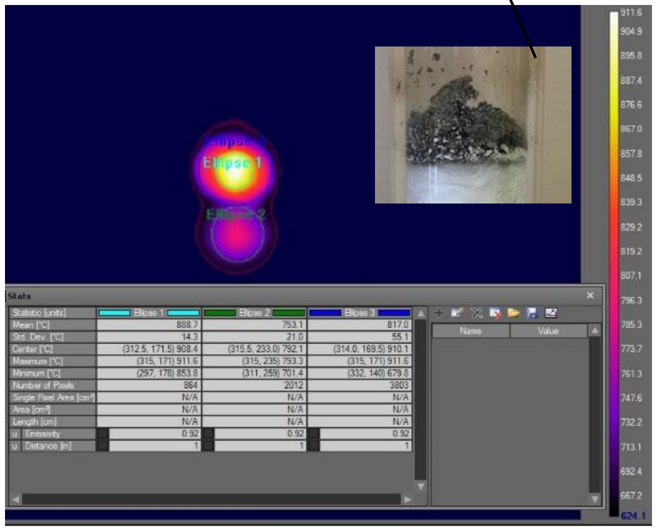
# MW activation under CO at different temperatures and powers (activation step)

- Rapid CO activation (5min) under MW compared to conventional at low temperature and power.
- At higher MW temperature a significant zeolite destruction was observed from XRD



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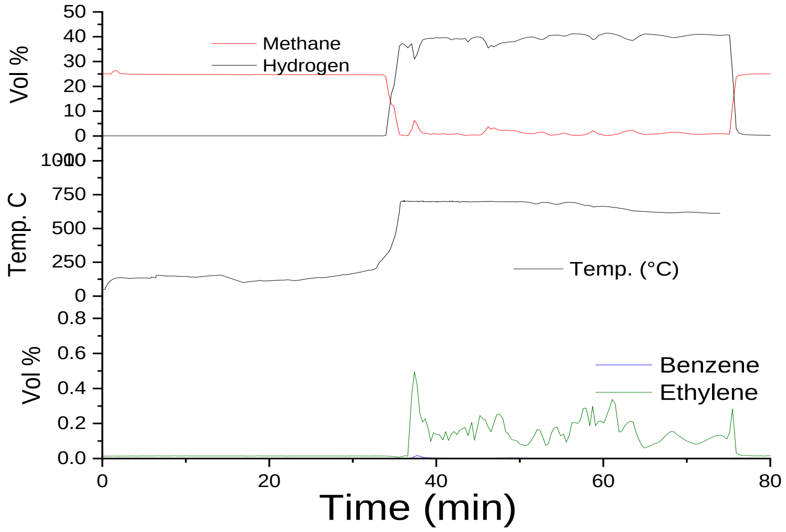
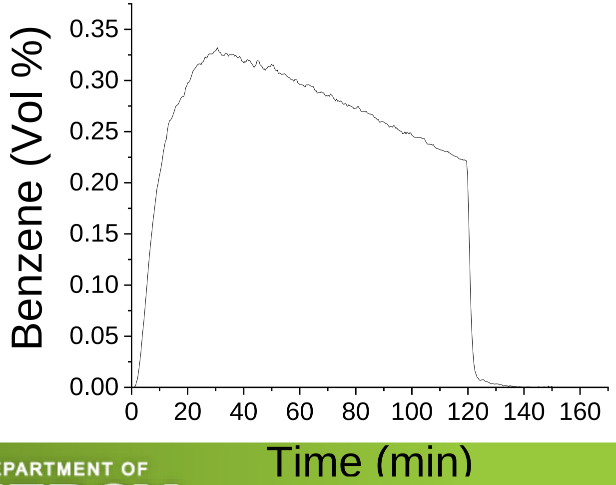
# Conventional Vs MW at 700C (high MW powers)

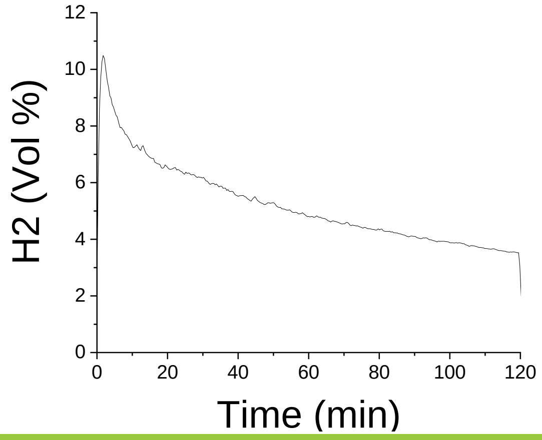
Under CO activation (900W, 700C)




- 700C MW is more selective to methane dehydrogenation reaction more than under conventional.
- Almost negligible BZ formation was observed at 700C under MW

Conventional studies @700C and CO activation



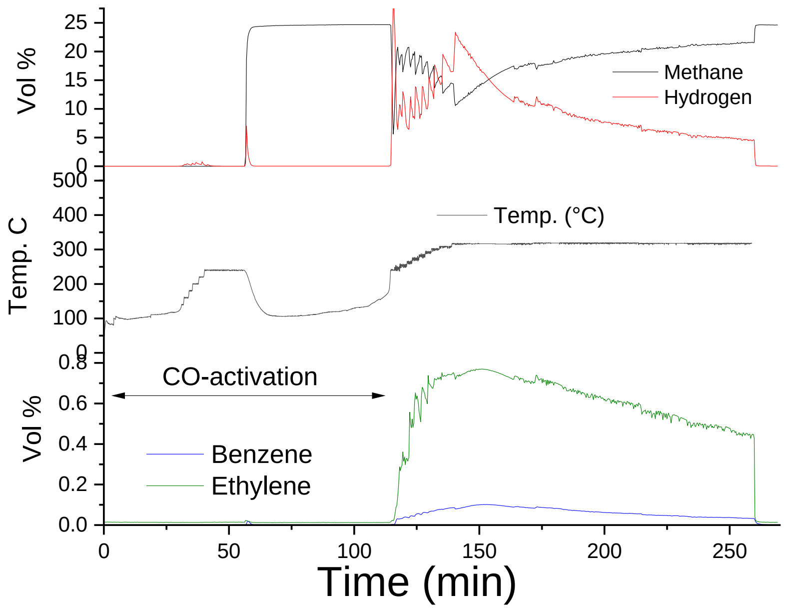

5Vol% H2 under conventional thermal reaction compared to 40% H2 under MW reaction



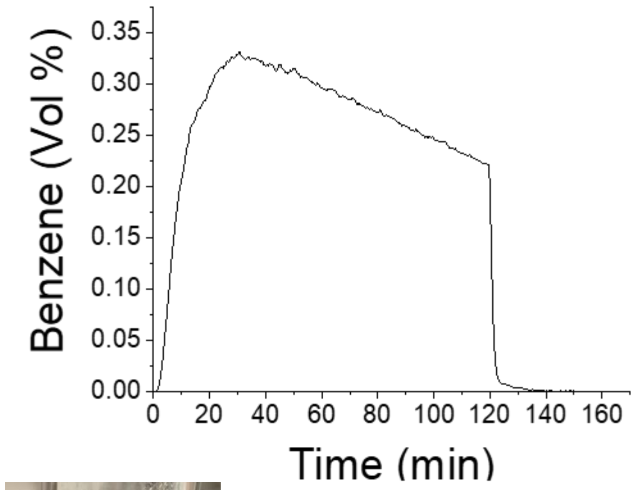
Mo 4wt% -HZSM-5 (SAR23)

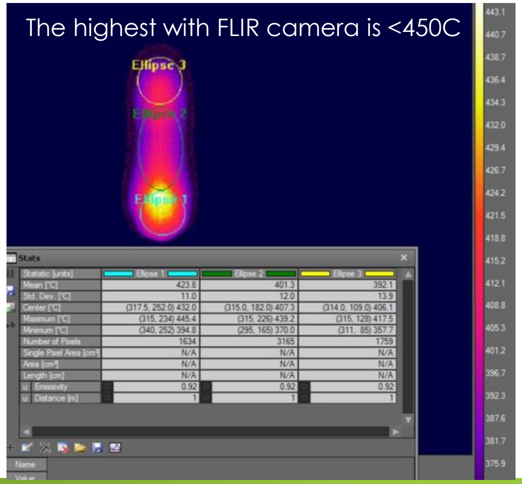
# MW conversion of methane at low temperatures (low MW powers)

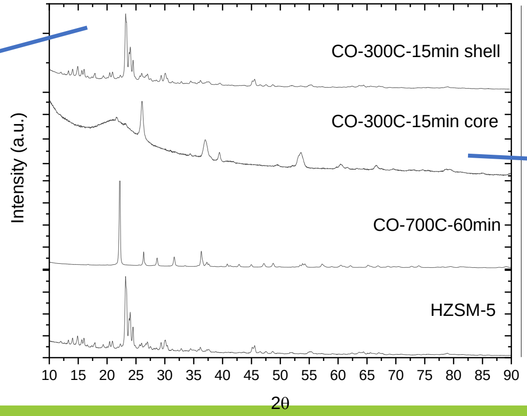
- The highest benzene yield (1100 ppm) was observed at **low MW power and temperature**
- Mo carbide species were observed in bed core suggesting that methane activation could preferentially occurring at the bed core while aromatization happening at the bed shell




Conventional studies @700C



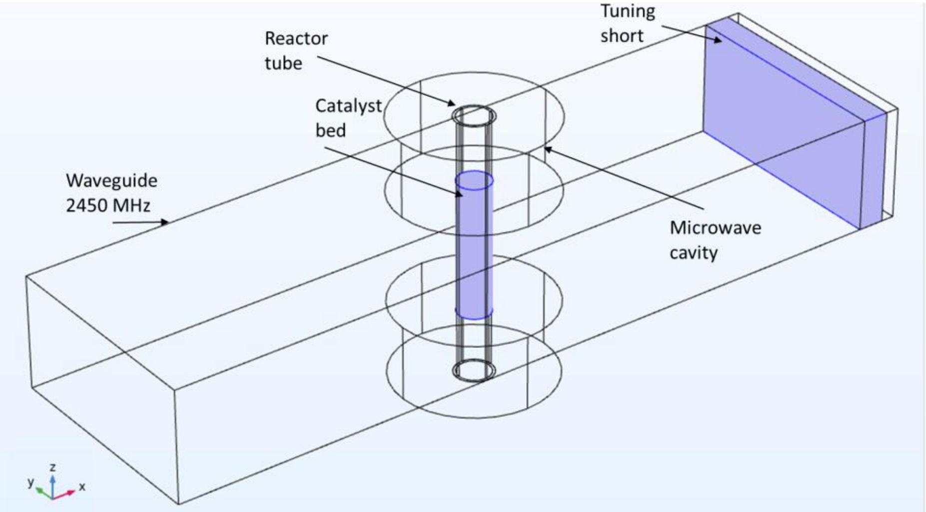




Mo 4wt% -HZSM-5 (SAR23)

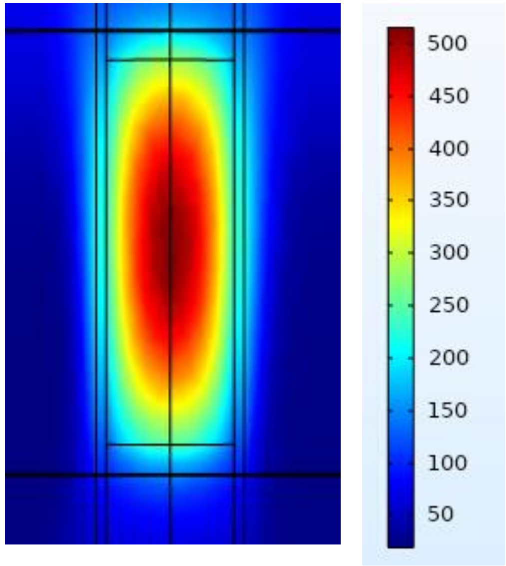
# Microwave Catalyst Development- COMSOL Modeling

- Numerical modeling to predict catalyst temperature inside the microwave reactor
- Used COMSOL Multiphysics software to develop numerical model for coupling electromagnetics, heat transfer and flow physics
- Tested effect of various reaction parameters to predict temperature uniformity and maximum achieved temperature
  - Reactor tube geometry
  - Reactor cavity dimensions
  - Effect of tuning position
  - Effect of addition of Silicon Carbide



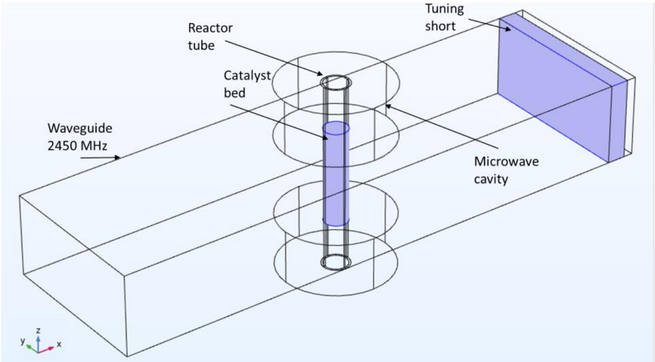
# COMSOL Modeling of Reactor Cavity

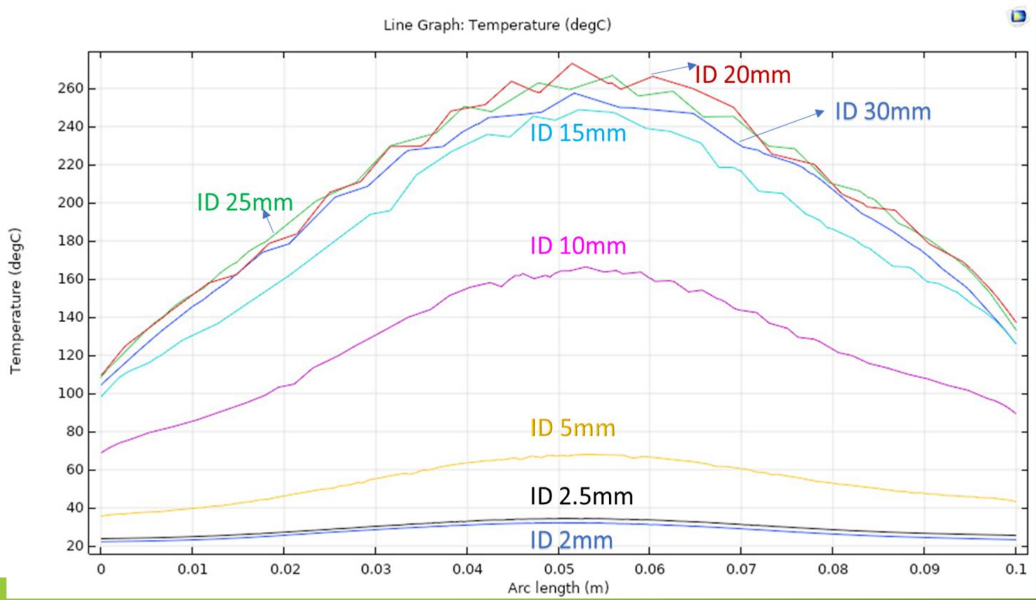
- Mo-ZSM-5 catalyst heating within the microwave cavity
  - Bed height 1.5 in
  - Reactor tube ID 0.5 in
  - Power in 100 W and time 30 min
- Mo-ZSM-5 catalyst heats inside out with significant temperature gradient along the reactor diameter
  - Temperature gradient 250 C
  - Very low thermal conductivity
  - Low loss material – not as MW- interactive
- Possible solutions
  - Mixing inert microwave absorbing material such as SiC
  - Changing tube and cavity ID to achieve uniformity
  - Changing tuning parameters



# Optimization of Temperature

- Effect of reactor tube size
  - T increases with increase in tube diameter up to 20 mm, then decreases
  - Penetration depth of Mo-ZSM-5 is 19.1 mm
  - Not enough material to absorb MW effectively at lower tube diameter
  - >20mm ID, too much material and maximum T-drops
  - 20mm tube diameter is ideal for the tested reactor type

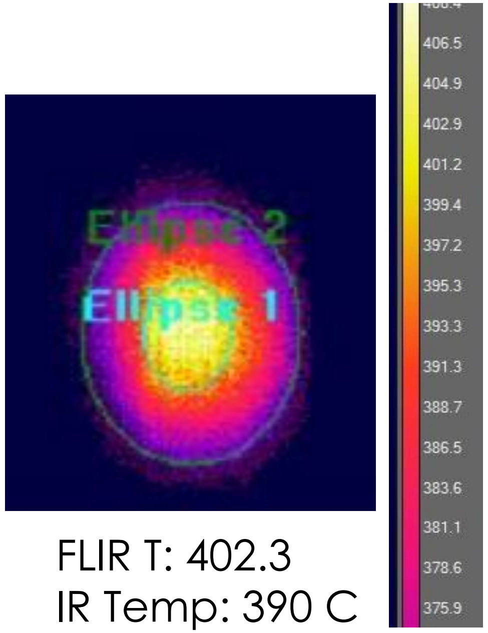


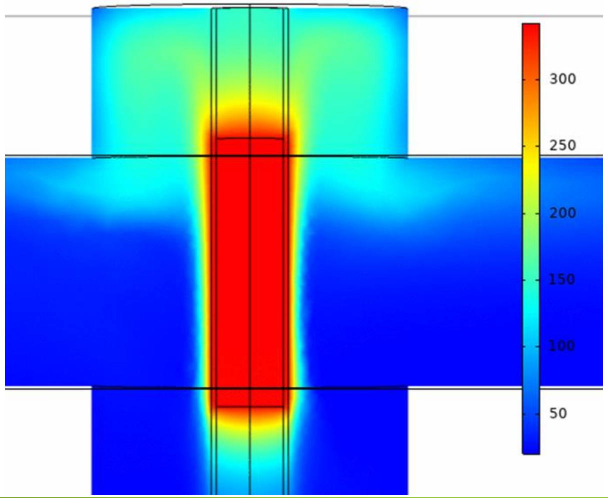

Arc length in x-axis inside catalyst bed

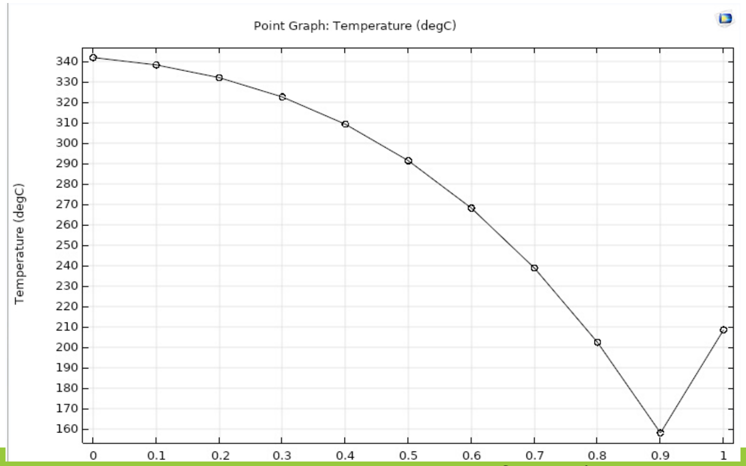
# COMSOL Heating Study with Silicon Carbide

- Mixing Mo-ZSM-5 and SiC powder in different ratios
  - Uniform temperature obtained when SiC is added
  - Higher temperature is achieved with addition of SiC
  - Experimental results in agreement with the model
  - < 10% reflected power with addition of SiC




FLIR T: 402.3
IR Temp: 390 C



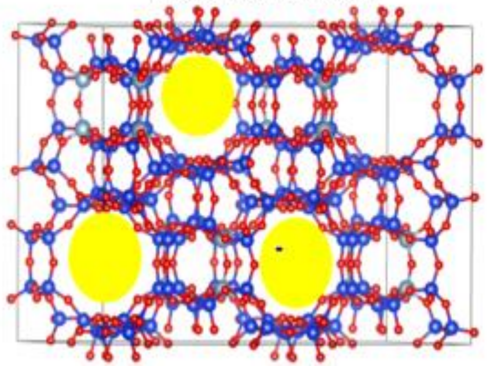




Catalyst mole fraction

# Computational Modelling of Mo-HZSM-5 for Methane Conversion

## DFT Modeling





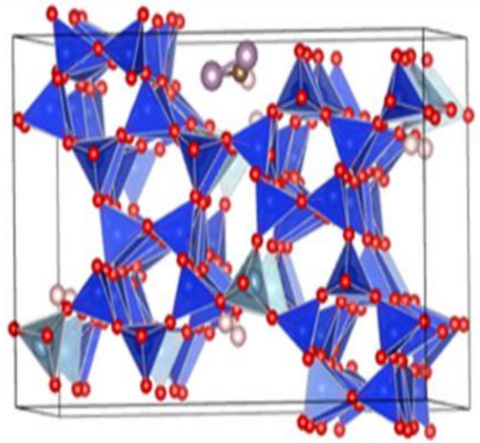
Constructing atomic scale model of Mo/ZSM-5 to understand how MW material interactions may impact the reaction chemistry

- Provide design considerations to improve absorption and enhance activity

- Optimized the structures of ZSM-5 to create system with a certain ratio of Silicon (Si) to Aluminum (Al) in reference to experimental result.

- Introduced Hydrogen (H) in the system to create Bronsted acid site and monitor adsorption energy change with respect to H doping level.

- Formation of single and bi Mo carbide were compared Higher concentration of the Brönsted acid sites leads strong chance of forming di-metal carbide type chemical compound within HZSM-5



# Accomplishments

- Understand heating and activation behavior of Mo/HZSM-5 in MW
  - Need to control carbon and MW field/absorption
- Developed a numerical model to predict temperature profiles within the catalyst bed when heated in a microwave cavity
- Established effect of baseline parameters on microwave heating of catalyst
- Tested different reactor designs to achieve temperature uniformity as well as optimum temperatures with applied power

# Challenges

- COVID quarantines in MW reactor lab
- Due to very low thermal conductivity of Mo-ZSM-5 catalyst, the catalyst heats non-uniformly
- Carbon formation changes dielectric properties of the catalyst during reaction
- Very high temperatures at the center of the catalyst bed causes structural changes to the catalyst, affecting catalyst activity
- Mixing SiC with the catalyst results in more uniform temperature profile
- Optimization of the catalyst and microwave field interaction requires an understanding of how the composition and other features (particle shape) effects on reaction kinetics under microwave irradiation.

# Summary/Next Steps

**Goal** is to control MW absorption and carbon formation to improve catalyst performance

Experimental

- Studies with SiC monolith and powder mixtures for homogeneous catalyst heating
- Begin to modify catalyst to enable resistance to carbon
- Parametric analysis- duty cycling (pulsing), effect of C2+ liquids

COMSOL

- Develop numerical model for catalyst coated SiC monolith to predict temperature profiles
- Use temperature dependent material properties to reach higher prediction accuracy of models

DFT

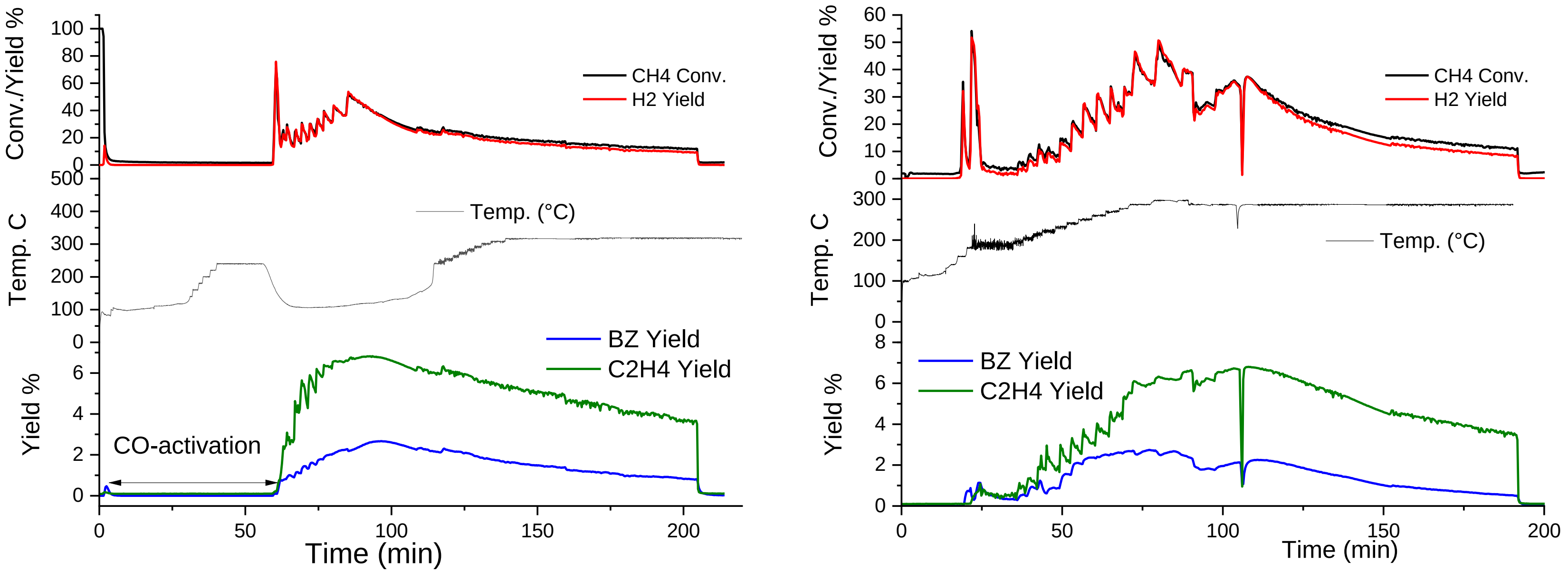
- Continue building Mo/ZSM5 model and evaluation of active sites and begin introduction of $CH_4$ determination of transition states

SSEA

- High level TEA analysis of MW system

# DHA rxn under low MW power

## Under with CO activation (left) and methane activation (right)



# Extra slides

# Technical Status

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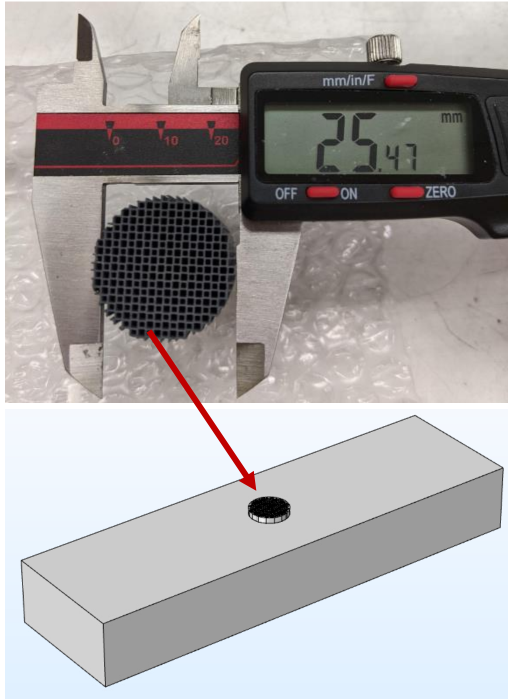
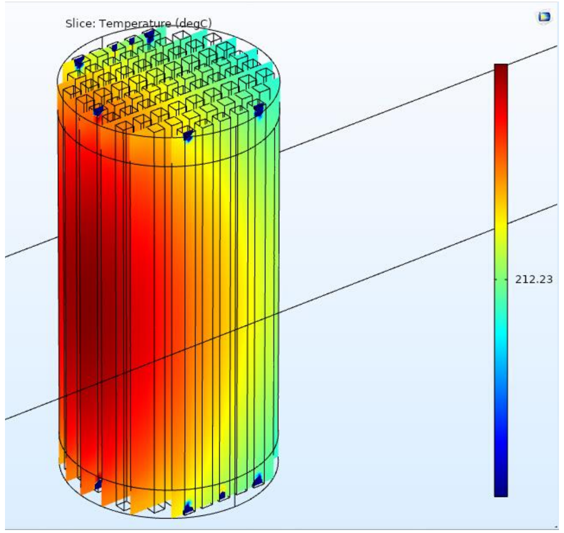
- Heating of SiC monolith in microwave reactor
  - ID = 2.54 cm or 1 in; Height – 2in
  - Dielectric constant – 10, loss – 1
  - Penetration depth Dp = 6cm (0.06m)
  - Each sq. void = 1.5 mm
  - Uniform temperature throughout height and length of monolith
  - Next step: Study the effect of catalyst coating

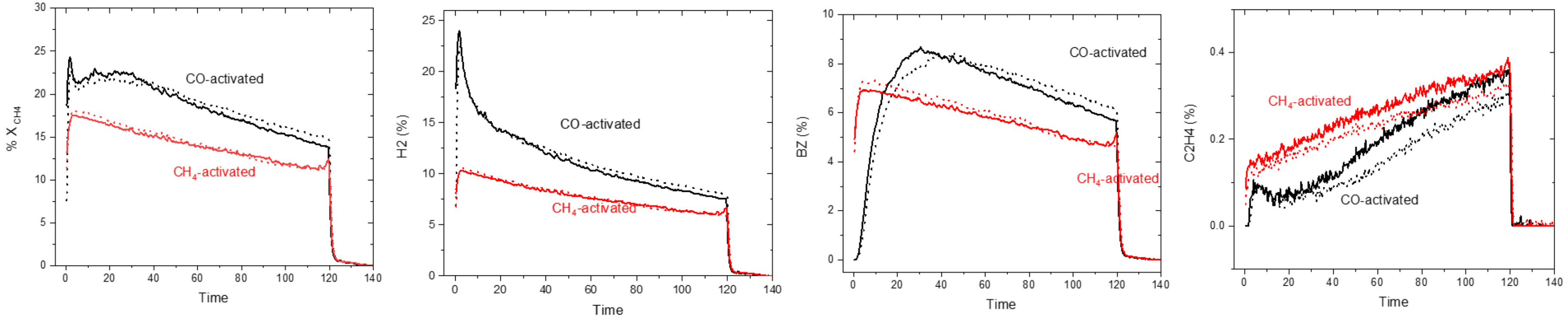


# Conventional studies @700C and different activation gases



**Catalyst was first activated then ran under methane for 2hr at 700C**




- CO activation of Mo catalyst gives higher yields compared to methane activation (likely to reduced carbon formation during activation)