Catalyst Deactivation and Stability in Microwave-assisted Methane Dehydroaromatization

Swarom Kanitkar
Research Scientist, NETL Support Contractor

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Authors and Contact Information

Swarom Kanitkar[1,2]; Victor Abdelsayed[1,2]; Xinwei Bai[1,2]; Evgeniy Myshakin[3,4]; Daniel Haynes[1]

[1]National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26505, USA

[2]NETL Support Contractor, 3610 Collins Ferry Road, Morgantown, WV 26505, USA

[3]National Energy Technology Laboratory, 626 Cochran Mills Road, Pittsburgh, PA 20136, USA

[4]NETL Support Contractor, 626 Cochran Mills Road, Pittsburgh, PA 20136, USA

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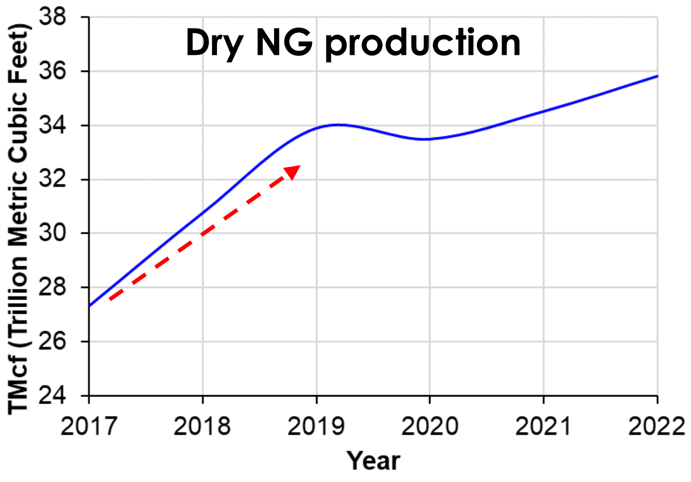
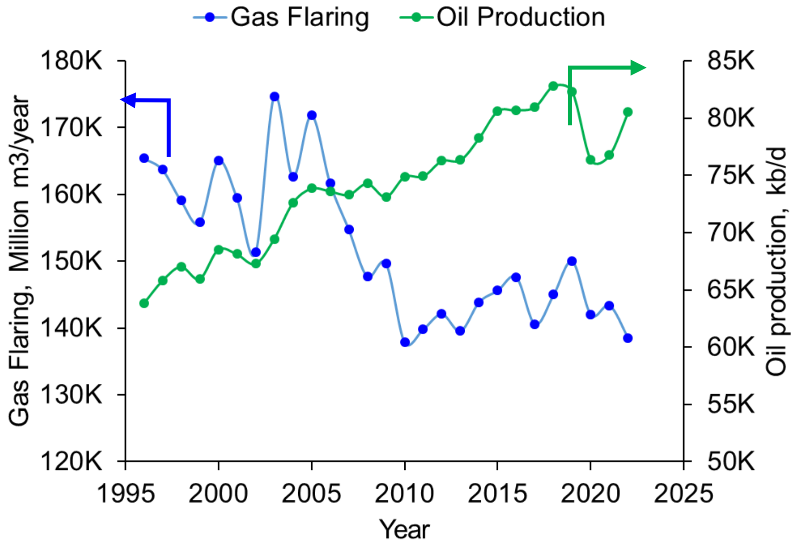
  - Reaction performance
  - Post reaction characterizations
- **Conclusions**
- **Acknowledgements**

Introduction

Natural Gas (NG) Scenario





NG flaring

- Inefficient and wastage of natural resources

- Point source for **<u>greenhouse gas emissions</u>**, e.g., CO_2 and CH_4
- Point source for volatile organic compounds (VOCs) and other hazardous air emissions
- **<u>Lost revenue</u>** for oil/gas producer and mineral rights owner
- **<u>Lost tax revenue</u>** for governments at various levels

❖ Energy Information Administration (EIA)
❖ ACS C&EN
❖ Shutterstock

Introduction

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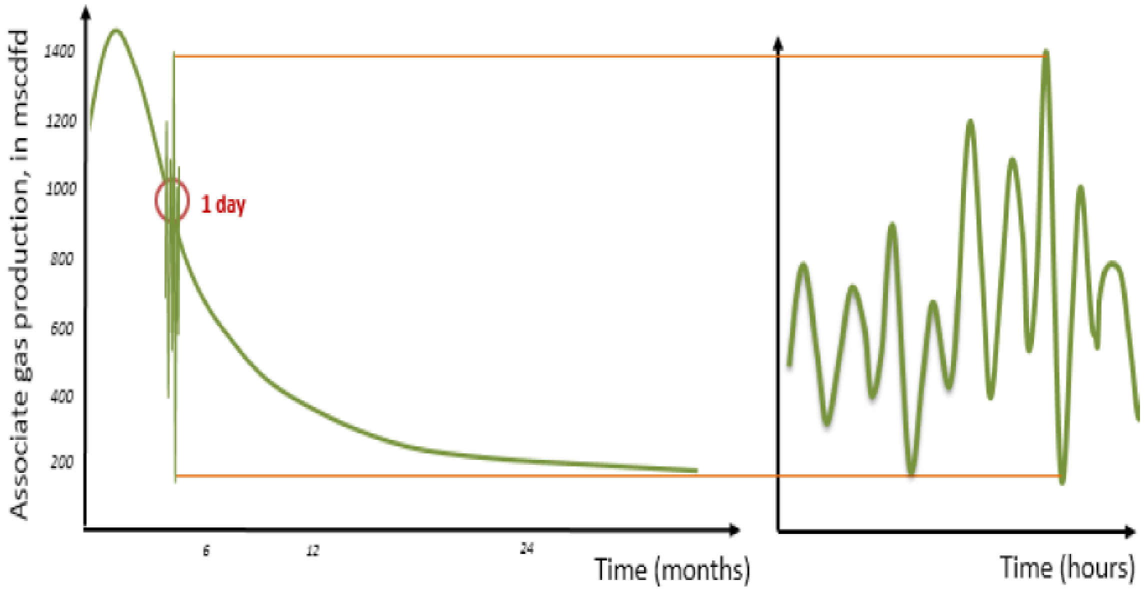
Challenges for Flare Gas Utilization

- Gas volumes and pressures vary significantly
  - Difficult to size equipment
- Composition varies between basins and wells



- **Technologies exist today** to convert methane, ethane, etc., to value-added, energy dense liquids and solid products
- However, they are only **efficient and cost effective** at **large-scales** employed in petrochemical industry
- Need alternative technologies for utilizing associated gas
  - New catalysts
  - Alternative conversion technologies (plasma, microwaves)
  - Reactor designs

Introduction

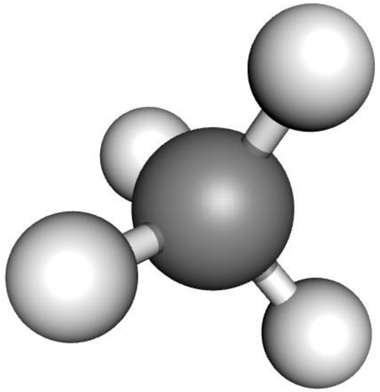
Flare Gas Utilization - Methane Dehydroaromatization

Component	Composition
Methane, CH_4	50-60%
Ethane, C_2H_6	20-25%
Propane, C_3H_8	10-12%
N-butane, C_4H_{10}	1-5%
Nitrogen, N_2	0-3%
Carbon Dioxide, CO_2	1-3%

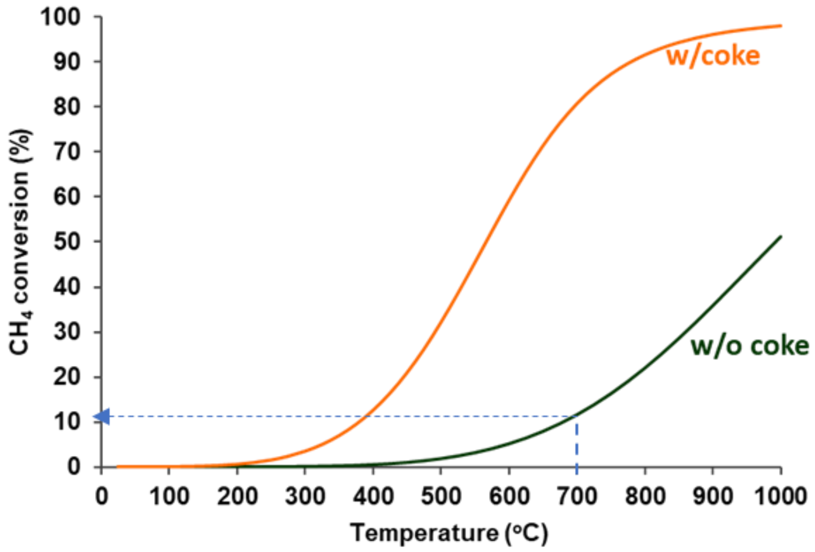
Bakken Oil Field, North Dakota

- **Single step conversion**:

$$6\,CH_4(g) \rightarrow C_6H_6(g) + 9\,H_2(g)\uparrow,\ \Delta G_{298\,K} = 433\ \text{kJ/mol}$$



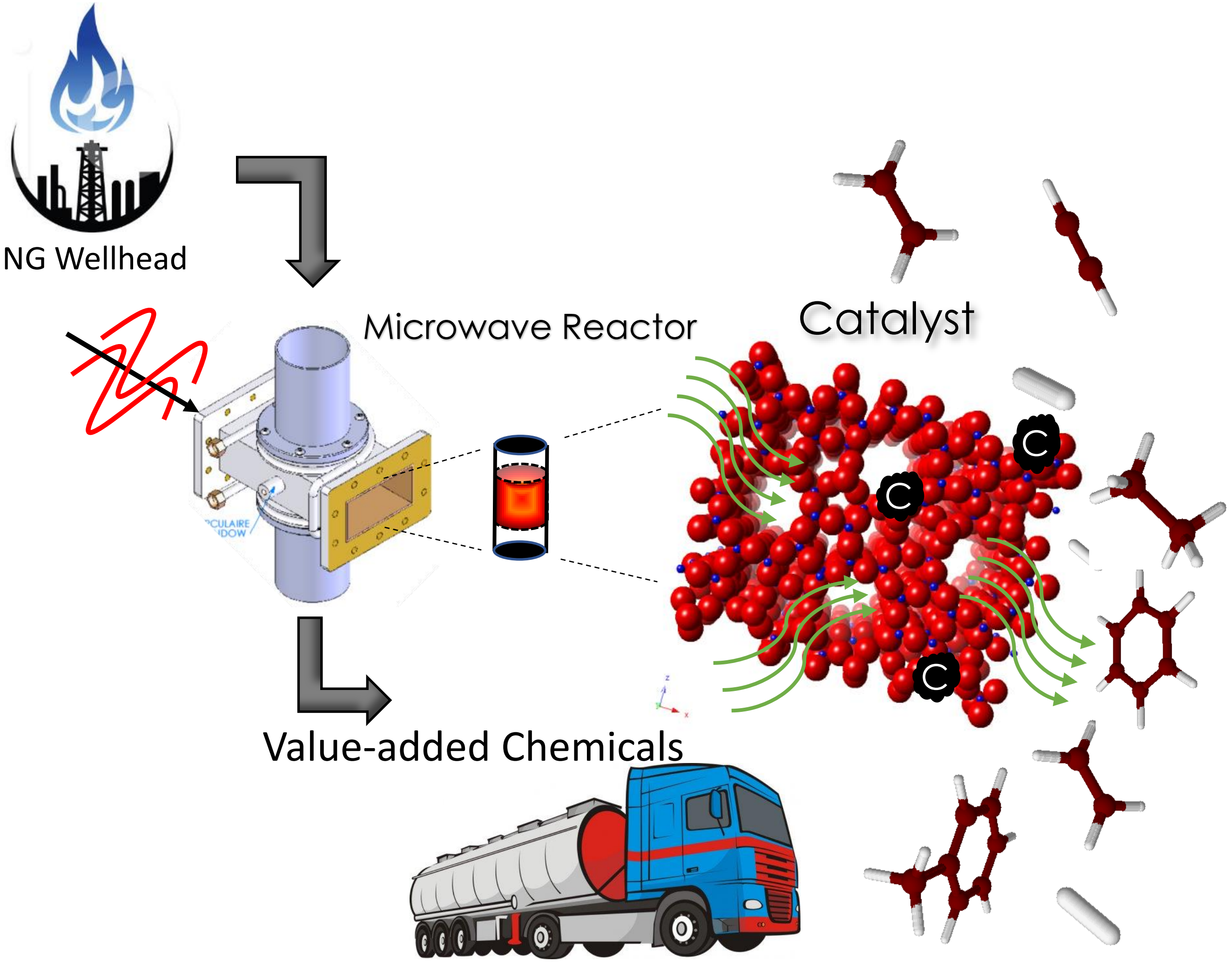
- State of the art catalyst - **Mo/HZSM5**
- **Challenges**:
  - Equilibrium constrained (~12%)
  - High temperatures (700 °C)
  - Carbon deposition



- https://ndpipelines.files.wordpress.com/2020/09/assessment-of-bps-produced-gas-compositions-sep20-final.pdf
- molview.org
- HSC Chemistry 10

Introduction

Why Microwaves?

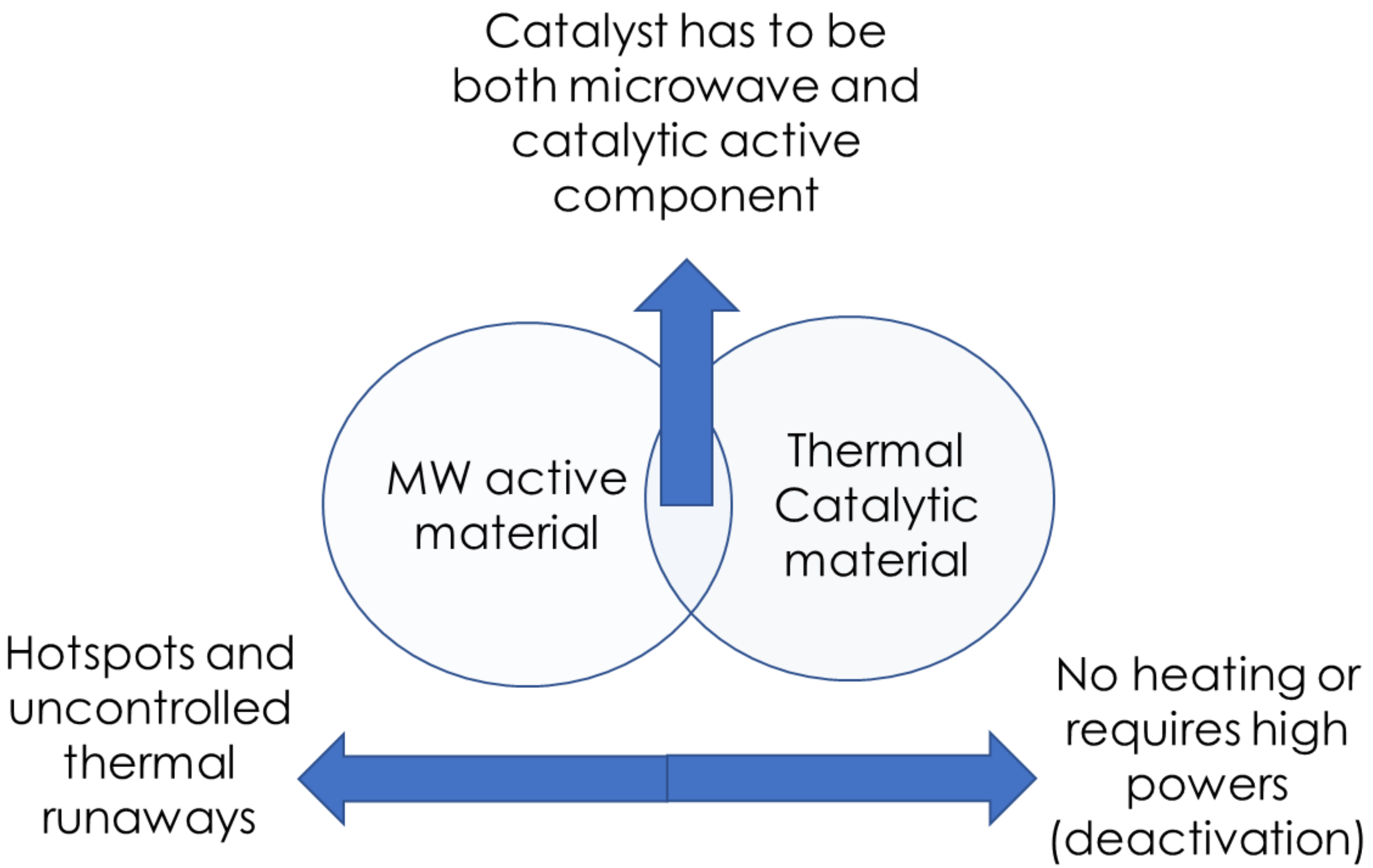


- Selective volume-based heating
- Rapid startup/shutdown
- Enhanced reaction rates and selectivities
- Direct natural gas – additives already present

❖ Abdelsayed, V. et al. *Catal. Tod. 2021*, ***365***, *88.*

Catalyst

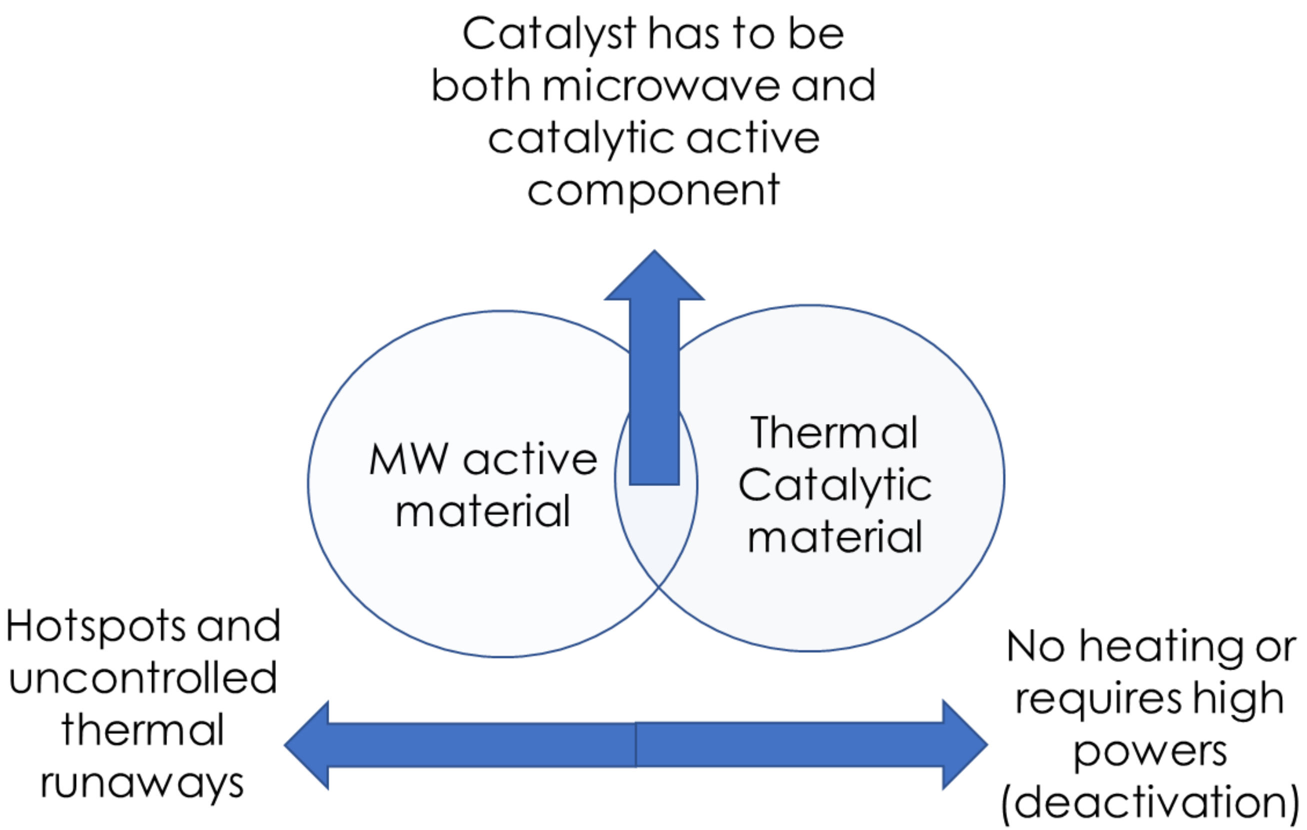
Requirements for Microwave Catalysts

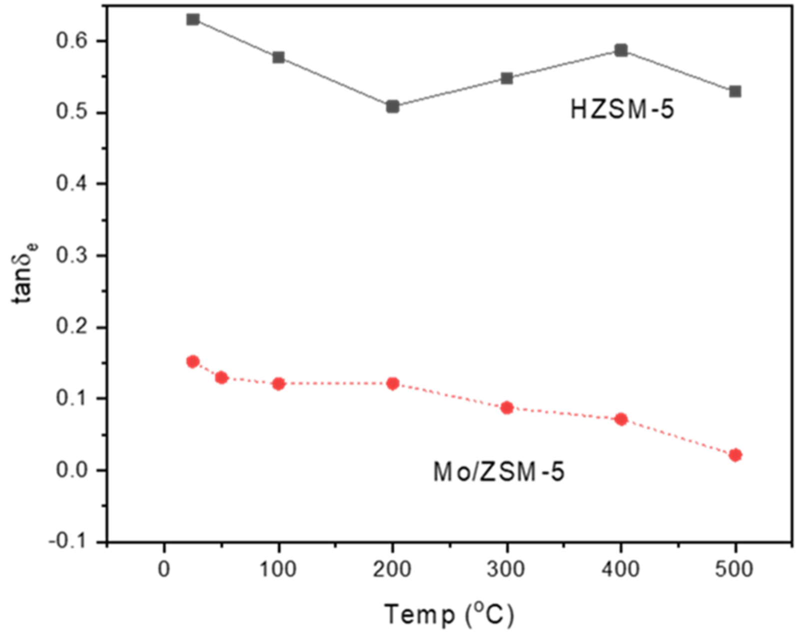


❖ Abdelsayed, V. et al. *Catal. Tod.* *2021*, ***365***, *88.*

Catalyst Characterizations

Dielectric Properties



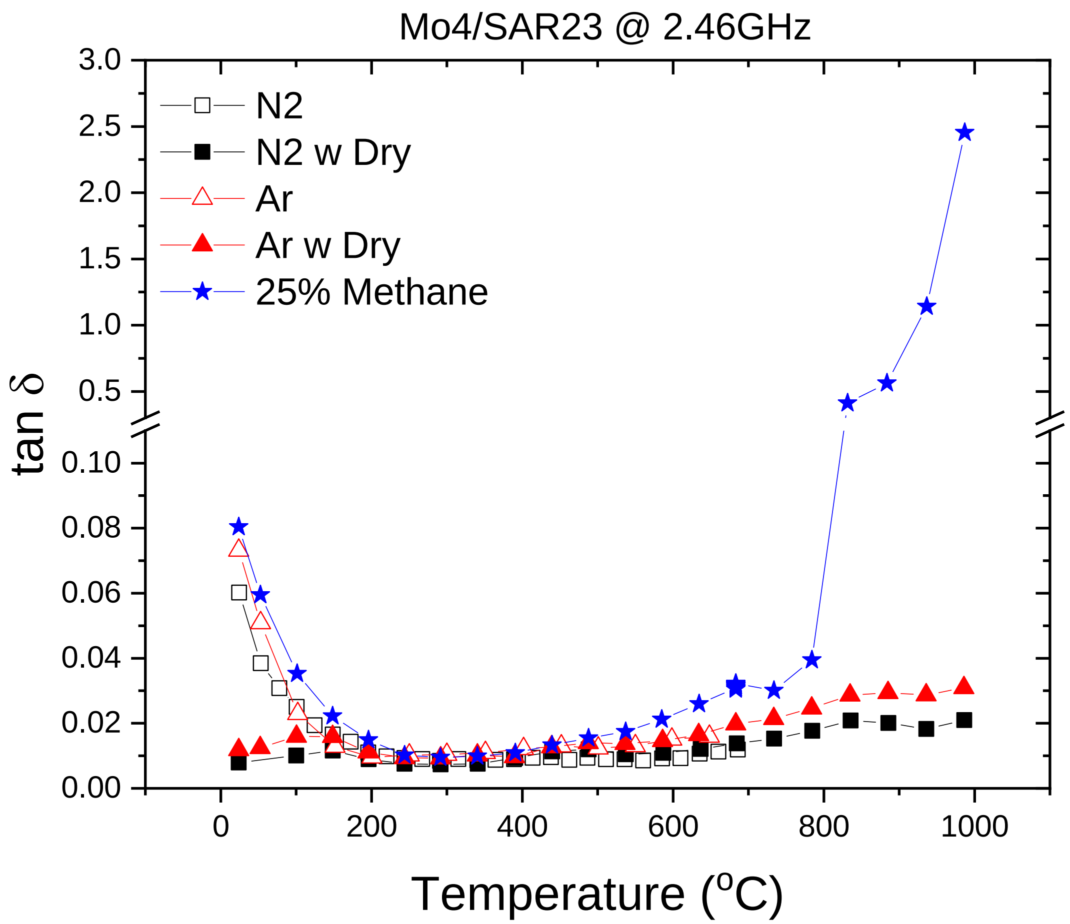


- Catalyst needs to be modified to improve MW absorption
- Combining catalyst with silicon carbide as a heating aid
  - Powder form
  - Monolith form

❖ Abdelsayed, V. et al. *Catal. Tod.* 2021, ***365***, 88.

Catalyst Characterization

Dielectric Properties

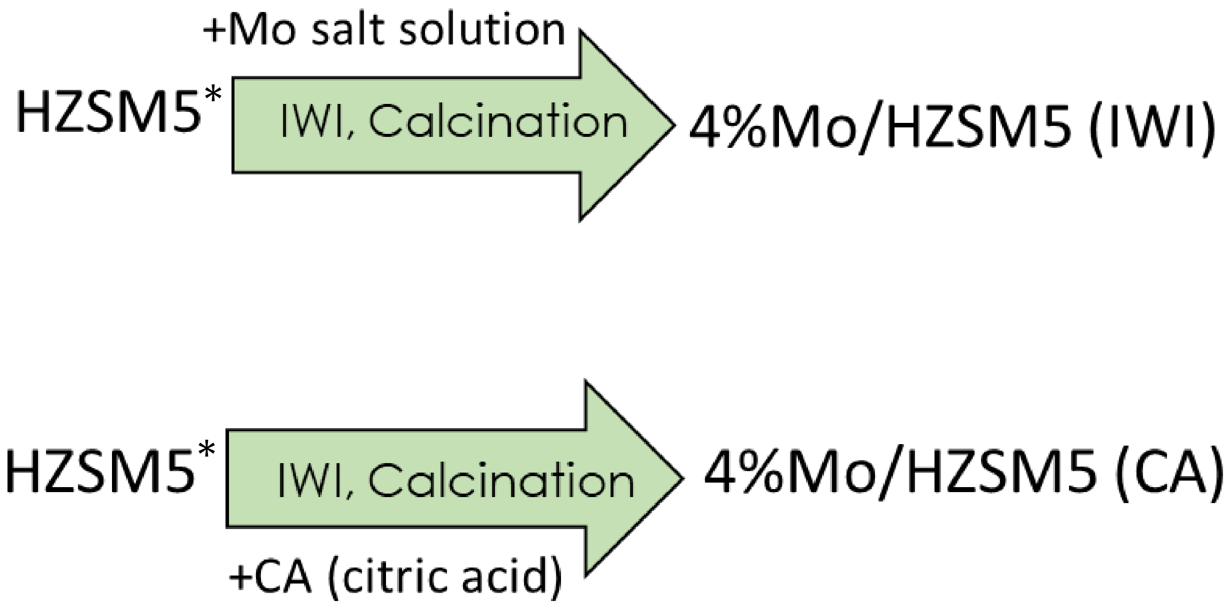


- Enhanced MW absorption under carbon environments
- Further facilitates more carbon production by generating hotspots

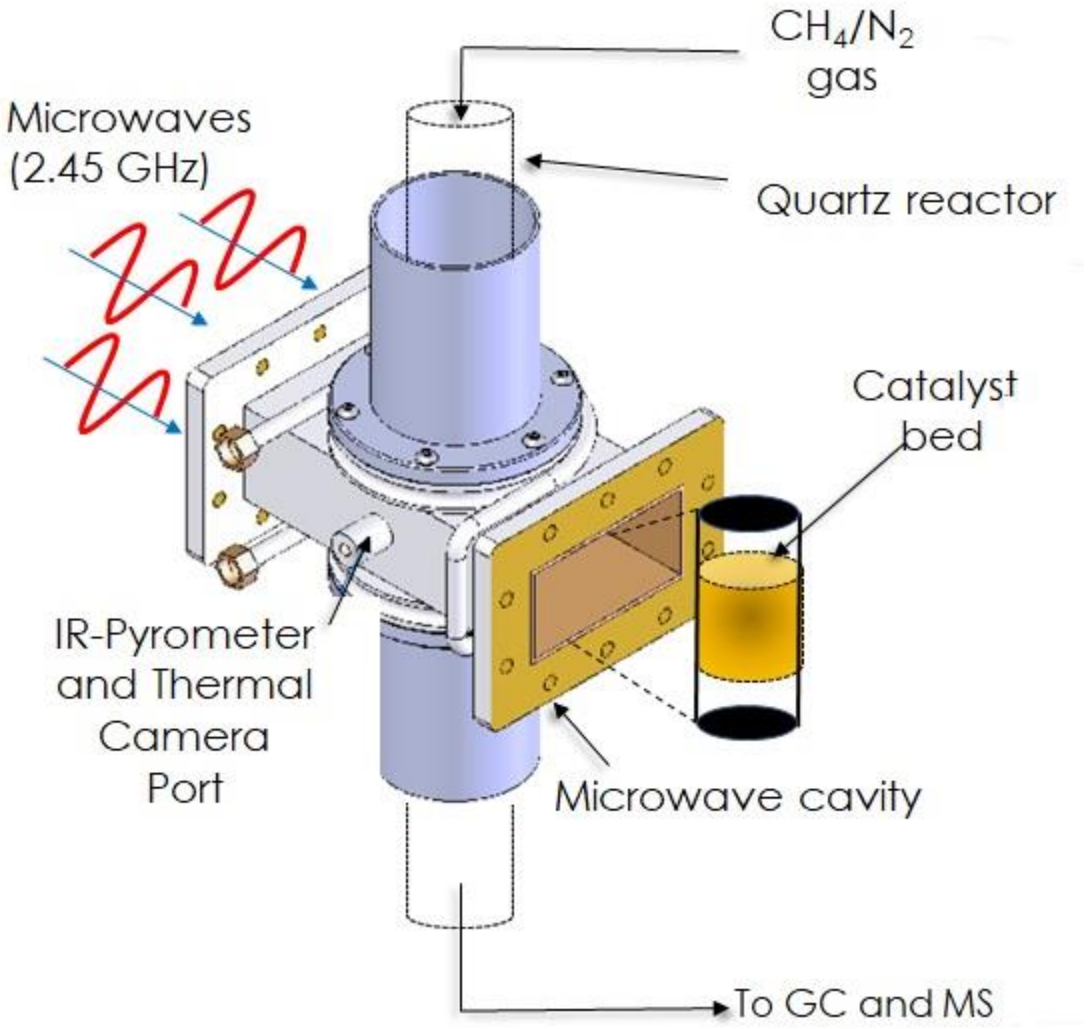
❖ Abdelsayed, V. et al. *Catal. Tod. 2021*, ***365***, *88.*

Experimental Details

Catalyst Synthesis and Microwave Reactor Schematic



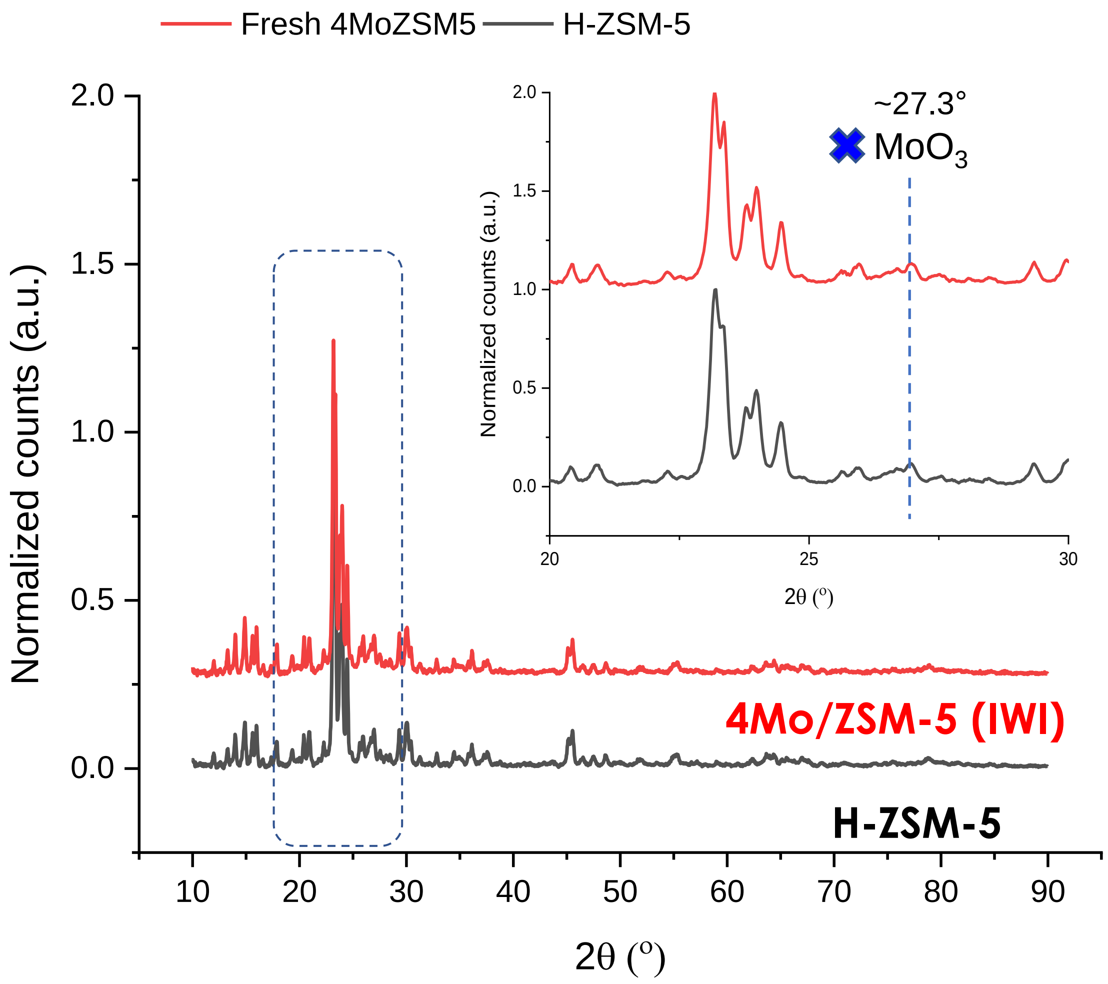
^IWI – Incipient Wetness Impregnation
* SiO_2/Al_2O_3 ratio = 23:1



❖ Abdelsayed, V. et al. *Catal. Tod.* *2021*, ***365***, *88.*

Catalyst Characterization

X-ray Diffraction (XRD) & Surface Area



- XRD shows finely dispersed Mo
- CA-based catalysts – probably more Mo in pores[1] (so more decrease in surface area)

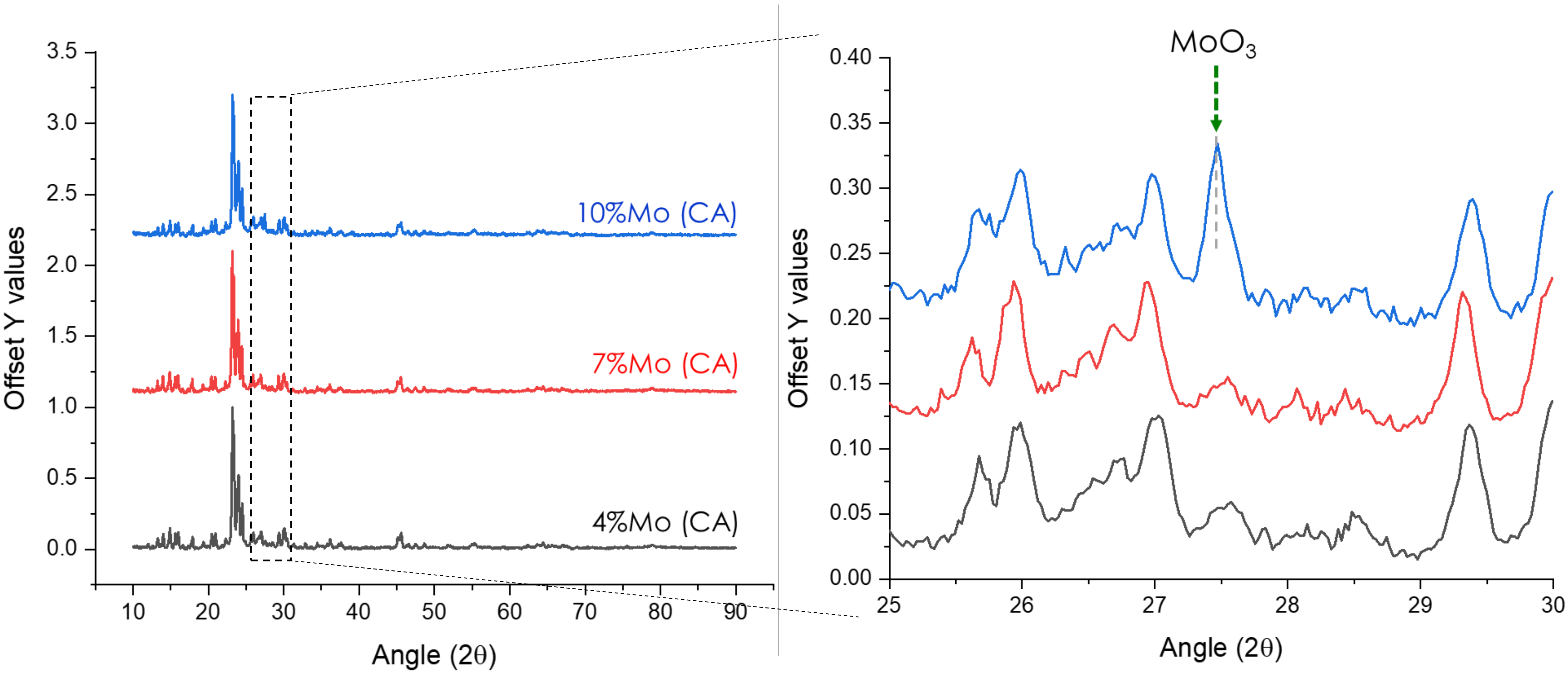
Catalyst	BET* Surface area (m^2/g)
H-ZSM-5	379
4Mo/H-ZSM-5 (IWI)	354
4Mo/H-ZSM-5 (CA)	324
7Mo/H-ZSM-5 (CA)	294
10Mo/H-ZSM-5 (CA)	272

*Brunauer Emmett Teller

1. Chen et al. *Inorg. Chem. Front.*, 2022,9, 4642-4650

Catalyst Characterization

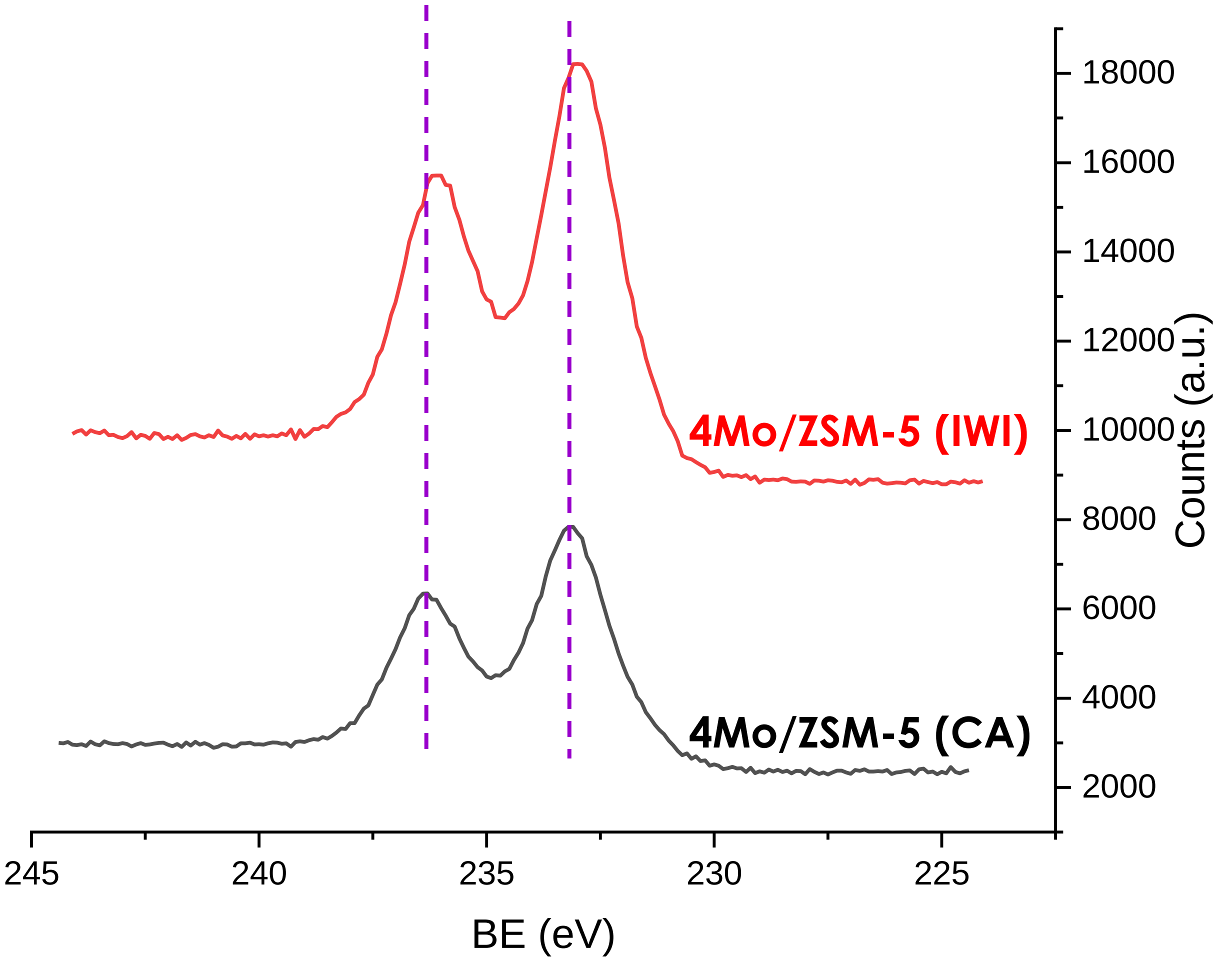
XRD

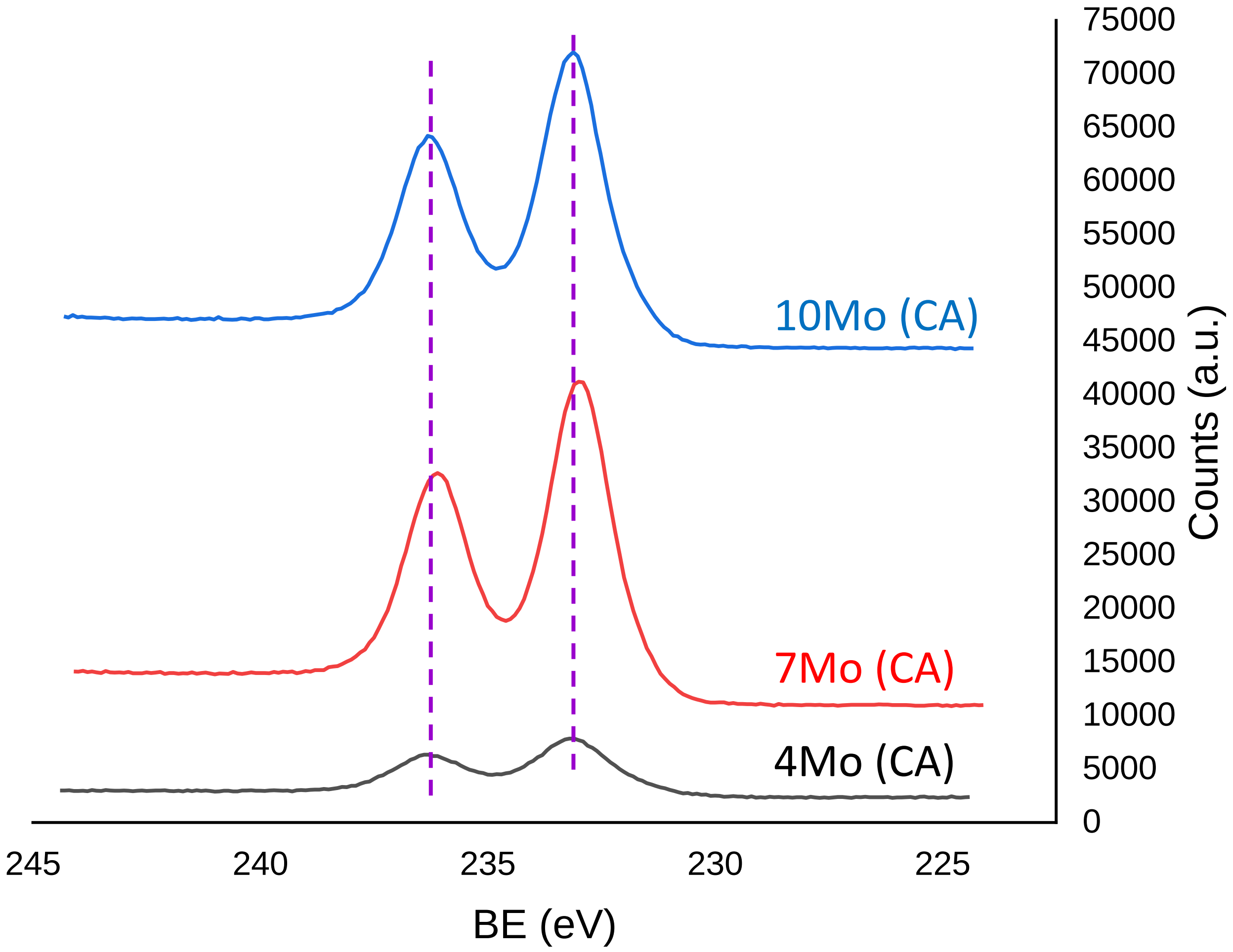


❖ Sridhar et al. *App. Cat. A.*, 2020, 589, 117247

Catalyst Characterizations

X-ray Photoelectron Spectroscopy (XPS)





Catalyst Characterization

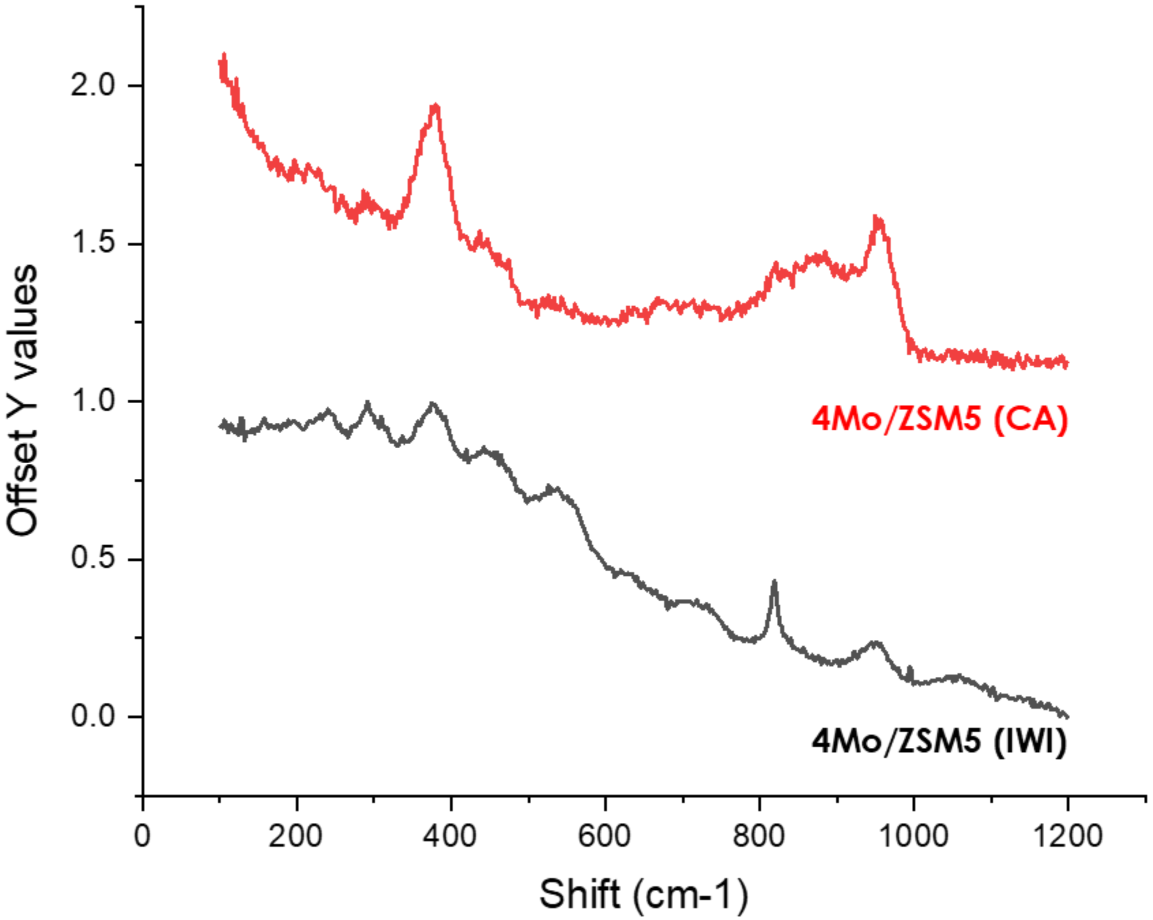
Fresh-XPS

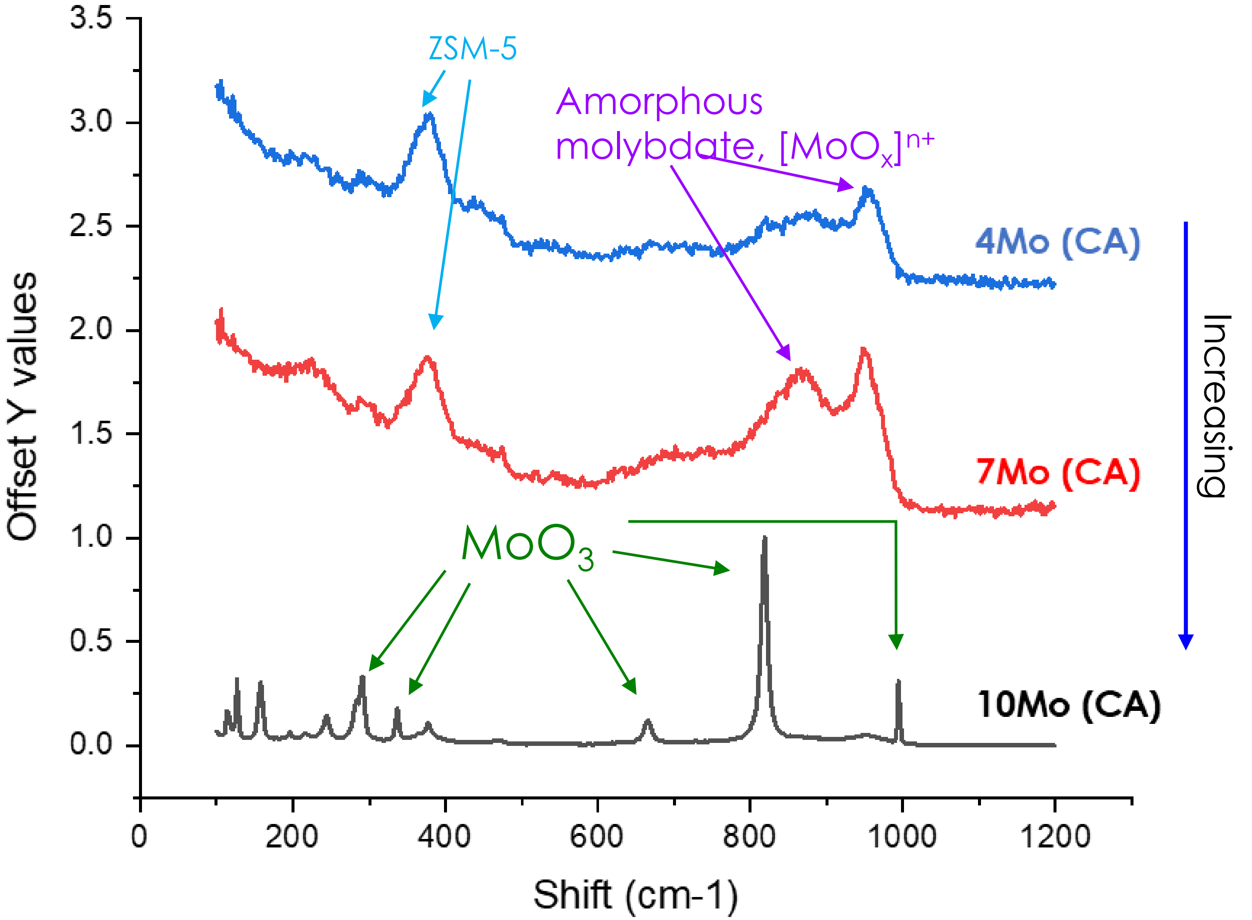
						Mo 3d5		% of Total Mo		Surface Composition (atomic %)				
	C-C	C-O	C=O	C(=O)-O	pi-pi*	Mo3d (VI)	Mo3d (V)	Mo(VI)	Mo(V)	C	O	Mo	Si	Al
4Mo (CA)	284.8	286.2	287.9	289.2	290.8	233.1	231.6	88.5	11.5	11.4	62.2	2.0	22.9	1.6
7Mo (CA)	284.8	286.2	287.9	289.2	290.8	232.9	231.5	94.6	5.4	11.9	61.7	9.50	15.3	1.6
10Mo (CA)	284.8	286.2	287.9	289.2	290.8	233.1	231.2	92.5	7.5	15.1	59.4	10.30	13.8	1.4
4Mo (IWI)	284.8	286.2	287.9	289.2	290.8	232.9	231.2	94.5	5.5	11.2	62.7	3.60	20.4	2.0

- Much lower surface concentration of Mo in CA-based catalysts compared to IWI
- Higher Mo loadings showed high surface Mo concentrations (especially 7 wt.% loading)

Catalyst Characterization

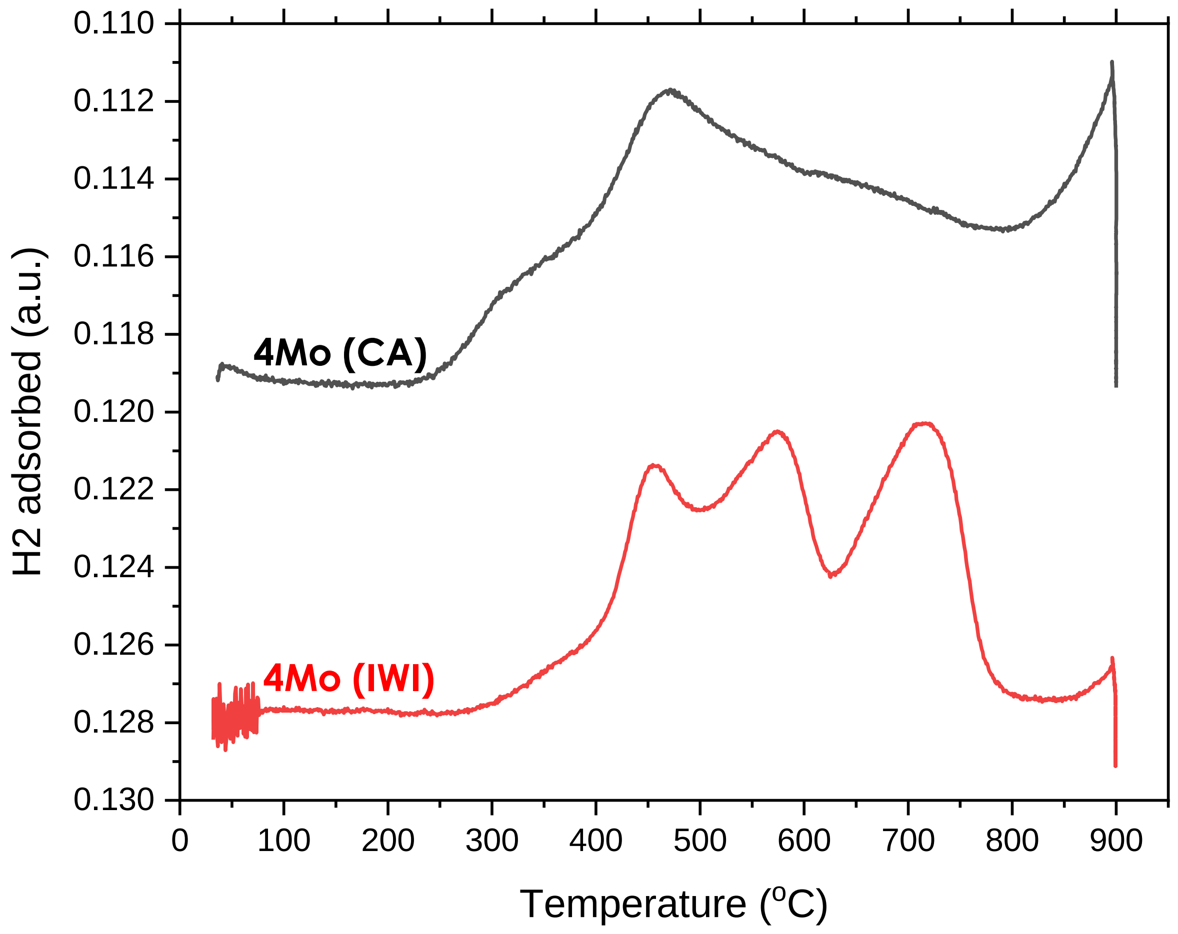
Raman

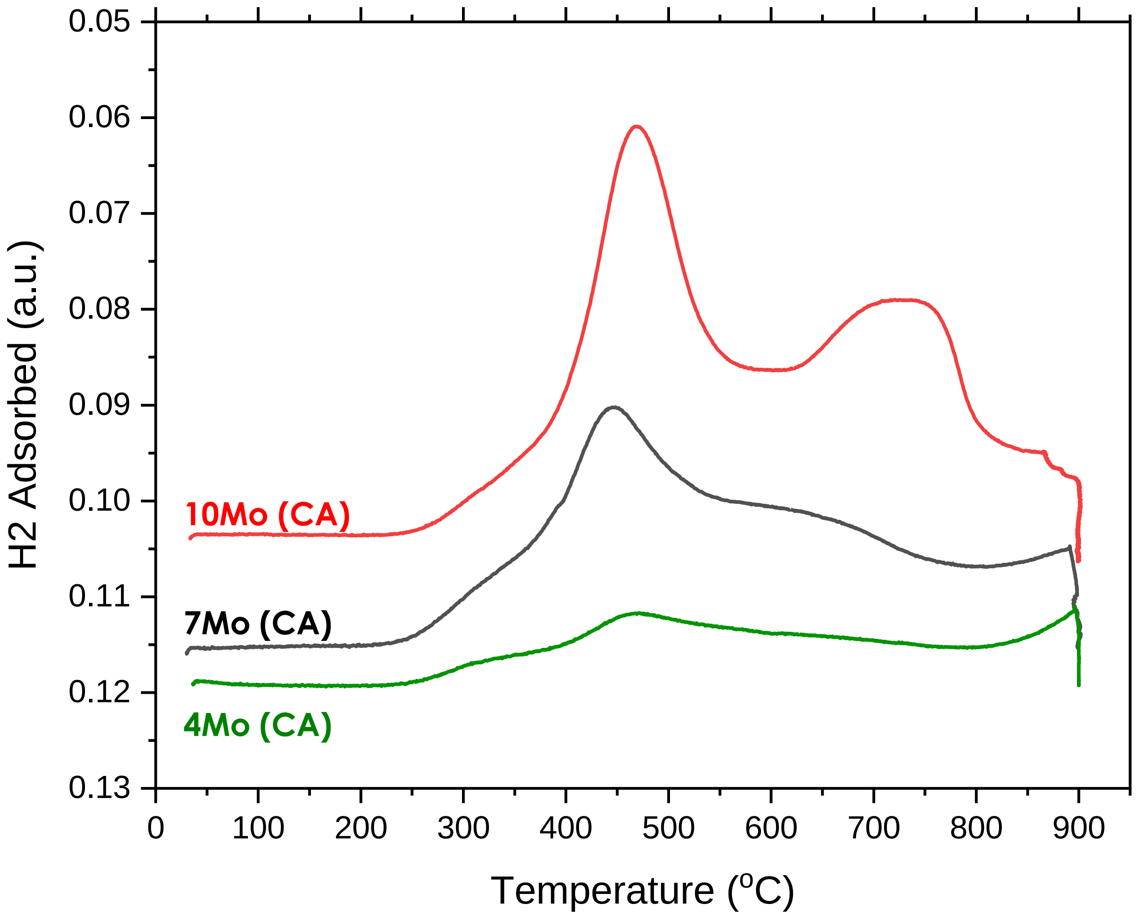




Catalyst Characterization

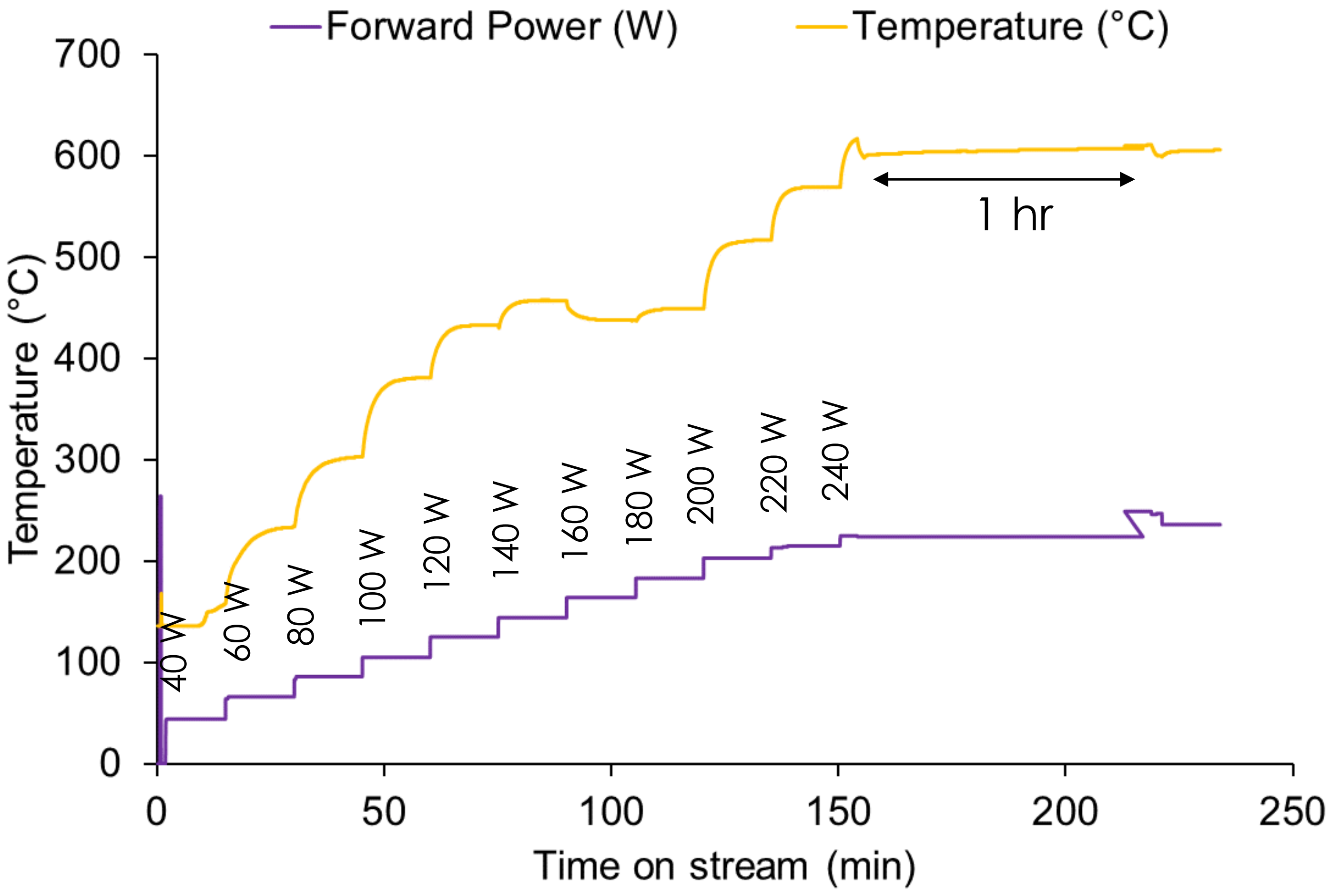
H_2-TPR





Experimental Details

TPSR (Temperature Programmed Surface Reaction)



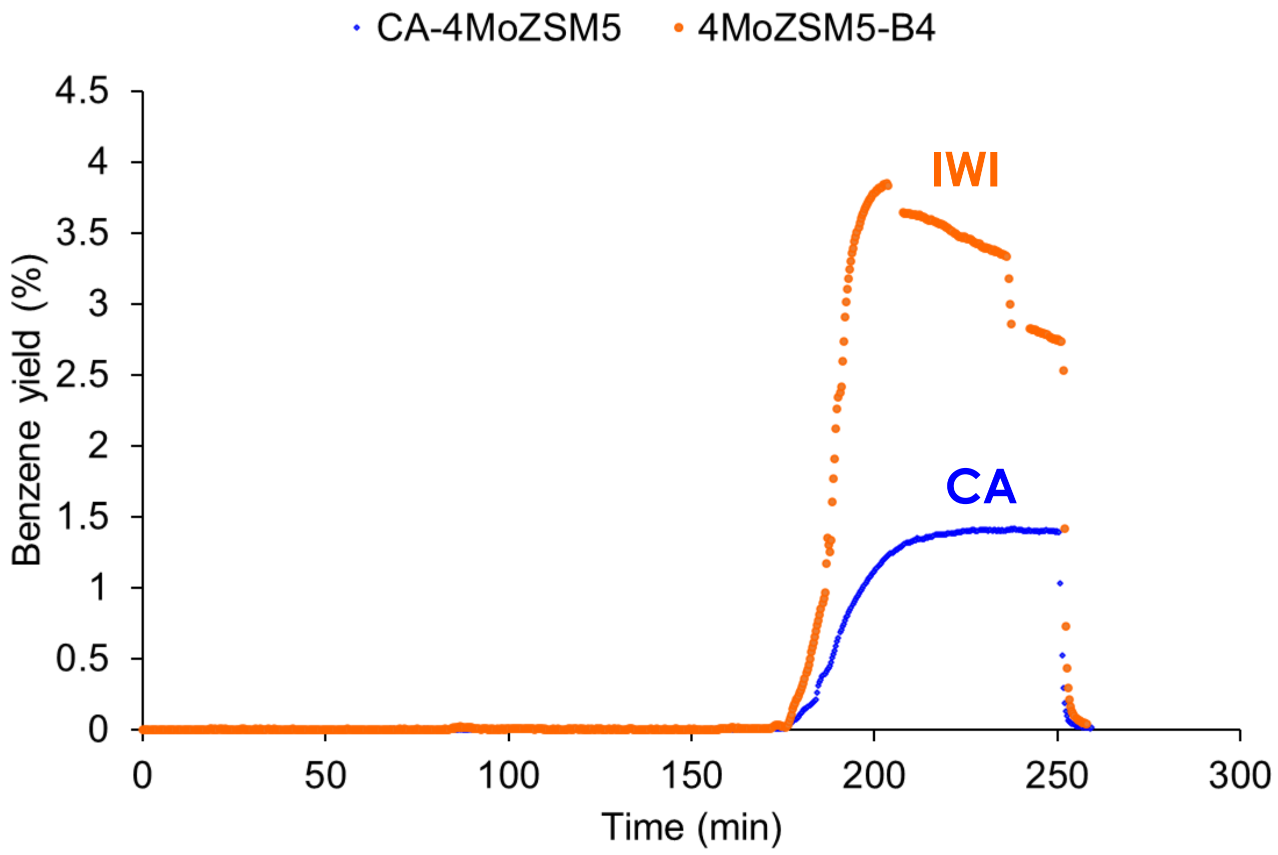
- TPSR up to 600 °C with MW power increments

MW Power	Temperature* (°C)
80	300
120	440
160	440
200	520
240	600

*measured using Pyrometer

Microwave Reaction Data

Performance Comparison - With and Without CA

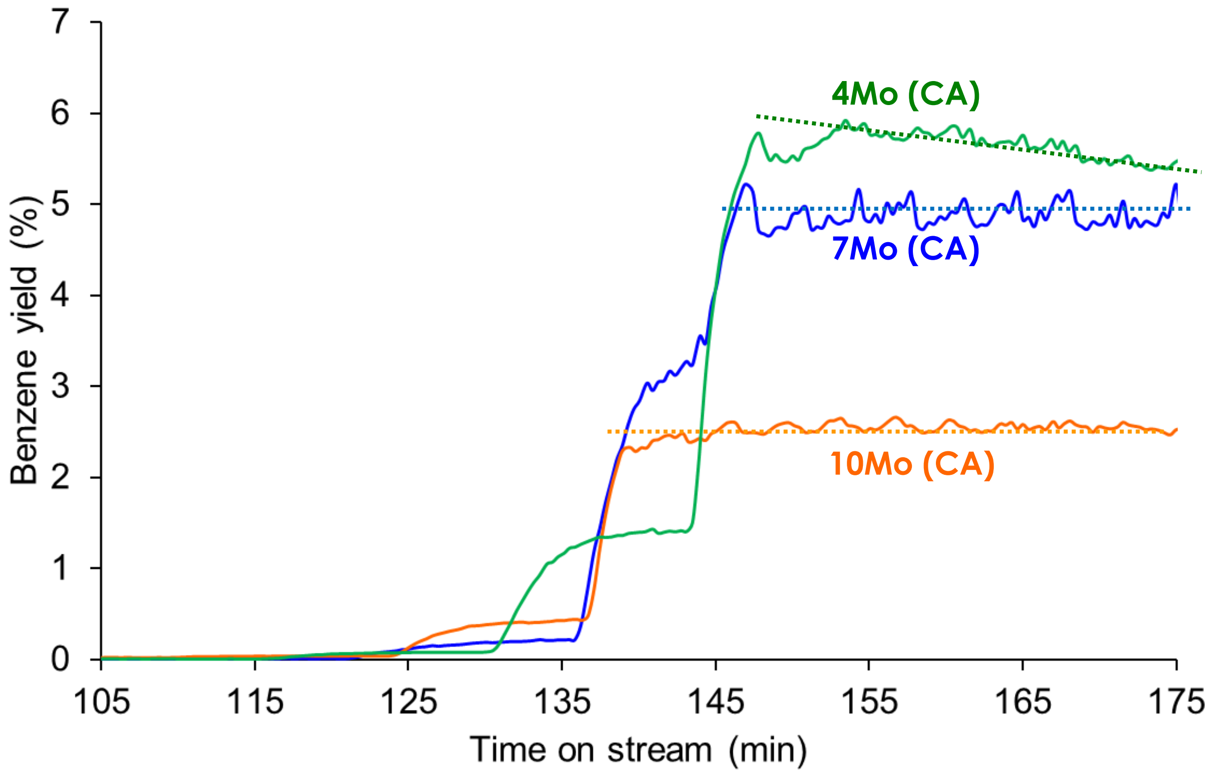


- 4Mo (IWI) showed higher benzene yield but faster deactivation
- 4Mo(CA) showed lower benzene yields but relatively stable productivity

Reaction conditions: 600 °C, 6000 mL/g_{cat}.hr, 1 atm

Microwave Reaction Data

Effect of Mo Loading

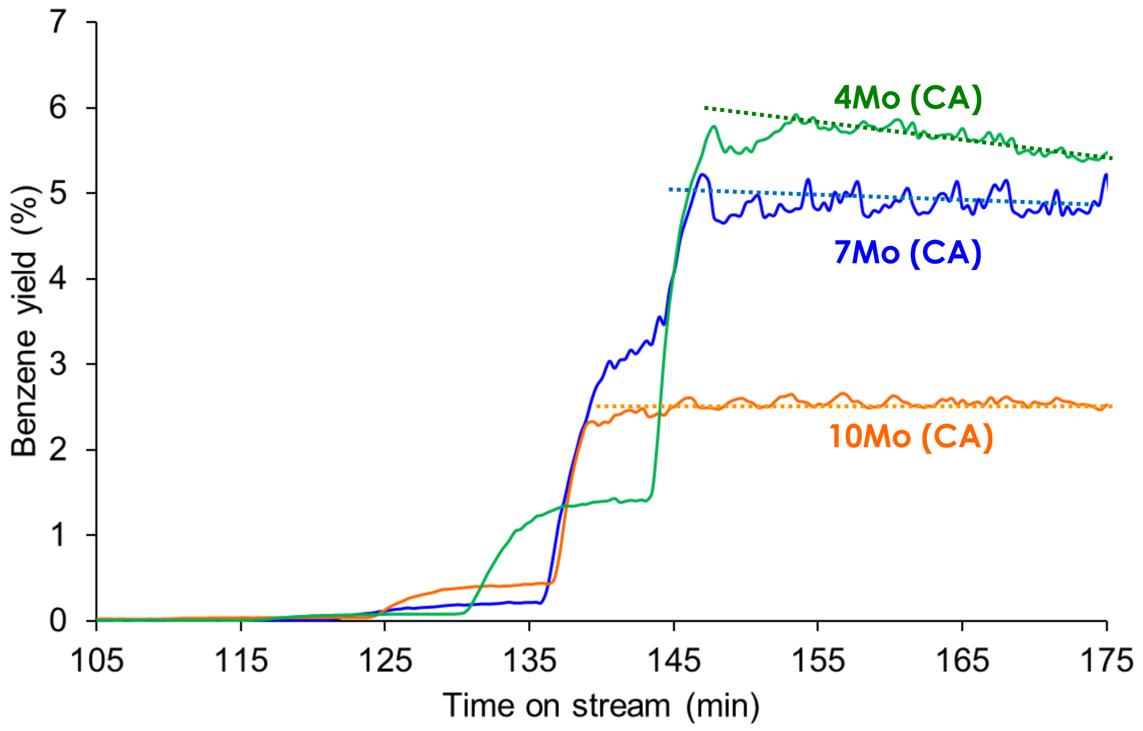


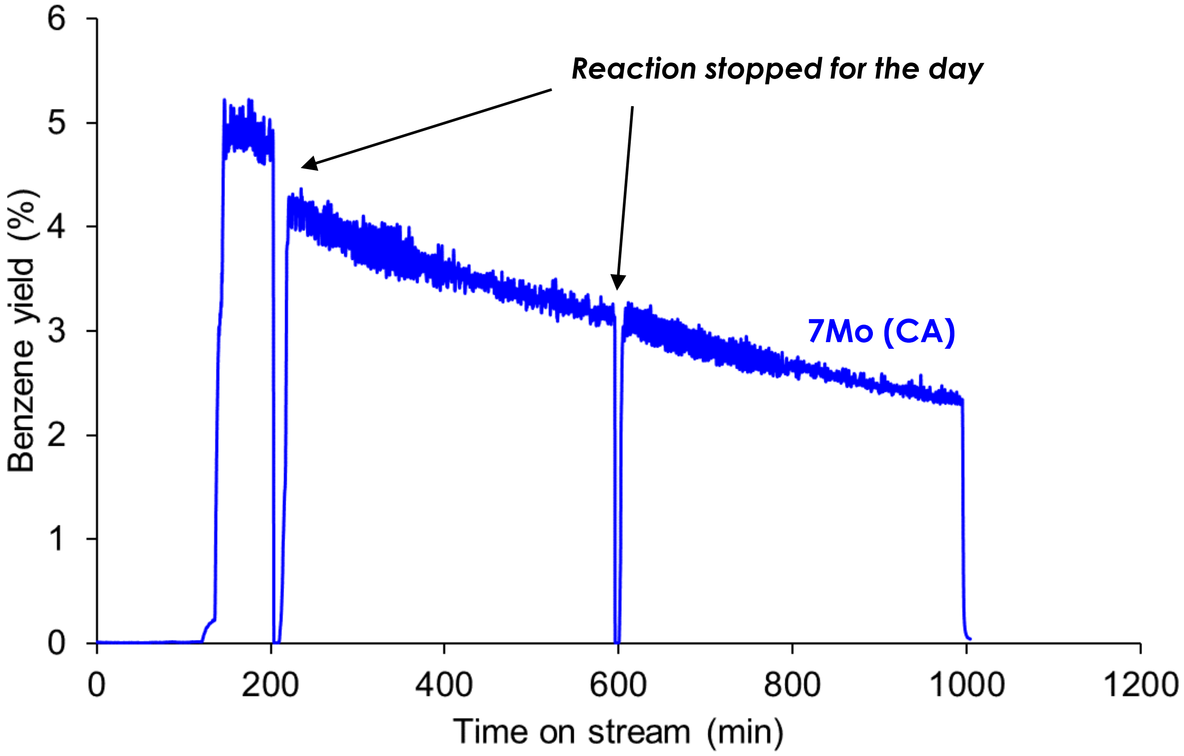
- 4Mo(CA) showed highest benzene yield but faster deactivation too
- 6Mo(CA) showed high benzene yields and relatively stable productivity
- 8Mo(CA) showed lower benzene yields but relatively stable productivity

Reaction conditions: 600 °C, 6000 mL/g_{cat}.hr, 1 atm

Microwave Reaction Data

Effect of Mo Loading

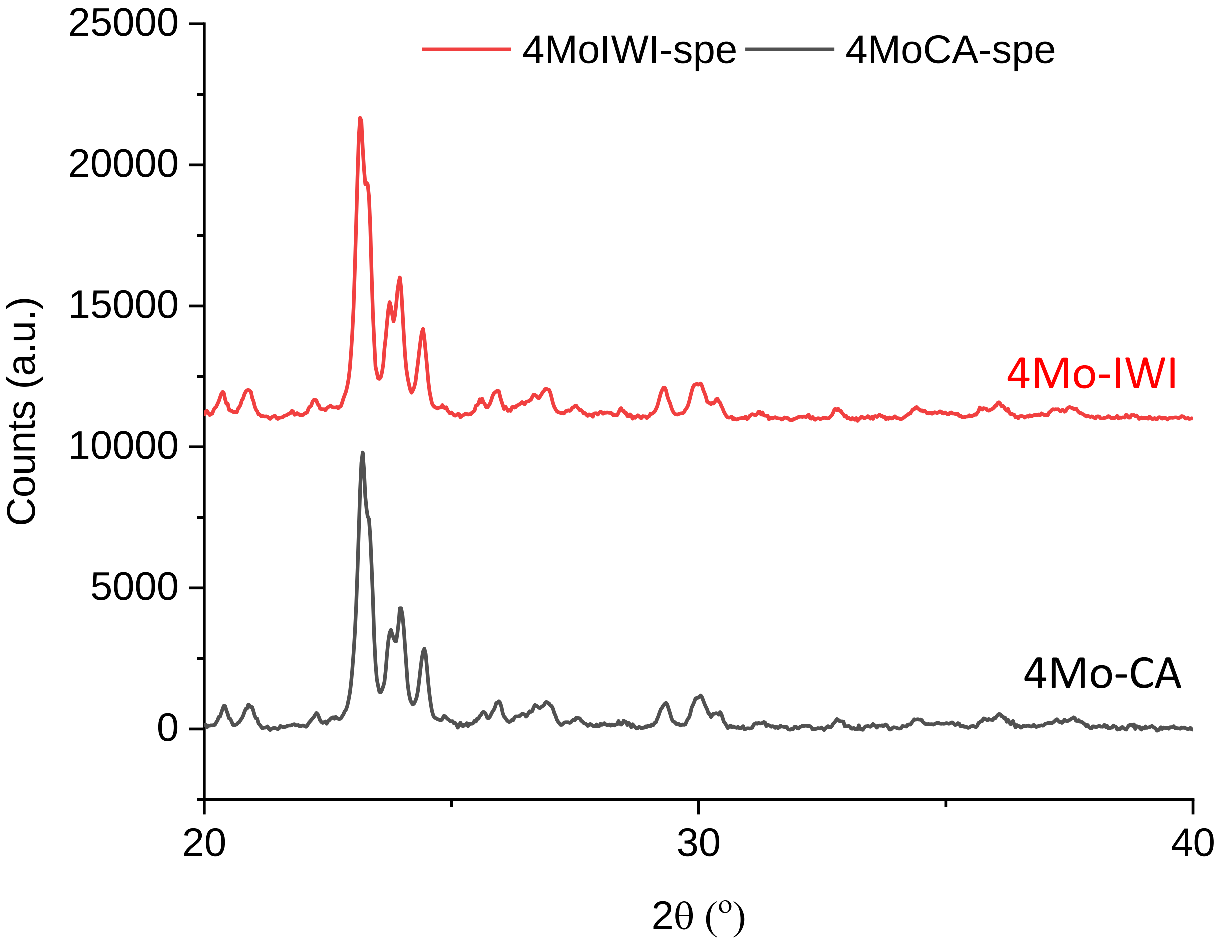




Reaction conditions: 600 °C, 6000 mL/g_{cat}.hr, 1 atm

Spent Catalyst Characterization

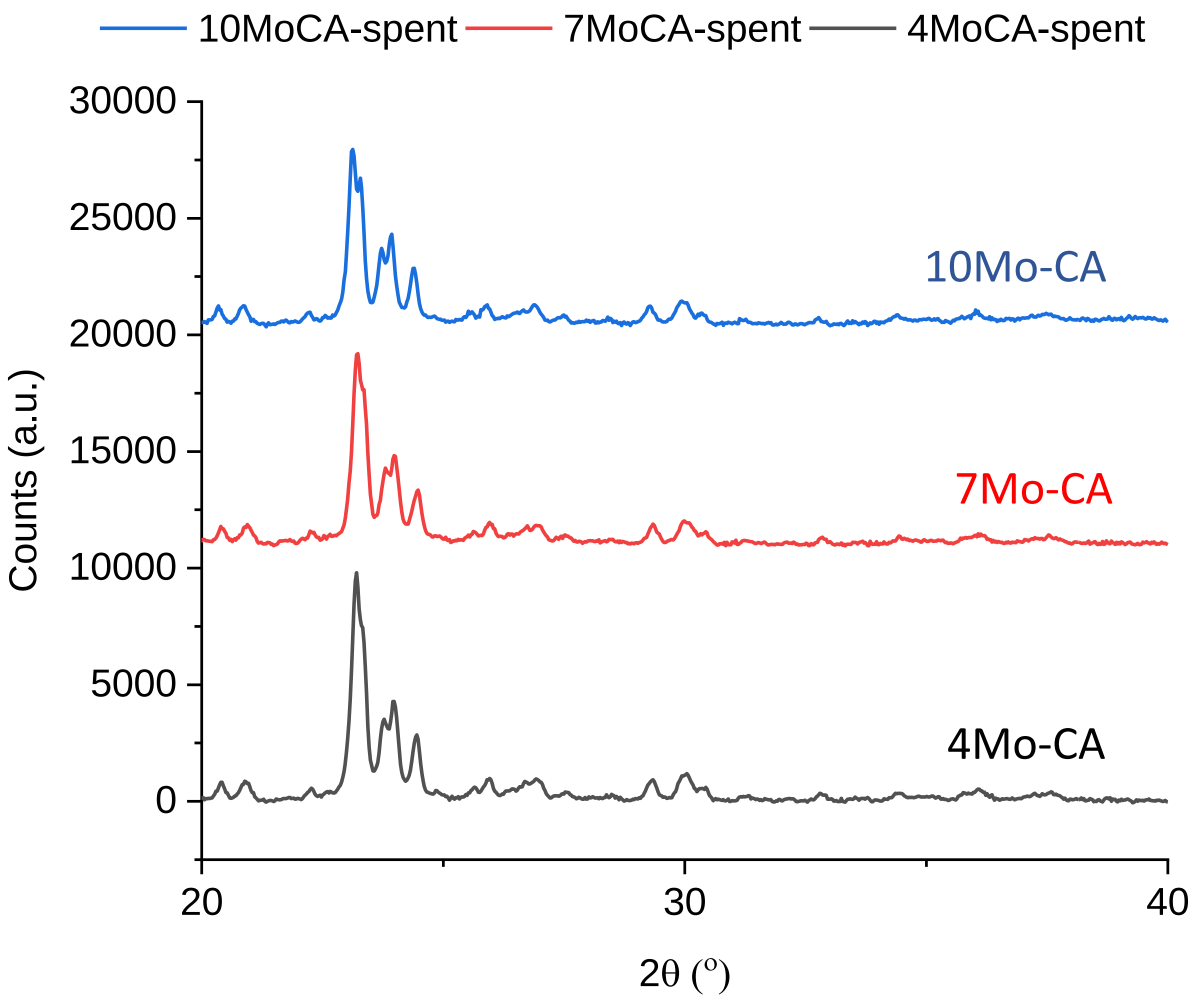
XRD



- No significant peaks for Mo or Mo_2C can be observed
- Mo still finely dispersed
- No apparent difference for CA vs. IWI catalysts

Spent Catalyst Characterization

XRD



- Higher loadings (10 wt.%) showed loss of MoO_3 peak
- Slight shift in zeolite peaks - carbon deposition in pores

Conclusions

- BET, Raman, and XPS results confirmed that citric acid helped in getting more Mo in the pores.
- Citric acid based catalysts can help in dispersing higher Mo weight loadings up to 7 wt.%.
- Deactivation under microwave conditions was slowed down.
- More detailed understanding is underway.

Acknowledgements

NATIONAL ENERGY TECHNOLOGY LABORATORY

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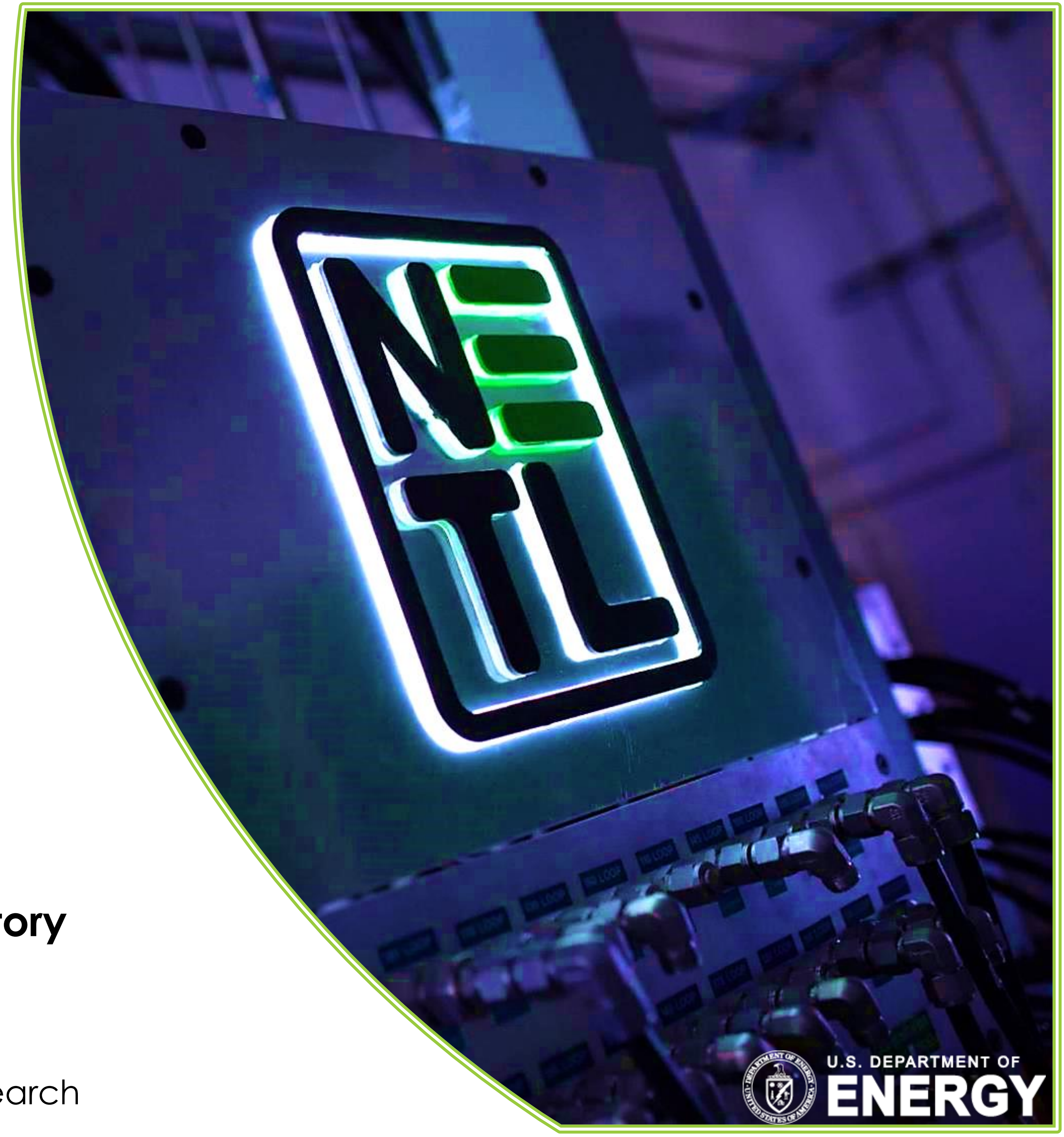
Contact: Dushyant Shekhawat
Dushyant.Shekhawat@NETL.DOE.GOV

for more information on Microwave Chemistry Research



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