DE-FE0031869

Core-Shell Oxidative Aromatization Catalysts for Single Step Liquefaction of Distributed Shale Gas

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NC State University

Project Partners: **West Virginia University, Lehigh University, Susteon Inc. and Shell**

DOE/NETL Project Manager: **Anthony Zammerilli**

04/03/2024

Outline

- Project Overview and Technology Background
- Technical Approach and Current Status
- Future development plan
- Summary

Project Overview

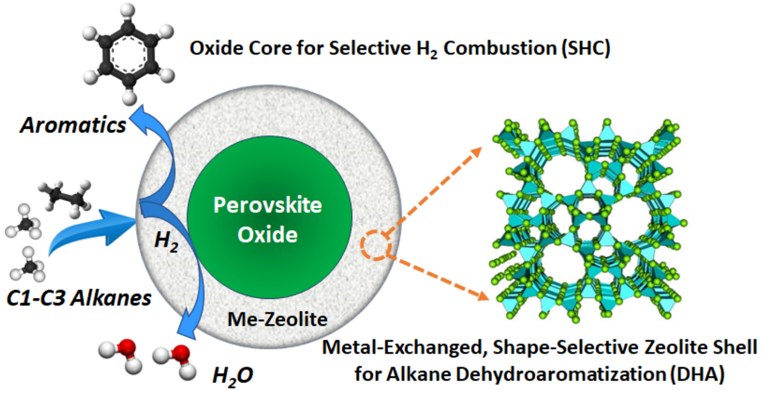
Period of Performance: 04/01/2020 - 06/30/2024 (two budget periods)

	DOE Funds	**Cost Share**
NC State Univ. *Dr. Fanxing Li*	***$359,940***	***$68,452***
Lehigh Univ. *Dr. Israel Wachs*	***$290,000***	***$80,268***
West Virginia Univ. *Dr. John Hu*	***$270,001***	***$67,500***
Susteon Inc. *Dr. Raghubir Gupta*	***$80,030***	***$15,000***
Shell (CS Only)	***$0***	***$25,000***
Total ($)	***$999,971***	***$256,220***

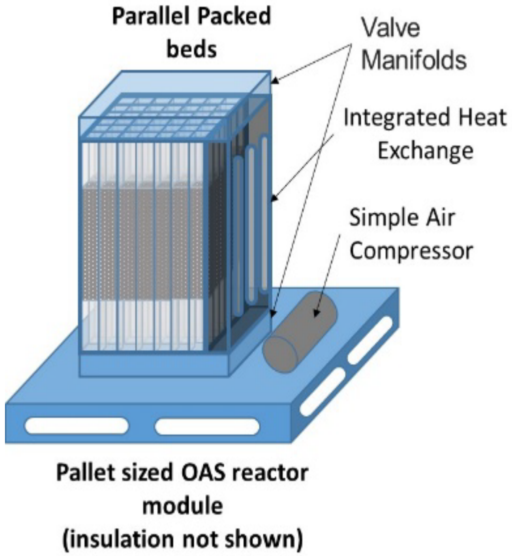
Project Objective: To design and demonstrate multifunctional catalysts to convert the light (dry) components of shale gas into liquid aromatic compounds and water in a modular oxidative aromatization system (OAS).

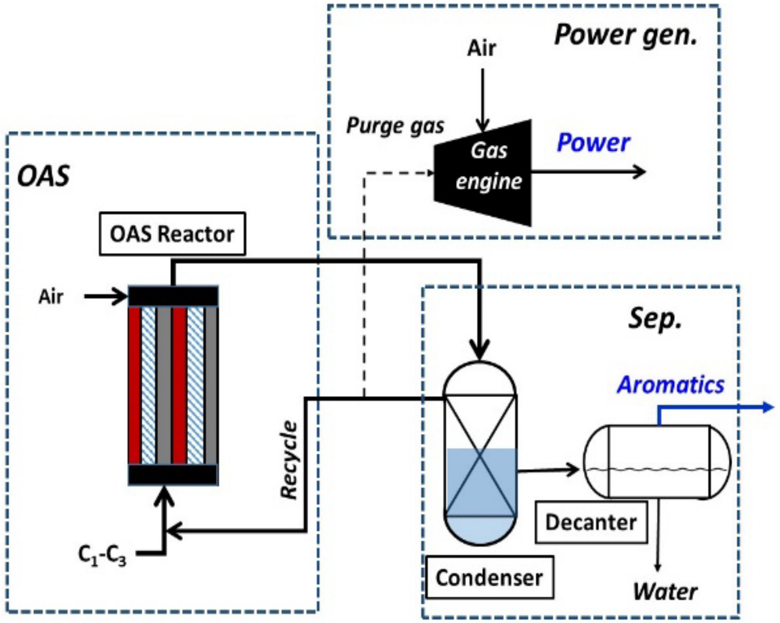
End of Project Goals: (1) Report SHC-DHA catalysts for 100 hours of continuous operation with >20% single pass aromatics yield; (2) Confirm 25% return on investment using a refined process model.

Modular Oxidative Aromatization System (OAS)



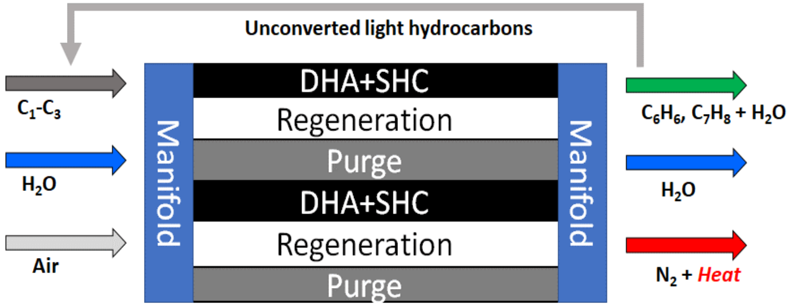
Original Idea





Cyclic operation in two steps:

- **DHA+SHC:** $6CH_4 + 9[O] \rightarrow C_6H_6 + 9H_2O$
- **Regeneration:** $O_2 \rightarrow 2[O]$ + heat
- Steam purge between steps, also prevents CO_x accumulation;



Conventional methane and ethane dehydroaromatization (DHA) are both highly endothermic and equilibrium limited.

$$6CH_4 \leftrightarrow C_6H_6+9H_2 \qquad (\Delta H=722\ kJ/mol)$$

Integrating a zeolite catalyst shell on a perovskite oxide-based selective hydrogen combustion core can: (a) facilitate autothermal operation; (b) eliminate equilibrium limitation; (c) inhibit coke formation; (d) allow modular conversion of C1-C3 alkanes to aromatics in a greatly simplified process.

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Technical Approach

BP1 (Q1-Q6): SHC, DHA, and SHC-DHA catalyst optimizations and preliminary design/TEA.

Task 2 (Q1-Q4). SHC redox catalyst optimization (NCSU) and DHA catalyst optimization (WVU and Lehigh)

Milestone 2.1: SHC catalyst screening, Q1
Milestone 2.3.1: DHA catalyst screening, Q3
Milestone 2.3.2: DHA catalyst characterization, Q3

Task 3 (Q4-Q6). SHC-DHA catalyst development (NCSU, Lehigh, and WVU)

Milestone 3.1: SHC-DHA catalyst screening, Q5
Milestone 3.2: Go/No-go, Q6

Task 4 (Q3-Q6). Process design, optimization and simulation (Susteon)

Milestone 4.0: Process Model, Q4

BP2 (Month Q7-Q16): OCM-DHA catalyst optimization, OAS demonstration, and detailed TEA.

Task 5 (Q7-Q12). OCM-DHA catalyst optimization (NCSU, Lehigh, and WVU)

Milestone 5.1: Catalyst synthesis/screening, Q8
Milestone 5.2 : Catalyst synthesis scale-up, Q10

Task 6 (Q12-Q16). Long term OAS demonstration

Milestone 6.1: Modular test unit commissioning, Q12
Milestone 6.2: Long-term OAS testing, Q16
Milestone 6.3: Post testing characterization, Q16

Task 7 (Q9-Q16). Process scale-up, comprehensive TEA, and commercialization plan development (Susteon)

Milestone 7.0: Final TEA, Q16

Success Criteria

BP1:

Report DHA/SHC physical mixture (or composite) with > 800 g/kgCat-hr aromatics productivity.

BP2 (End of Project Goals):

Report selected SHC-DHA catalyst for 100 hours of continuous operation with >20% single pass aromatics yield;

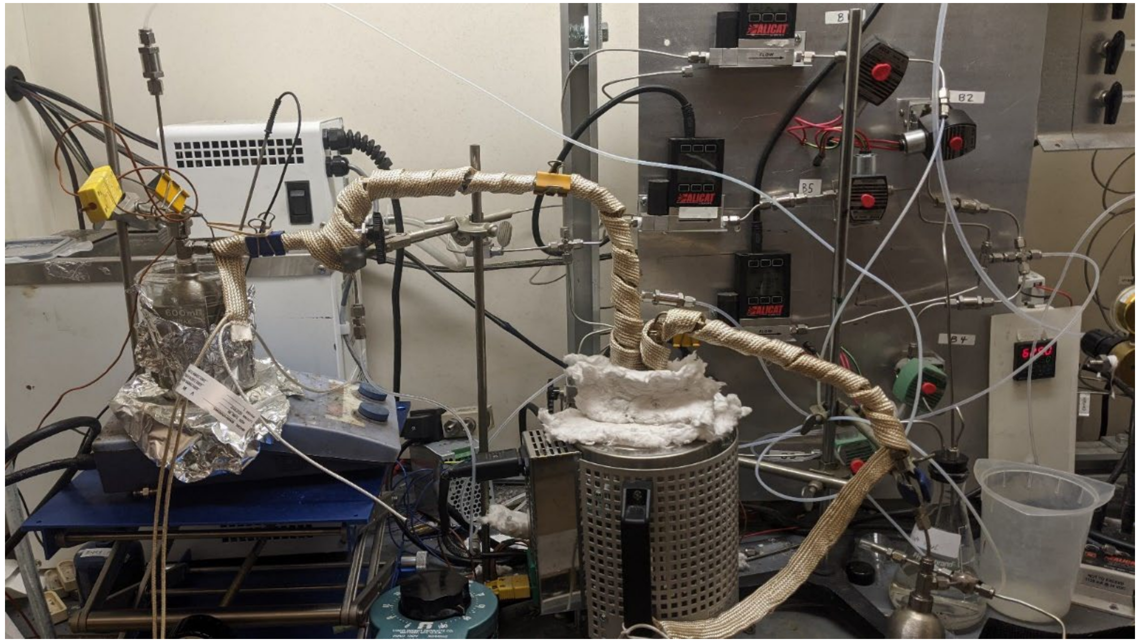
Risk Mitigation

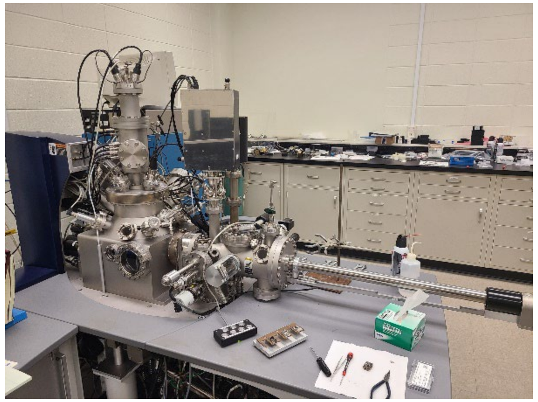
Cost/Schedule Risks:	**Probability**	**Impact**	**Overall**	**Mitigation Strategy**
Delayed/Extended negotiations	Med	Low	Low	Facilities are in place for rapid ramp up
Technical/Scope Risks:				
Insufficient DHA or SCH catalyst performance	Low	High	Med	Develop large library catalytic of materials and approaches; rationalized catalyst design based on molecular insights
Compatibility issues between DHA and SHC catalyst	Med	High	Med	Develop alternative schemes for yield enhancement.
Management, Planning, and Oversight Risks:				
Delayed personnel ramp-up	Low	Low	Low	Sufficient personnel are in place and/or quickly filled (e.g. Ph.D. students) for the project.

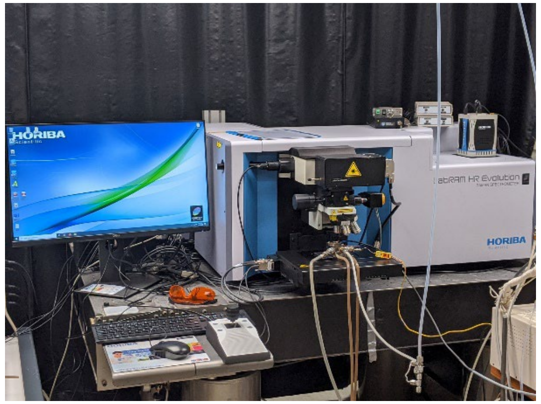
Synthesis Apparatus: CEM Microwave Synthesizer

- The zeolite synthesis of H-ZSM-5 and HGaAlMFI has been optimized using the new CEM MW synthesizer
- This will allow for shorter synthesis times and increased zeolite yields in comparison to the previous synthesis methods (conventional hydrothermal autoclaves and solid-state crystallization)
- Typically uses the same solution preparation as the original conventional hydrothermal autoclave method
- Two solutions are prepped and stirred for 4 hours before being placed in the two Teflon vessels with small stir bars
- The vessels are then placed in the CEM MW and run according to a temp/time set of conditions

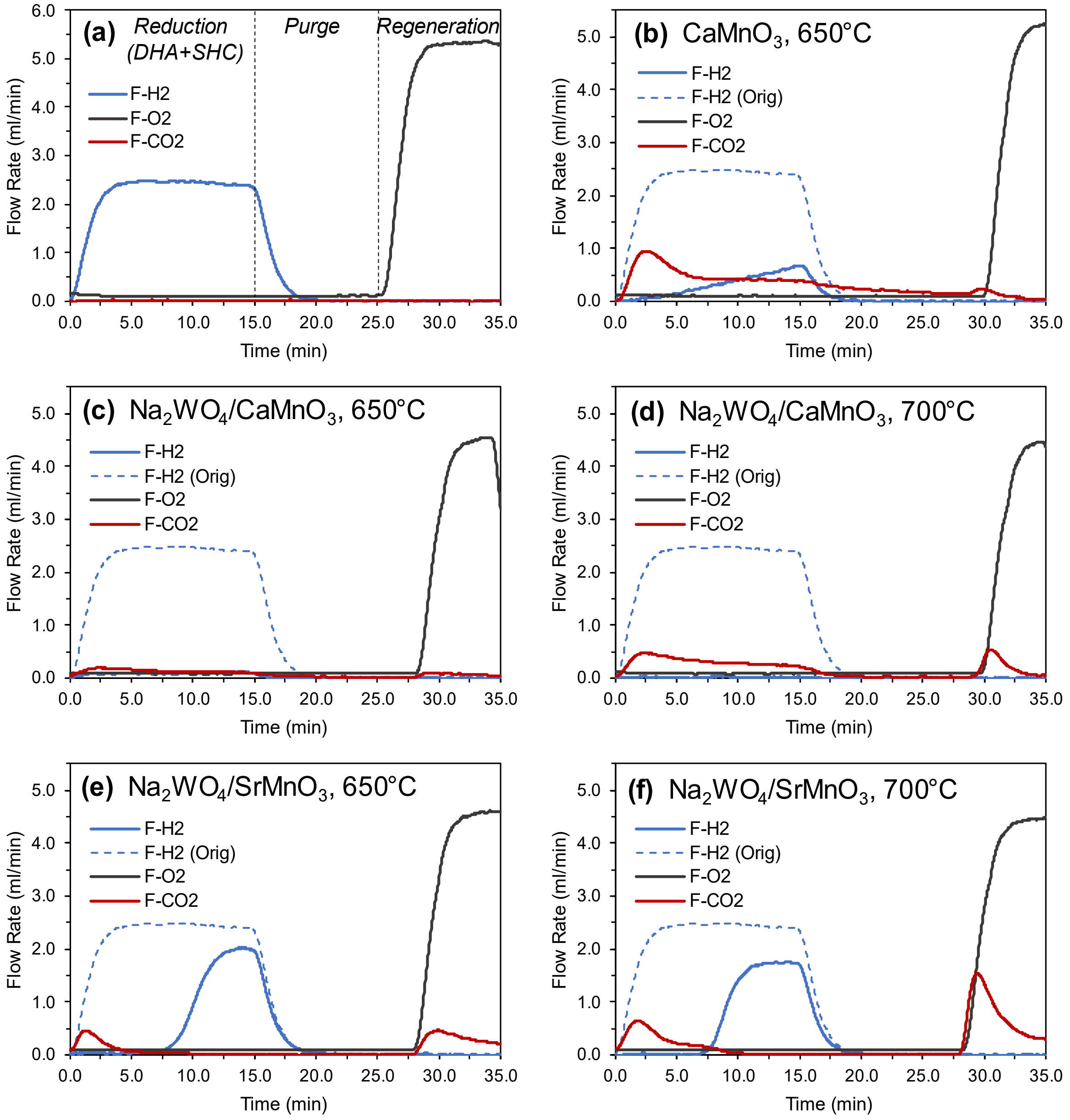
Catalyst Testing and Characterizations

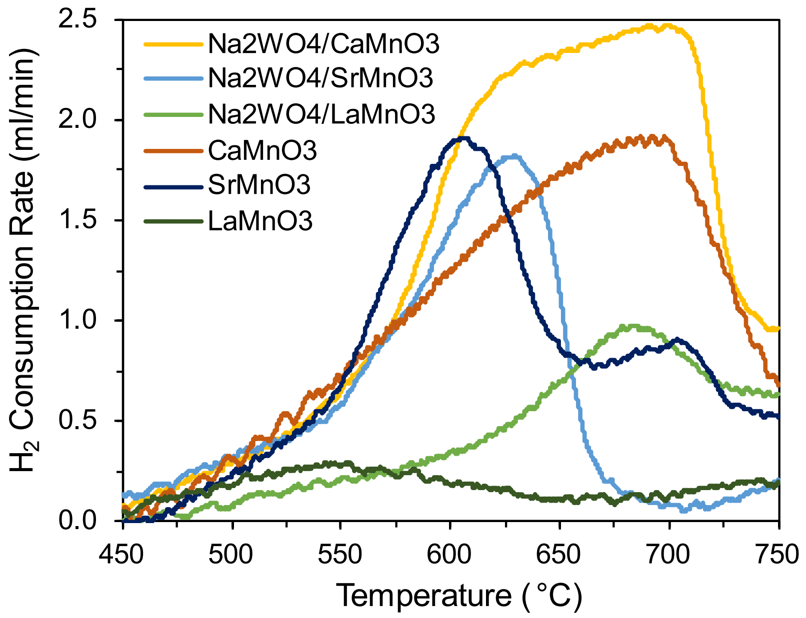






Summary of Project Progress – Selective Hydrogen Combustion (SHC)



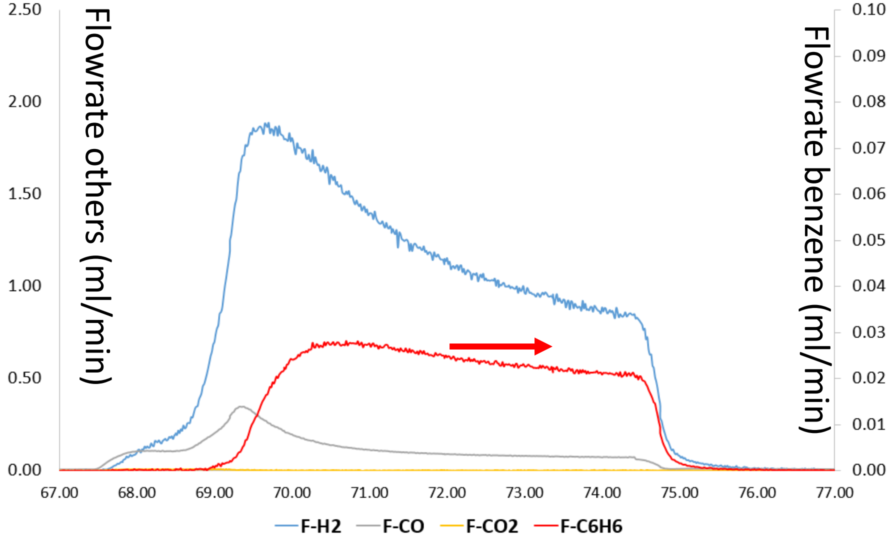


Sample	T (°C)	Total H_2 Combustion	Selectivity w/o Coke
$CaMnO_3$	650	1.40 mmol	70.4%
$Na_2WO_4/CaMnO_3$	650	1.55 mmol	89.7%
$Na_2WO_4/CaMnO_3$	700	1.60 mmol	79.6%
$Na_2WO_4/SrMnO_3$	650	1.16 mmol	90.2%
$Na_2WO_4/SrMnO_3$	700	1.15 mmol	82.5%

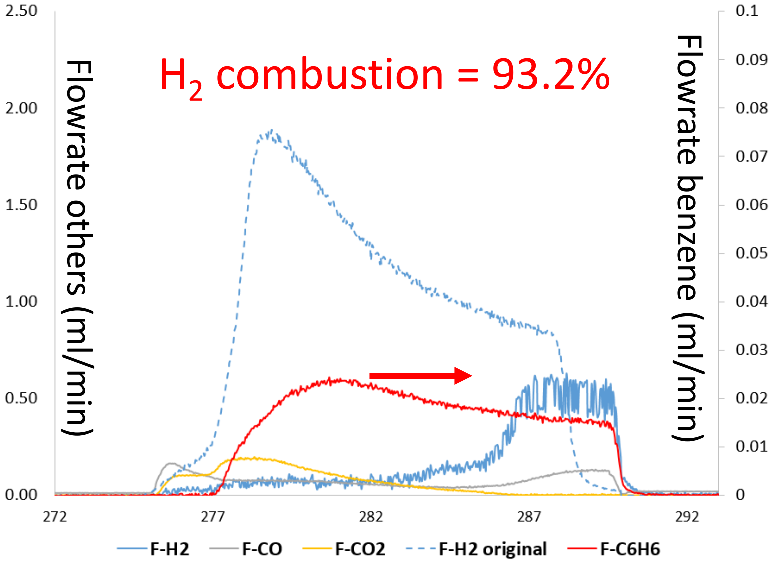
Co-feed of 1:1 H_2/C_6H_6 on 500 mg of redox catalyst particles. Selectivity based on oxygen distribution basis; 75% oxygen distribution selectivity corresponds to 97.8% selectivity (H_2 combusted v.s. C_6H_6 combusted).

Summary of Project Progress – DHA + SHC +DHA sequential bed

DHA
single bed

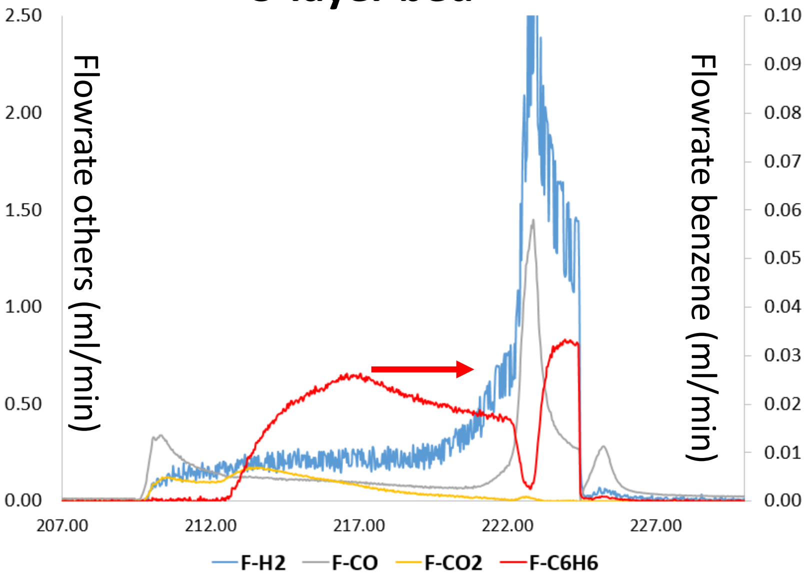


DHA+SHC
2-layer bed



H_2 combustion = 93.2%

DHA+SHC+DHA
3-layer bed



- $Na_2WO_4/CaMnO_3$ leads to H_2 combustion = 93.2%.
- CO by-product is also combusted into CO_2.
- Benzene formation rate is barely affected.

- H_2O formed in the SHC bed deactivates benzene formation from the 2nd DHA bed.
- 2nd DHA bed starts to form benzene only when the SHC bed is fully consumed of active lattice oxygen.

DHA → ***SHC*** → ***H_2O Removal*** → ***DHA***

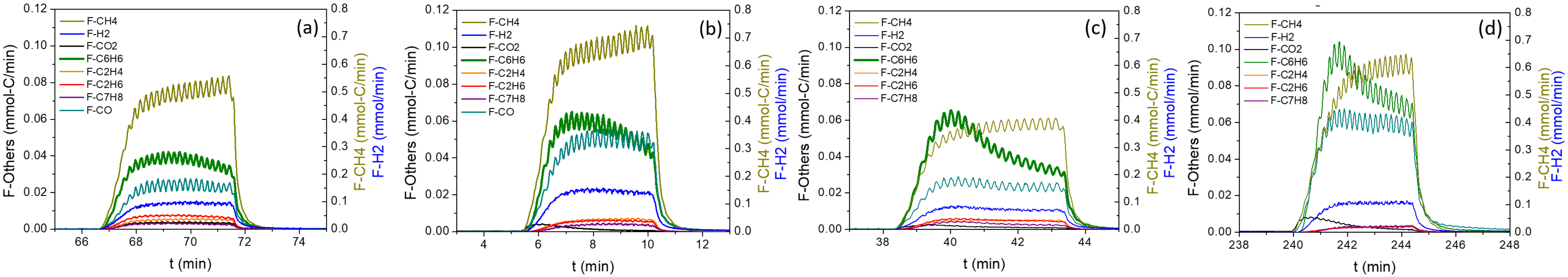
~40% yield increase but a very complex process configuration

Summary of Project Progress – Further Improvement OCM + steam resistant DHA Catalyst

Alternative approach :

Methane oxidative coupling → ***C2+ Dehydroaromatization (DHA)*** →

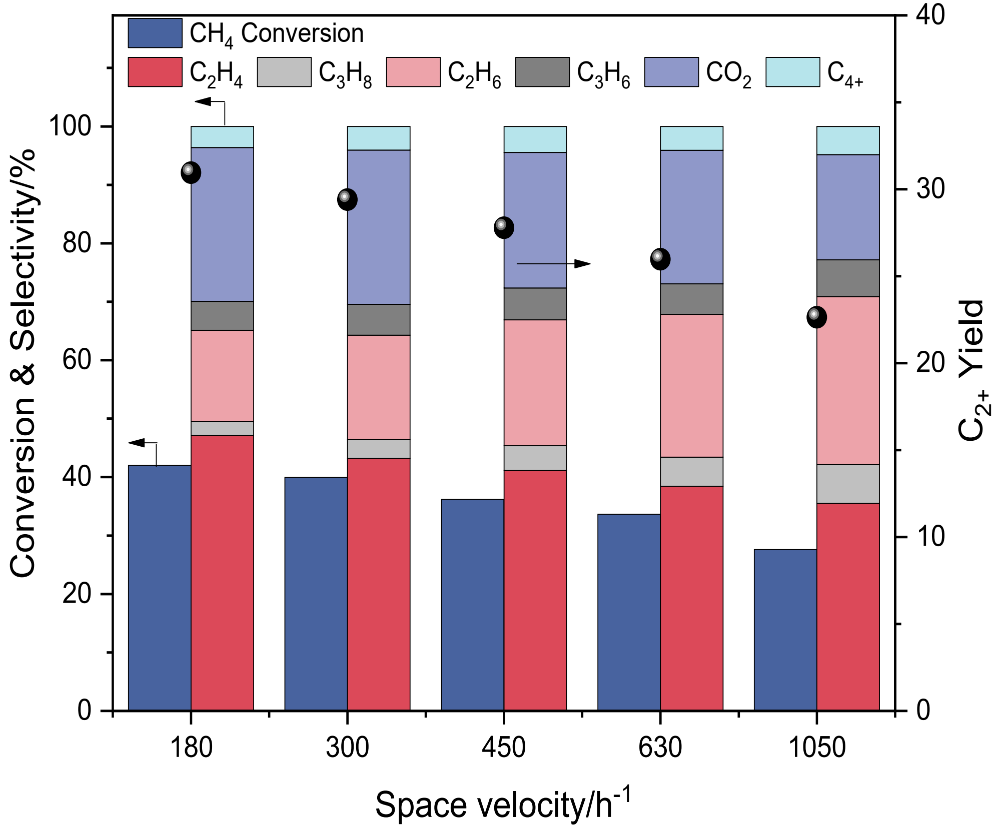
Surface promoted mixed oxide *Ga/ZSM based catalyst*

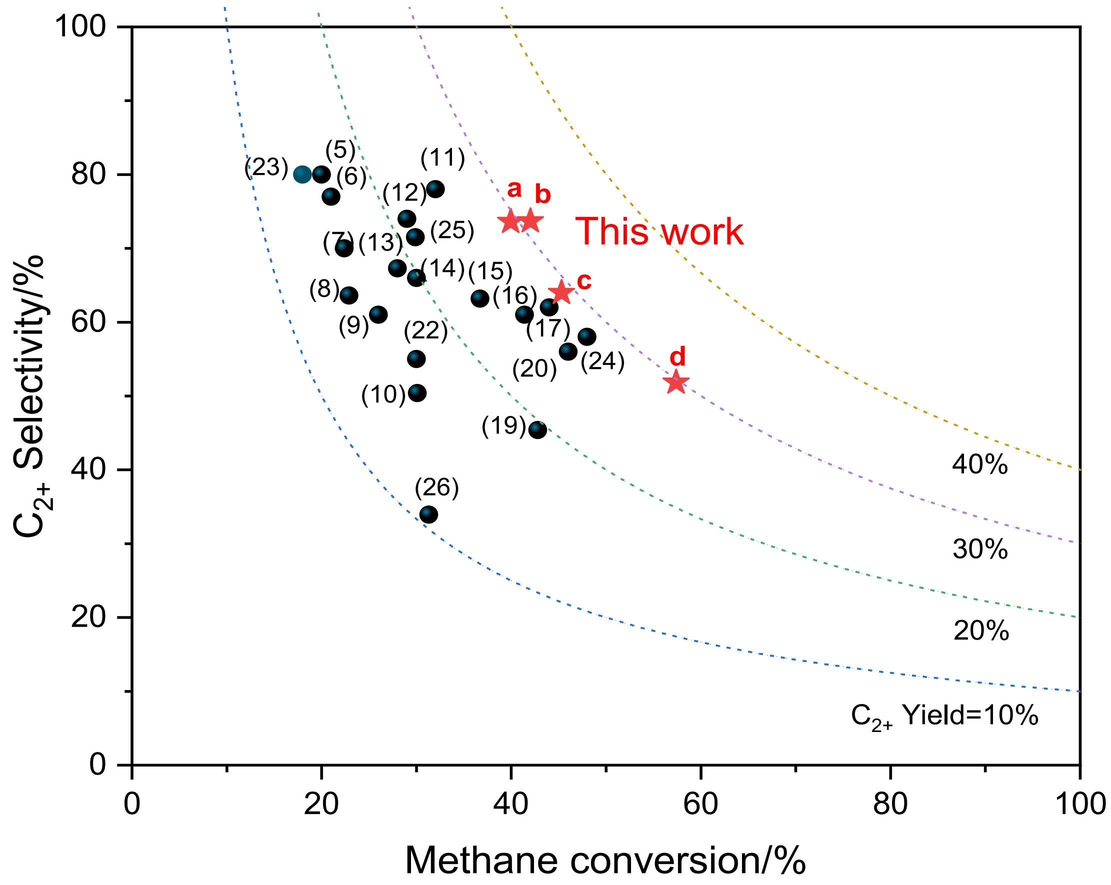


Methane DHA tests in OCM+DHA route at 700°C (a) without H_2-pretreatment, (b) with H_2-pretreatment and 720°C (c) without H2-pretreatment (d) with H_2-pretreatment.

Combining OCM with DHA shows promising aromatic yield

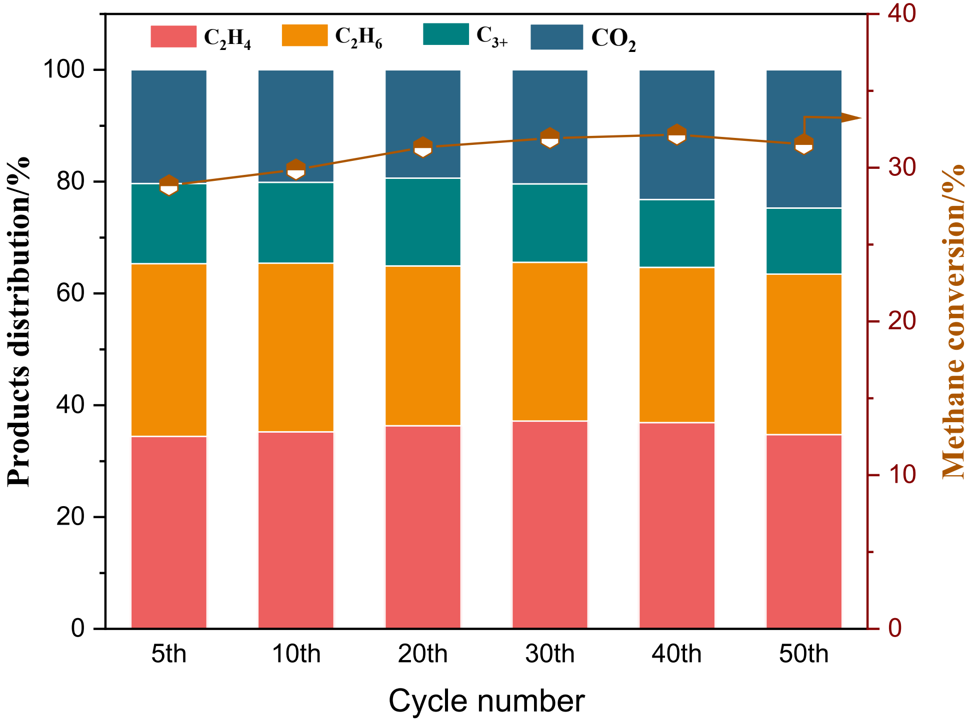
Summary of Project Progress – OCM Catalyst Optimization

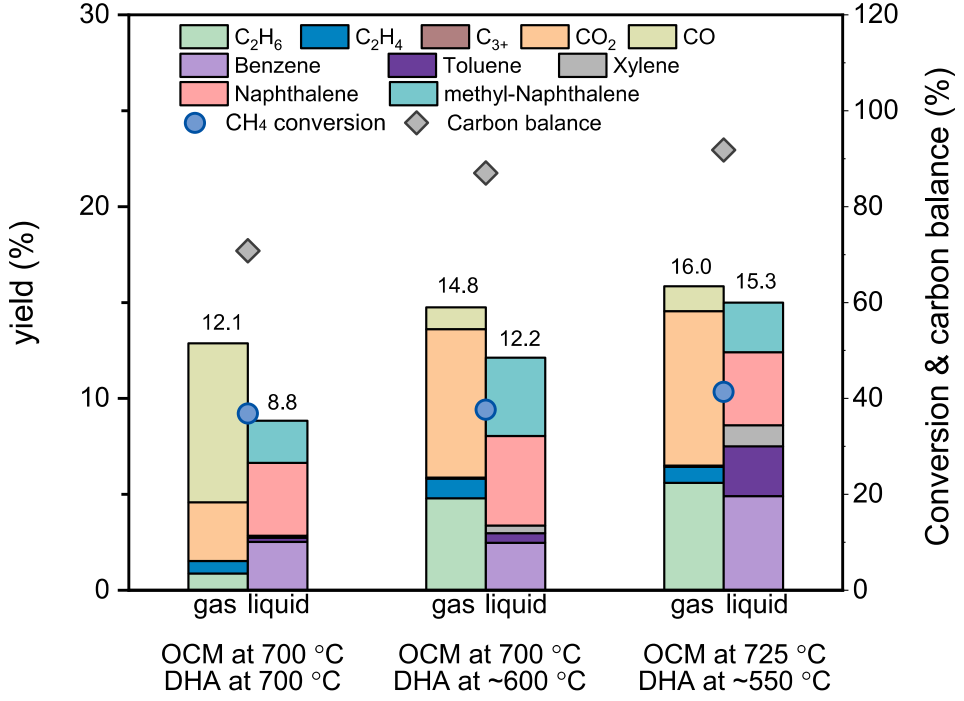




Our recently developed CL-OCM redox catalyst showed 30+% single pass C2+ yield

Summary of Project Progress – OCM Catalyst Stability and OCM+DHA Performance



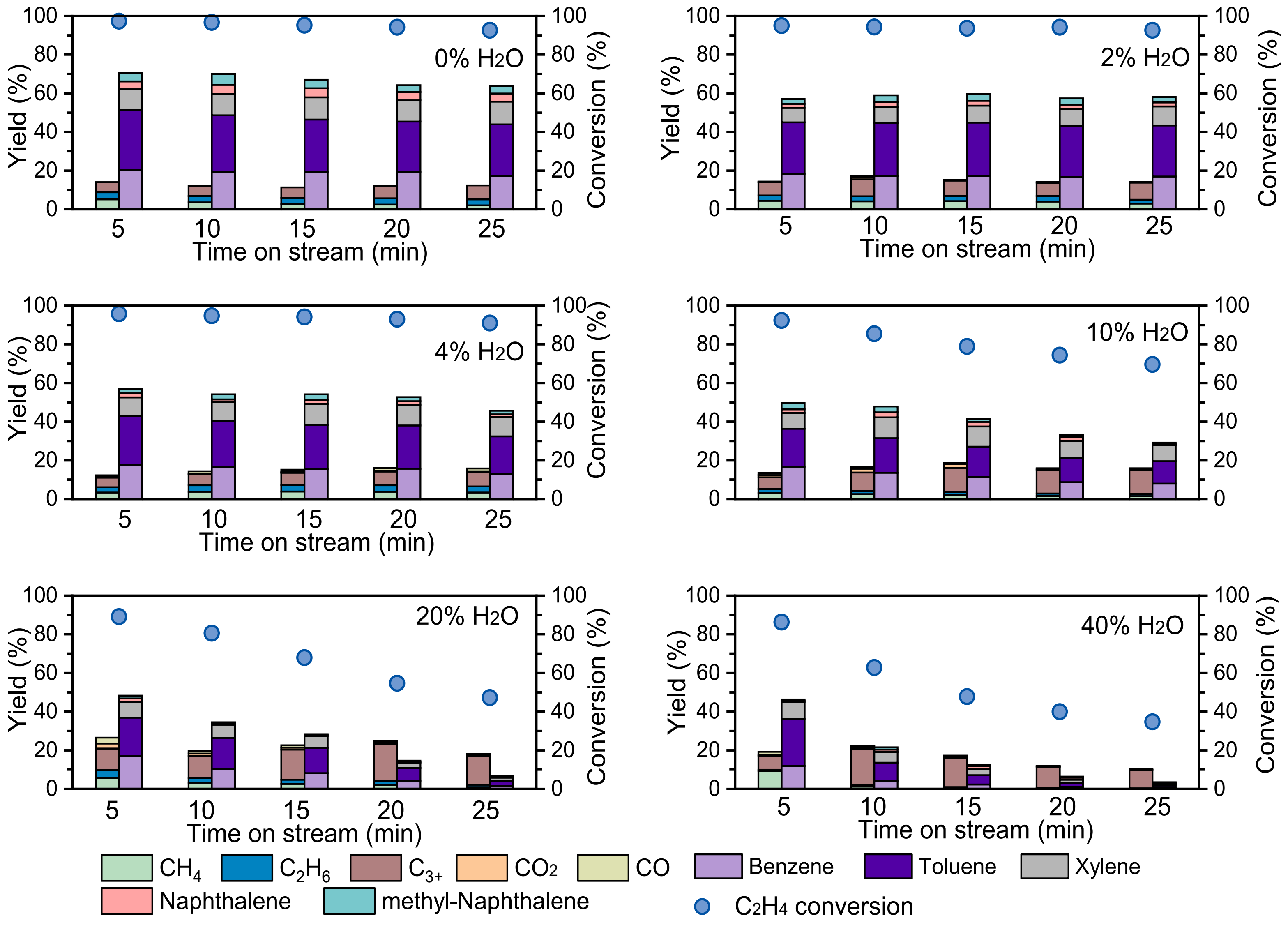


- OCM catalyst with core-shell structure enabled 30.9% C2+ yield and 42.7% methane conversion.
- OCM catalysts remained stable during the cycling test for over 50 cycles (~500 mins overall reaction time)

- OCM+DHA reached the aromatic yield milestone of 15%, nearly doubling the optimal yield from state-of-the-art methane DHA catalysts.

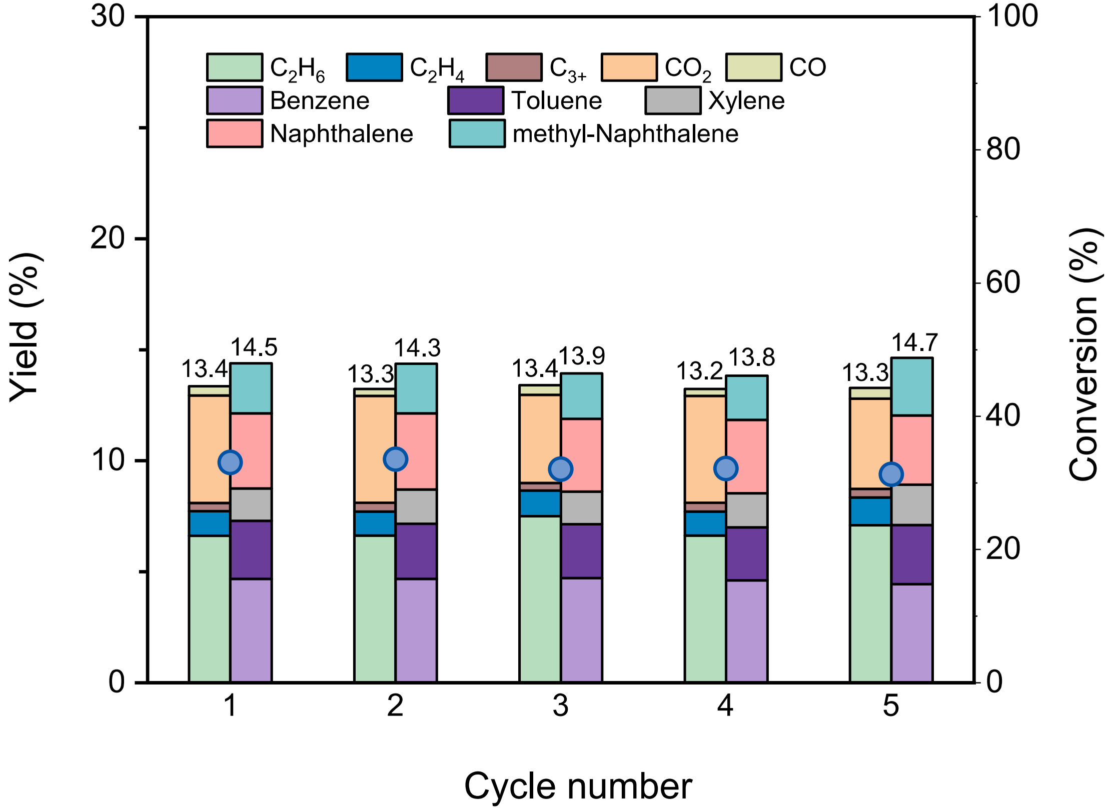
Milestone 5.1 : 15% single pass aromatics yield was achieved

Summary of Project Progress – OCM+DHA Stability

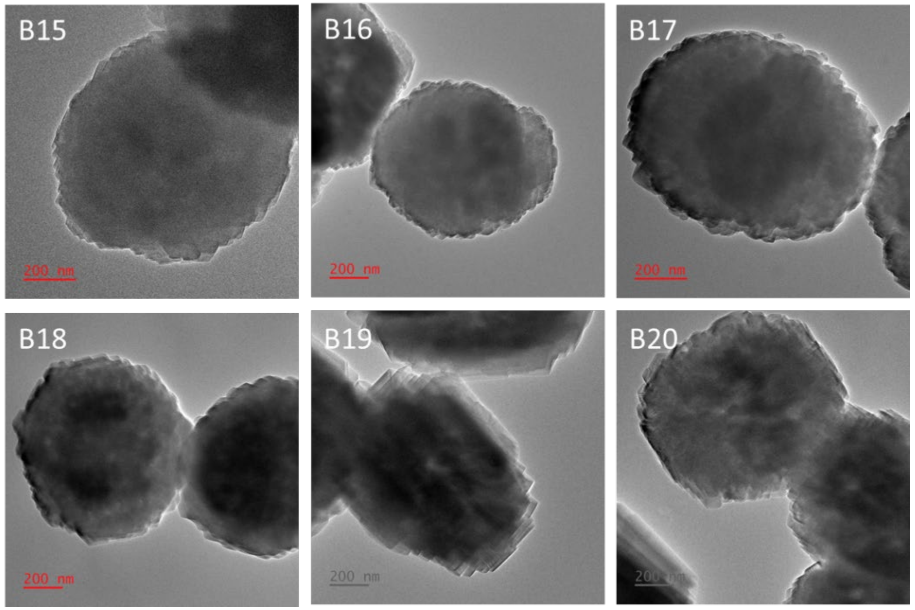


- Increased amount of water can deactivate the DHA catalyst.
- The current OCM reaction has 15-25% water as the side product.

Summary of Project Progress – OCM+DHA Stability and Catalyst Scalability



- ~15% single pass aromatic yield with almost no deactivation can be achieved by O_2-oxidation for OCM and H_2-reduction for DHA as the regeneration setup.



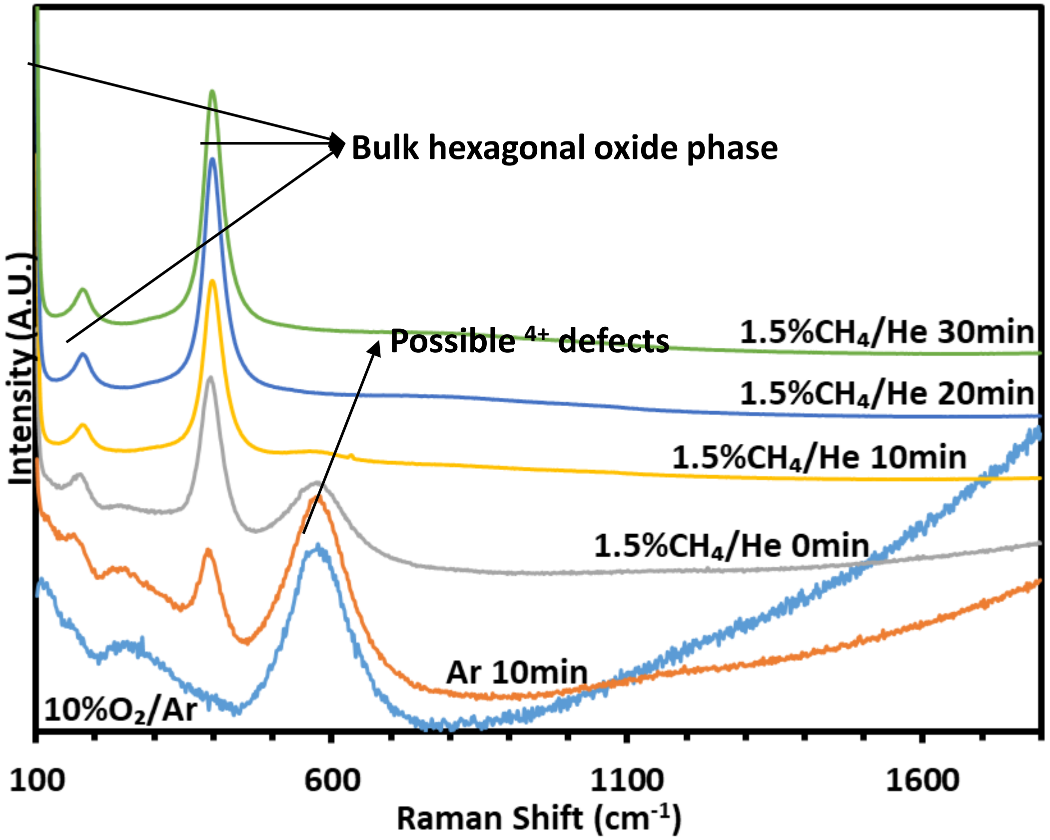
- SEM showed the synthesized DHA catalysts were highly repeatable.
- We validated the scale-up synthesis from 5g, 8g, 10g, and 20g with repeatable performance.

Task 6.2: Stable OCM+DHA operation achieved

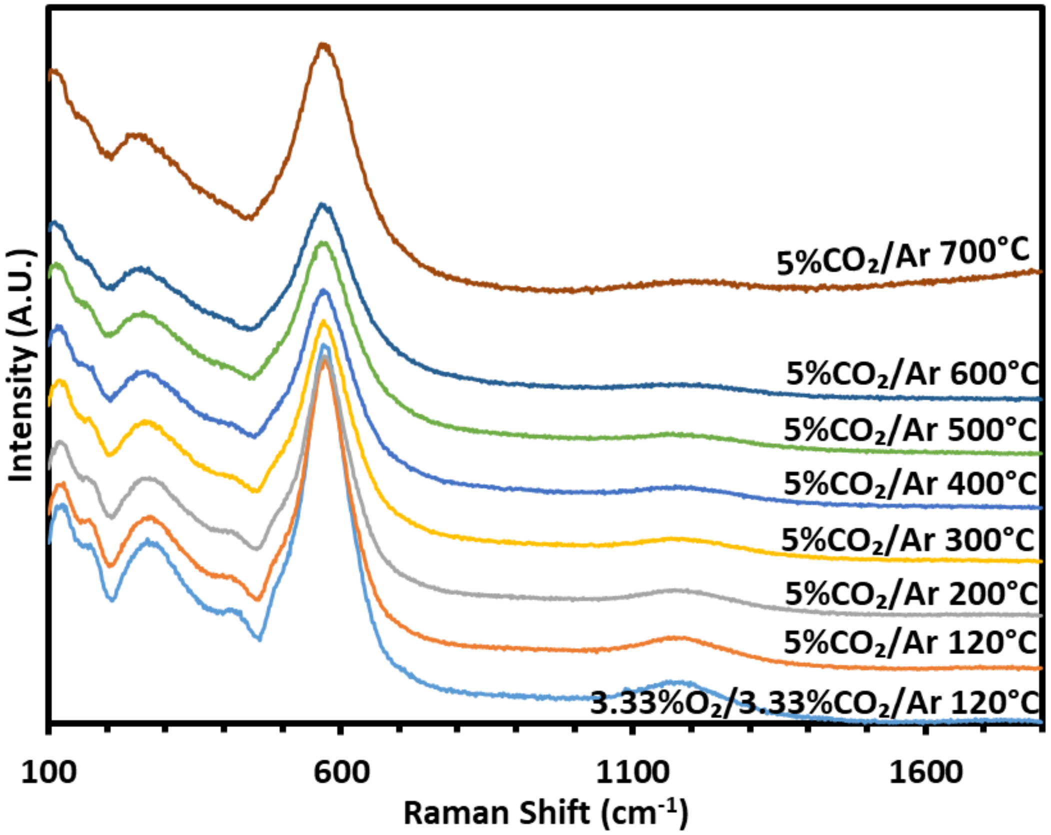
Task 5.2 : Scale-up synthesis was validated to be feasible.

In Situ Raman Characterization of OCM Catalysts

Bulk mixed oxide support dynamics under reaction conditions



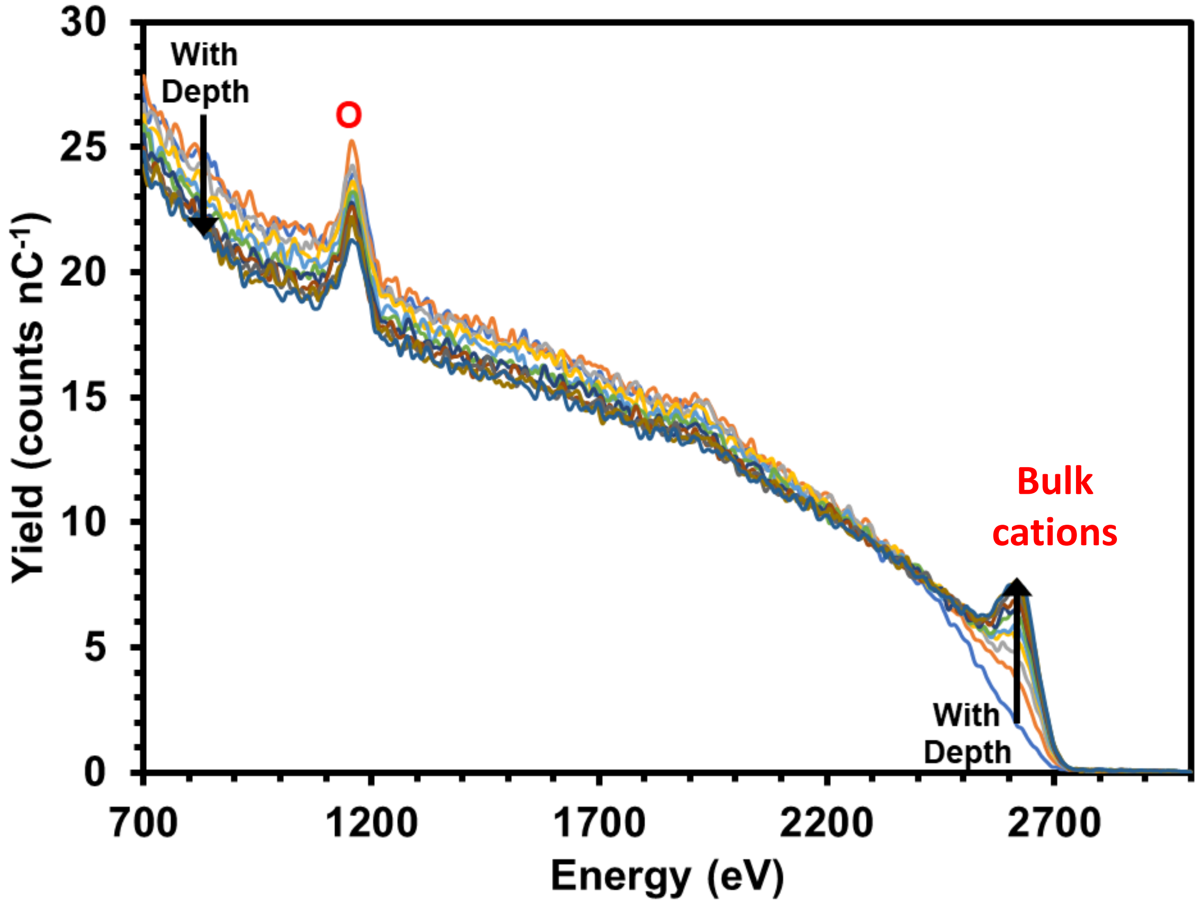
in situ Raman spectra of an oxidatively dehydrated OCM sample exposed to a reducing (1.5%CH_4/He) flow at 700°C, showing the gradual formation of a hexagonal phase from the 4+ defect rich oxidized structure.

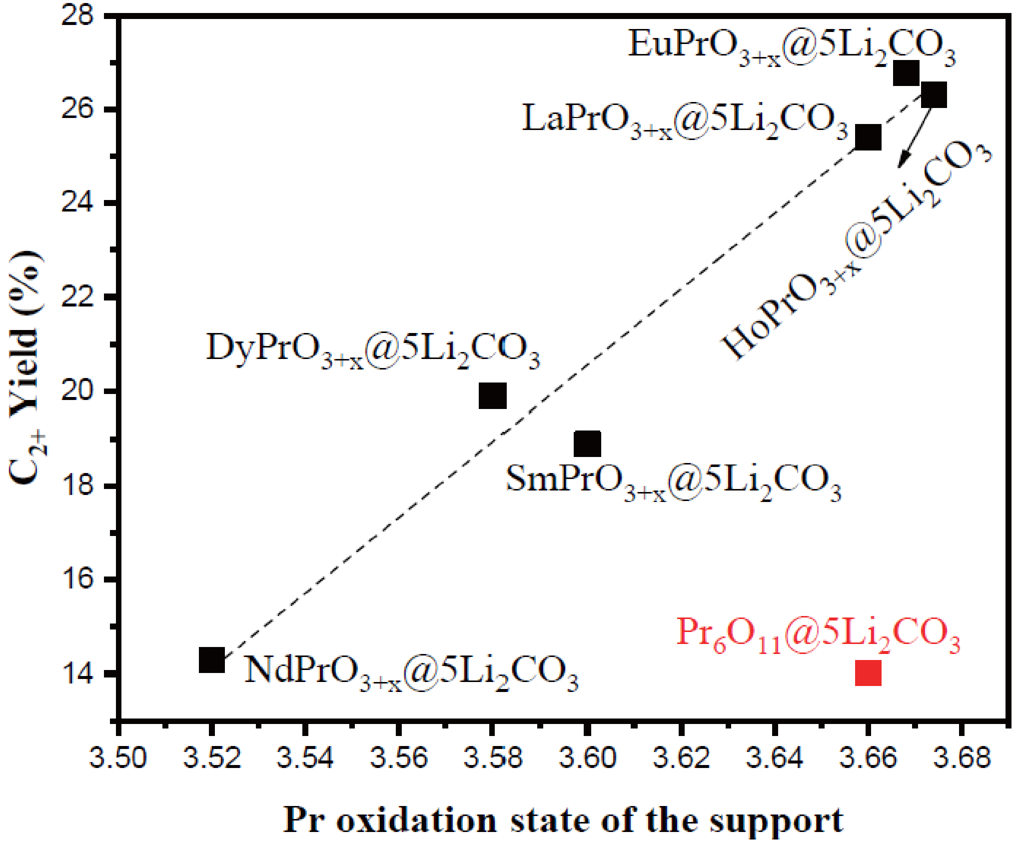


Oxidation with 3.3% O_2 re-created 4+ defects and exposure with CO_2 and Ar didn't show significant changes

In Situ HS-LEIS Characterization of the OCM Catalysts

High sensitivity low energy ion scattering characterization on an atomic layer basis

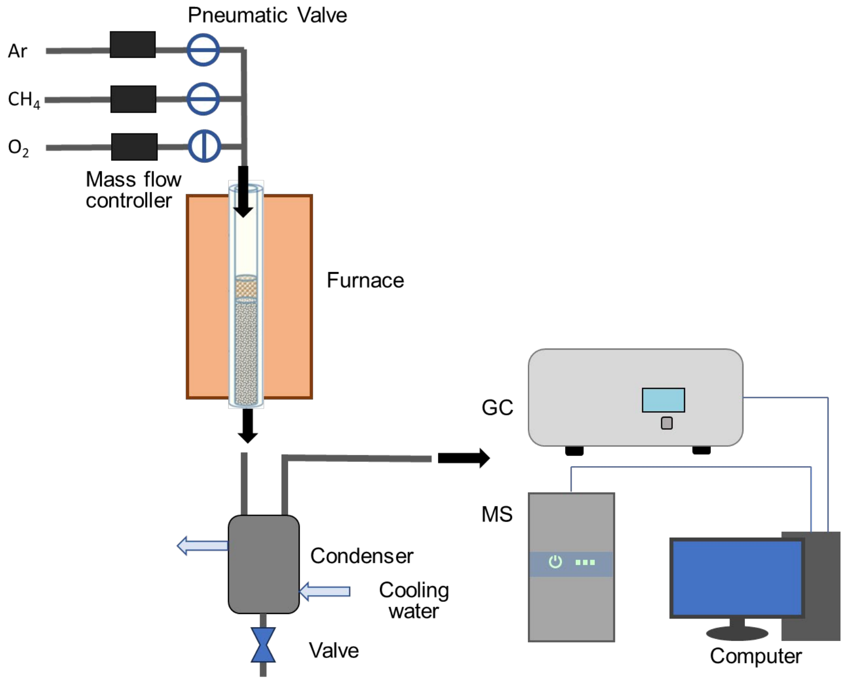


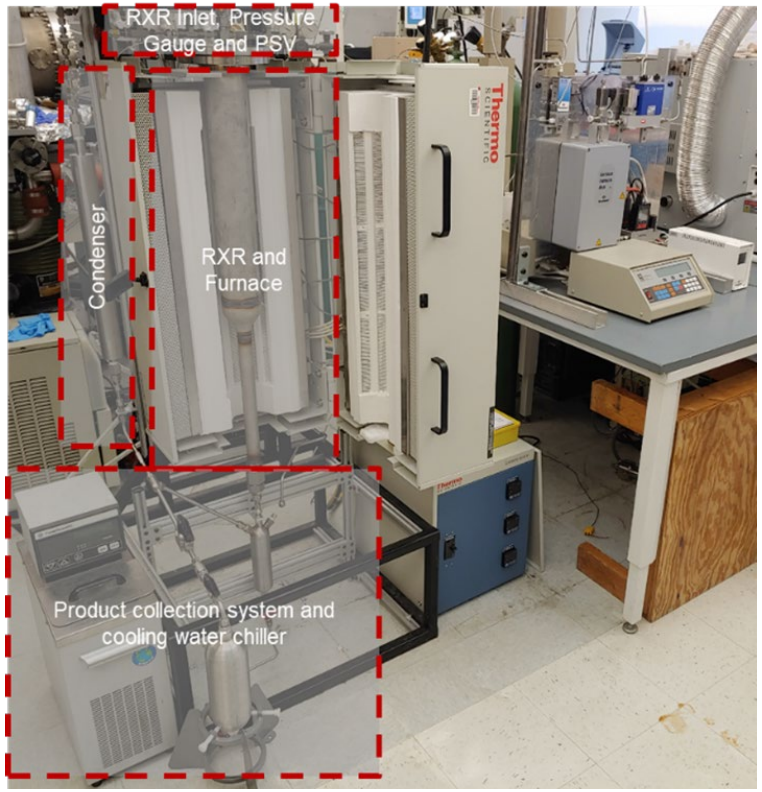


The HS-LEIS spectra for the oxidatively dehydrated OCM catalyst shows that no bulk cations are present in the outermost surface.

After approximately 2 atomic layers are sputtered then they start to show up, suggesting that the surface of the catalyst is completely covered by Li_2CO_3.

Summary of Project Progress – Reactor Scaleup and Shakedown





The reaction modular testing unit is being set up and commissioned by the NCSU, including reactant feedstock, the reactor, the separation unit, and the analysis instrument.

Task 6.1: The reaction modular testing unit has been set up

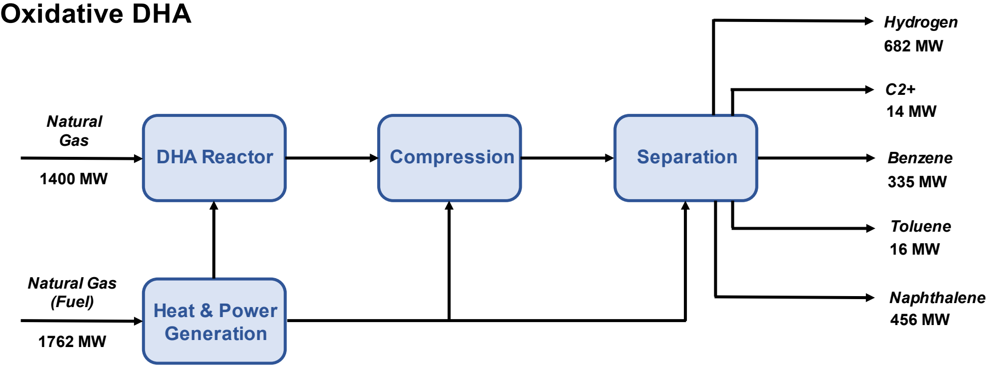
Energy Demand Comparison

Values in MW (unless otherwise noted)	Base Case	OAS 10%Y	OAS 20%Y	OAS 40%Y
NG for Heat (60% eff.)	1131.8	713.7	274.7	63.0
NG for Electricity (40% eff.)	655.5	344.9	0.0	-203.9
Fuel Requirement before Credits	1787.3	1058.5	274.7	63.0
Fuel NG Requirement after Credits	**1080.1**	**1026.1**	**233.1**	**-148.8**
Energy in Valuable Products	820.9	857.0	837.3	829.8
Net Energy Demand (Energy Lost)[d]	**1659.2**	**1569.1**	**750.8**	**352.0**
Aromatics Production Rate (kg/s)	18.8	19.4	19.0	18.8
Specific Net Energy Demand (MJ/kg)	88.3	80.9	39.6	18.7
% Reduction in Energy Demand	**--**	**8.4%**	**55.2%**	**78.8%**

* Aromatics production basis set at *19 kg/s*.

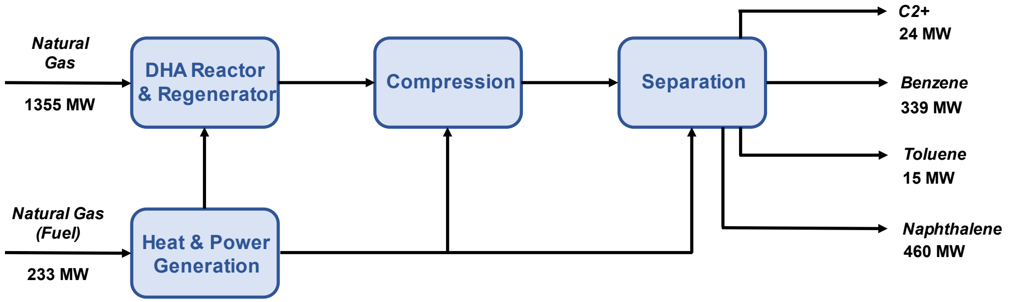
- The principal reductions in net energy input come from:
  - Reduction in overall process flowrate and resulting impacts on pre-heating, compression, and refrigeration duties
  - Simplified downstream separation requirements (particularly H_2/CH_4 cryogenic separation
- OAS technology enables modular operation
  - Non-oxidative DHA requires large scale demonstration due to H_2/CH_4 separation requirement
  - OAS able to economically produce Aromatics at **50 bbl/day scale**

Base Case:
Non-Oxidative DHA



Net Energy Input = 1659 MW
= 88.3 MJ/kg aromatics

Oxidative Aromatization System (OAS): 20% Yield



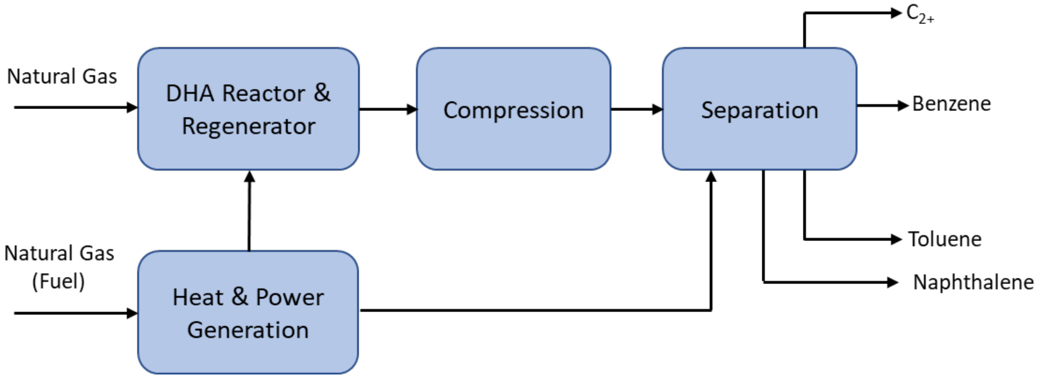
Net Energy Input = 751 MW
= 39.6 MJ/kg aromatics

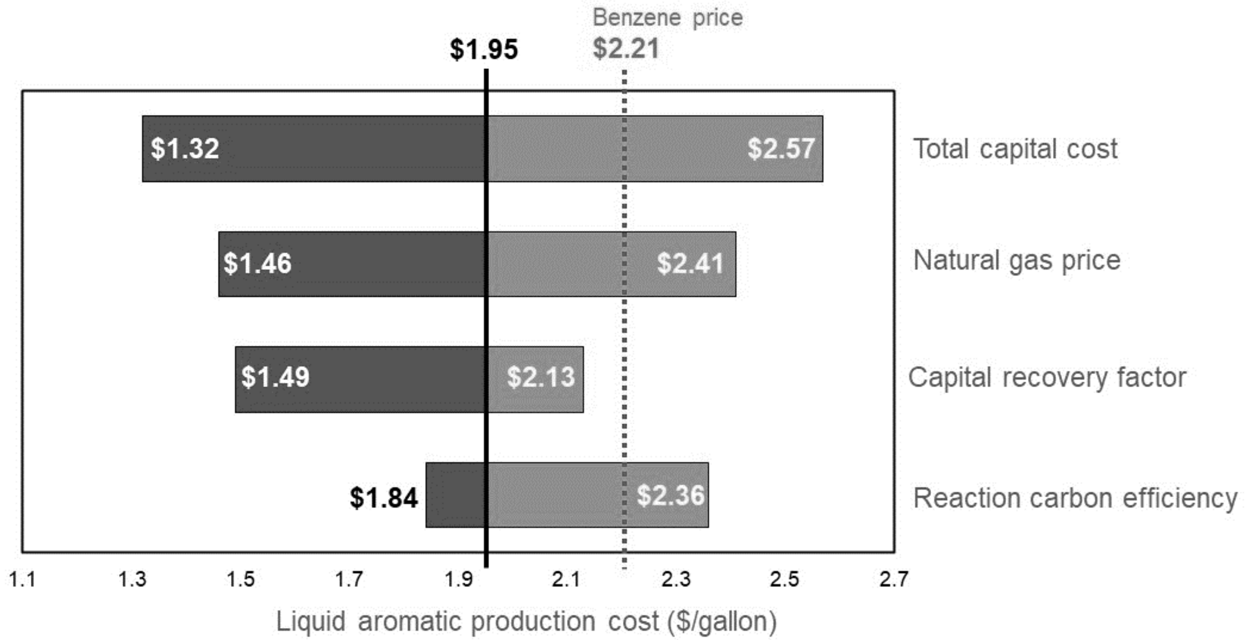
Preliminary Economics: 50 bbl/day Modular Plant

Susteon

- NCSU Oxidative Aromatization System (OAS) achieves a breakeven liquid aromatic production cost of $1.95/gal compared to a market price of $2.21/gal
- Capital expenditure and yield efficiency identified as major factors in final product cost
- Improving the reactor design can reduce the aromatic costs to <$1.50/gal

Parameter	**Units**	**Low**	**Base**	**High**
Total capital cost	$/bbl/day	50,000	100,000	150,000
Natural gas price	$/MMBTU	0	3	5
Capital recovery factor	%	6	12.4	15
Reaction carbon efficiency	%	50	80	95





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Plans for Future Development

Future work within the project:

- Optimization of the process scheme guided by TEA;
- Long-term OAS demonstration and post demonstration characterization;
- Finalization of TEA and scale-up roadmap.

Future work beyond the project:

- Further scale up testing (up to 1000 cuft/day);
- Detailed catalyst cost and scalability study; Detailed system design and costing;
- Demonstration and commercialization with industrial partner(s).

Synergistic Opportunities:

- Plasma or microwave enhanced conversions (*Jason Hicks and John Hu*);
- Advanced schemes, membrane/electrochemical enhancement (*Ranjani Siriwardane, Joshhua Tong, Dongixa Liu*)
- Advanced catalyst/mechanisms (*Andreas Heyden*)

Summary Slide

Various ZSM based DHA catalysts have been developed, meeting the 800 g/kgCat-hr and 80% aromatics selectivity target (go/no-go);

Effective SHC redox catalysts have been developed, demonstrating >200 mol/kgCat-hr activity and >80% selectivity at 700 °C;

Efficient hydrogen combustion resulted in high steam concentration, eliminating the active sites on the DHA catalyst;

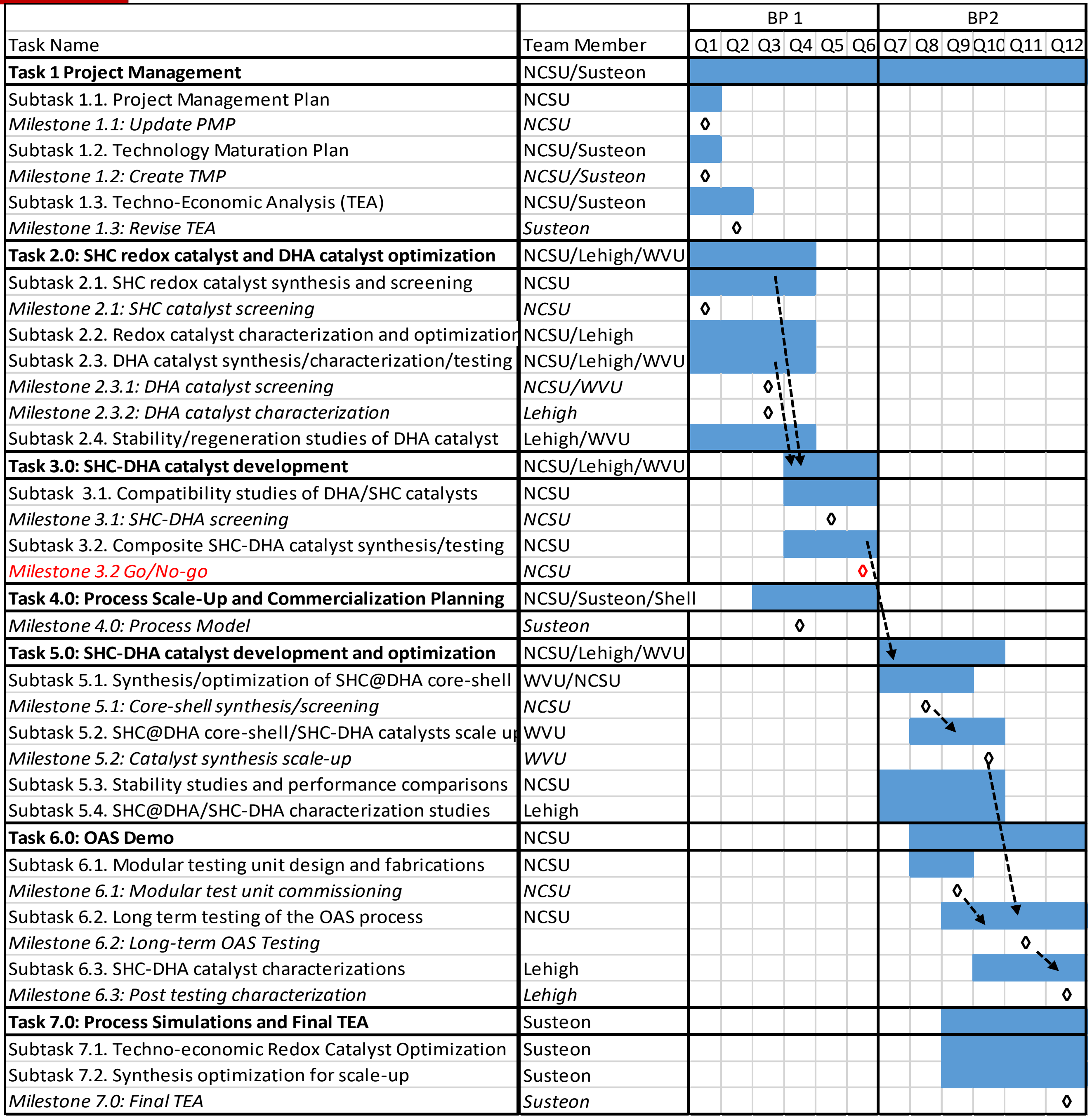
Alterative schemes for methane DHA have been developed, showing excellent aromatics yields;

In-situ characterization of the catalysts generated mechanistic insights;

TEA indicates that the proposed OAS technology has excellent potential for energy savings and emission reduction.

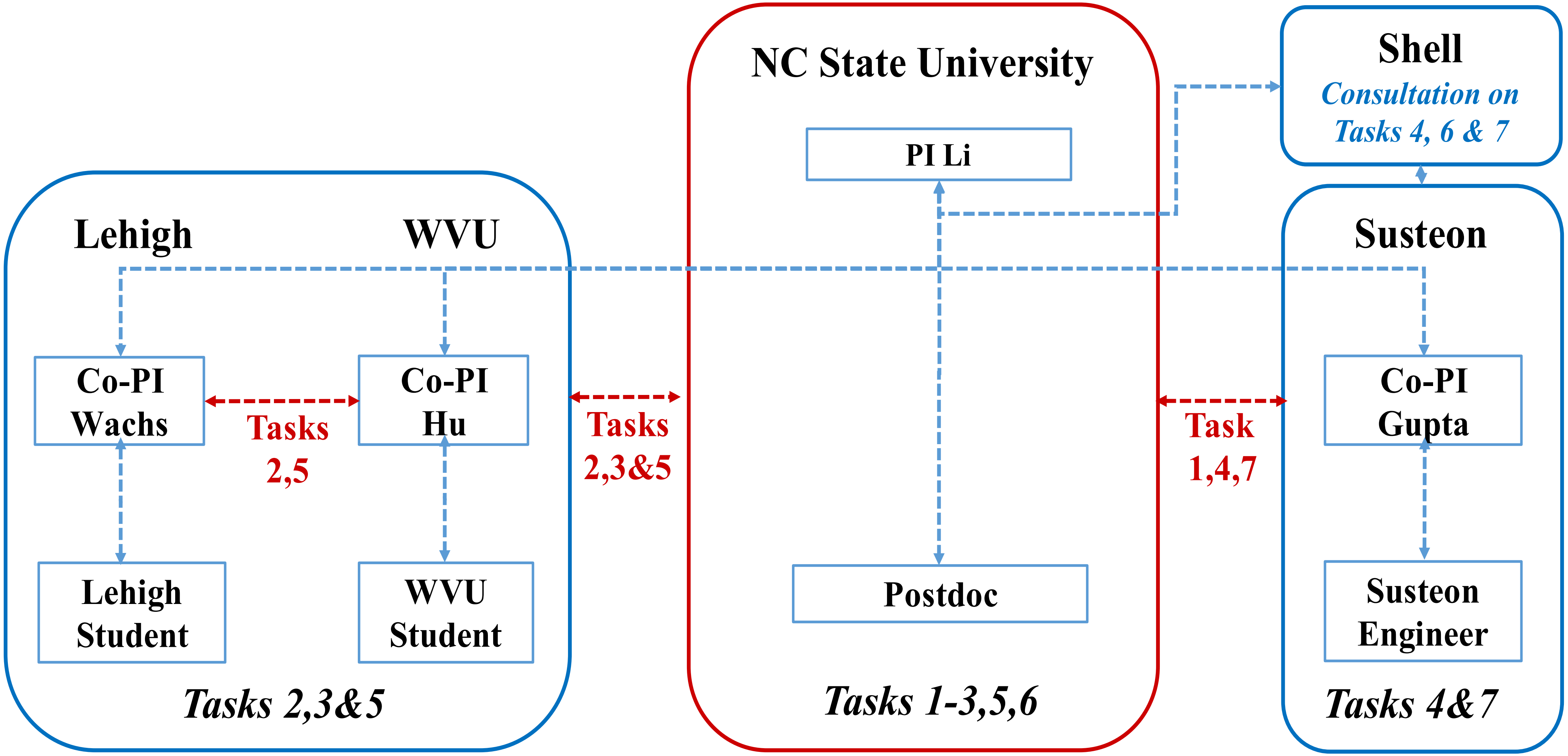
Thanks for the support!
Questions or suggestions?

Appendix: Project Schedule

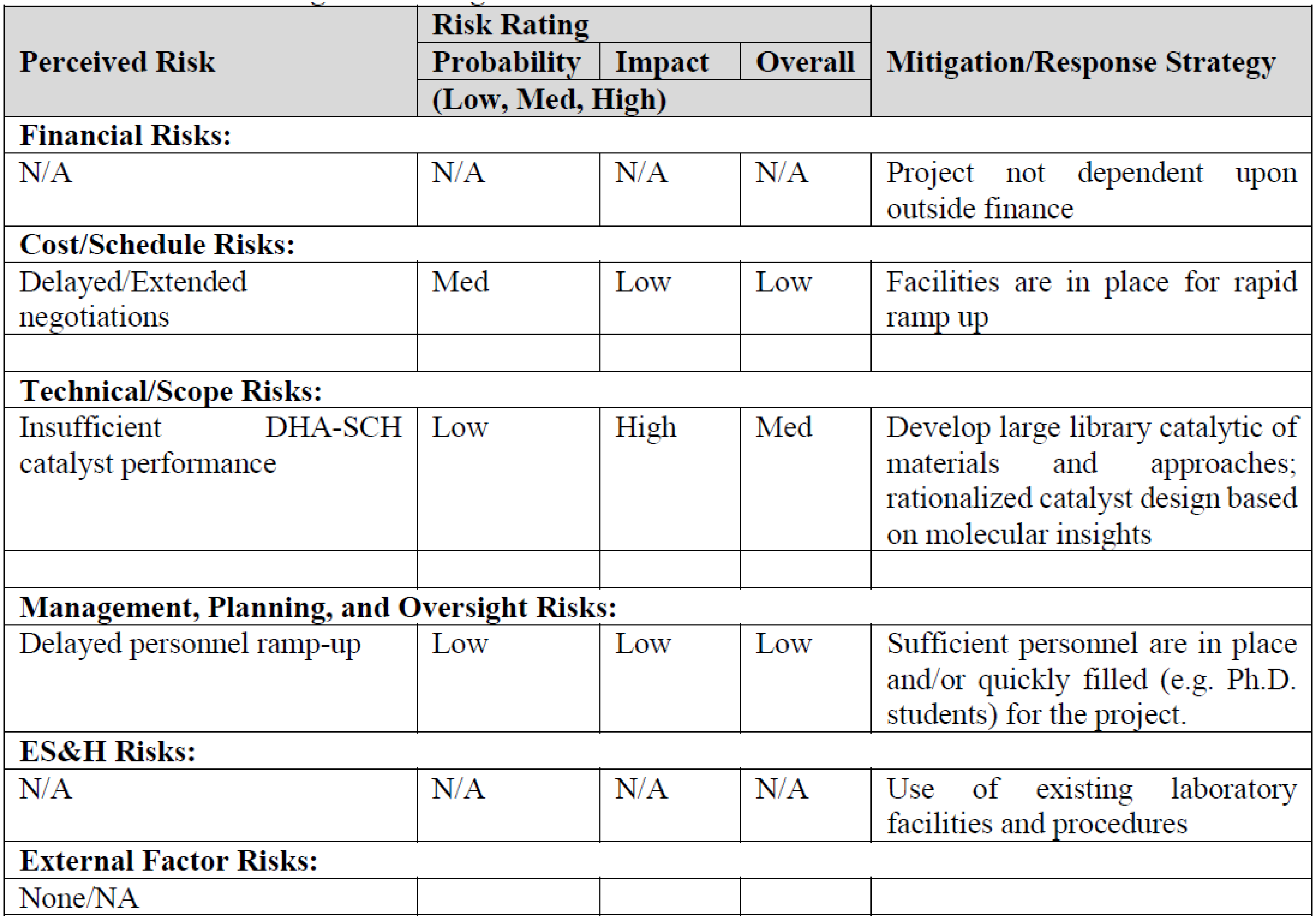


Task Name	Team Member	BP 1						BP2					
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1 Project Management	NCSU/Susteon	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Subtask 1.1. Project Management Plan	NCSU	🟦											
Milestone 1.1: Update PMP	*NCSU*	◊											
Subtask 1.2. Technology Maturation Plan	NCSU/Susteon	🟦											
Milestone 1.2: Create TMP	*NCSU/Susteon*	◊											
Subtask 1.3. Techno-Economic Analysis (TEA)	NCSU/Susteon	🟦	🟦										
Milestone 1.3: Revise TEA	*Susteon*		◊										
Task 2.0: SHC redox catalyst and DHA catalyst optimization	NCSU/Lehigh/WVU	🟦	🟦	🟦	🟦								
Subtask 2.1. SHC redox catalyst synthesis and screening	NCSU	🟦	🟦	🟦	🟦								
Milestone 2.1: SHC catalyst screening	*NCSU*	◊											
Subtask 2.2. Redox catalyst characterization and optimization	NCSU/Lehigh	🟦	🟦	🟦	🟦								
Subtask 2.3. DHA catalyst synthesis/characterization/testing	NCSU/Lehigh/WVU	🟦	🟦	🟦	🟦								
Milestone 2.3.1: DHA catalyst screening	*NCSU/WVU*			◊									
Milestone 2.3.2: DHA catalyst characterization	*Lehigh*			◊									
Subtask 2.4. Stability/regeneration studies of DHA catalyst	Lehigh/WVU	🟦	🟦	🟦	🟦								
Task 3.0: SHC-DHA catalyst development	NCSU/Lehigh/WVU				🟦	🟦	🟦						
Subtask 3.1. Compatibility studies of DHA/SHC catalysts	NCSU				🟦	🟦	🟦						
Milestone 3.1: SHC-DHA screening	*NCSU*					◊							
Subtask 3.2. Composite SHC-DHA catalyst synthesis/testing	NCSU				🟦	🟦	🟦						
Milestone 3.2 Go/No-go	*NCSU*						◊						
Task 4.0: Process Scale-Up and Commercialization Planning	NCSU/Susteon/Shell			🟦	🟦	🟦	🟦						
Milestone 4.0: Process Model	*Susteon*				◊								
Task 5.0: SHC-DHA catalyst development and optimization	NCSU/Lehigh/WVU							🟦	🟦	🟦	🟦		
Subtask 5.1. Synthesis/optimization of SHC@DHA core-shell	WVU/NCSU							🟦	🟦	🟦			
Milestone 5.1: Core-shell synthesis/screening	*NCSU*								◊				
Subtask 5.2. SHC@DHA core-shell/SHC-DHA catalysts scale up	WVU								🟦	🟦	🟦		
Milestone 5.2: Catalyst synthesis scale-up	*WVU*										◊		
Subtask 5.3. Stability studies and performance comparisons	NCSU							🟦	🟦	🟦	🟦		
Subtask 5.4. SHC@DHA/SHC-DHA characterization studies	Lehigh							🟦	🟦	🟦	🟦		
Task 6.0: OAS Demo	NCSU								🟦	🟦	🟦	🟦	🟦
Subtask 6.1. Modular testing unit design and fabrications	NCSU								🟦	🟦			
Milestone 6.1: Modular test unit commissioning	*NCSU*									◊			
Subtask 6.2. Long term testing of the OAS process	NCSU									🟦	🟦	🟦	🟦
Milestone 6.2: Long-term OAS Testing												◊	
Subtask 6.3. SHC-DHA catalyst characterizations	Lehigh										🟦	🟦	🟦
Milestone 6.3: Post testing characterization	*Lehigh*												◊
Task 7.0: Process Simulations and Final TEA	Susteon									🟦	🟦	🟦	🟦
Subtask 7.1. Techno-economic Redox Catalyst Optimization	Susteon									🟦	🟦	🟦	🟦
Subtask 7.2. Synthesis optimization for scale-up	Susteon									🟦	🟦	🟦	🟦
Milestone 7.0: Final TEA	*Susteon*												◊

Appendix: Project Organizational Structure



Risk Management



Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
	(Low, Med, High)			
Financial Risks:				
N/A	N/A	N/A	N/A	Project not dependent upon outside finance
Cost/Schedule Risks:				
Delayed/Extended negotiations	Med	Low	Low	Facilities are in place for rapid ramp up
Technical/Scope Risks:				
Insufficient DHA-SCH catalyst performance	Low	High	Med	Develop large library catalytic of materials and approaches; rationalized catalyst design based on molecular insights
Management, Planning, and Oversight Risks:				
Delayed personnel ramp-up	Low	Low	Low	Sufficient personnel are in place and/or quickly filled (e.g. Ph.D. students) for the project.
ES&H Risks:				
N/A	N/A	N/A	N/A	Use of existing laboratory facilities and procedures
External Factor Risks:				
None/NA				

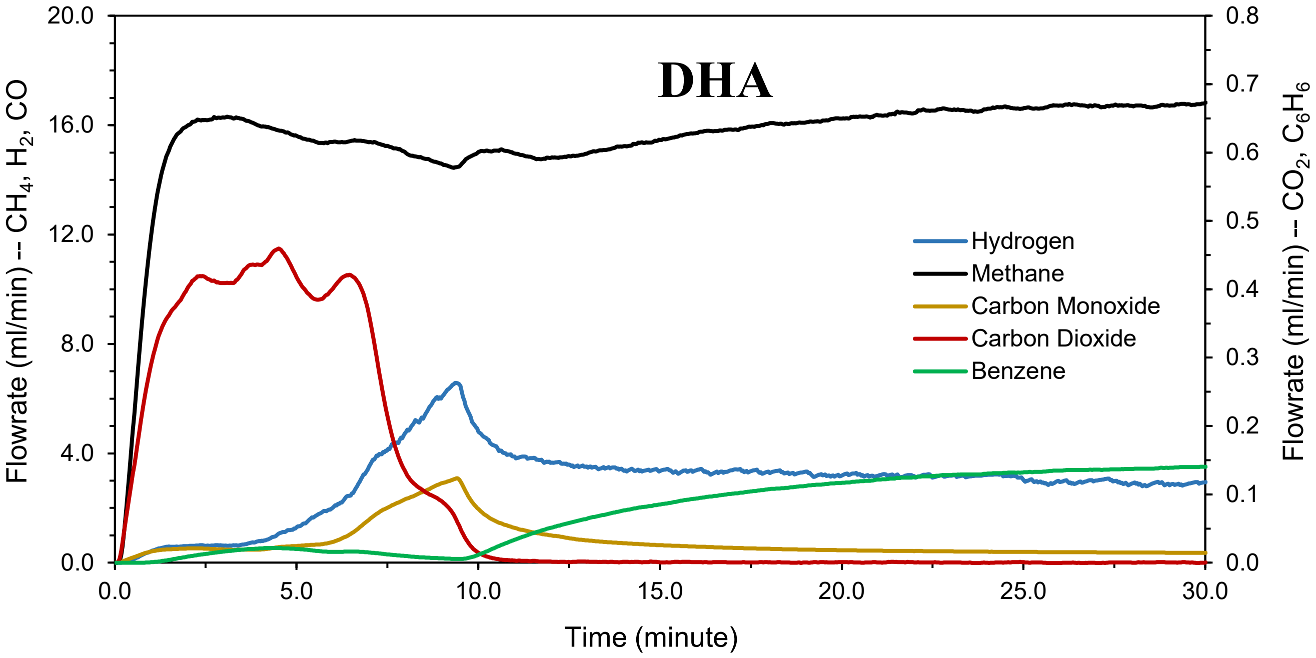
Milestones

Task#	Milestone Title & Description	Due	Verification method
1.1	Update PMP	BP1-Q1	Submit updated PMP
1.2	Create TMP	BP1-Q1	Submit TMP
2.1	SHC Catalyst Screening: Report 4 SHC redox catalysts with hydrogen combustion activity of 200 mol/kgCat-hr and 80% selectivity at 700 °C.	BP 1-Q1	Report reaction data in Q-Report
1.3	Revise TEA	BP1-Q2	Submit Revised TEA
2.3.1	DHA Cat. Screening: Report 3 or more DHA catalysts with > 500 g/kgCat-hr aromatics productivity and > 80% selectivity at <700 °C	BP1-Q3	Report reaction data in Q-Report
2.3.2	DHA Cat. Characterization: Identify DHA catalysts phases and structures under reaction conditions.	BP1-Q3	Report data for 2 DHA catalyst.
4.0	Process Model: Report ASPEN models for a base case (non-oxidative DHA) reactor and OAS showing >50% reduction in net energy demand	BP1-Q4	Report energy demand for OAS vs. base-case
3.1.	SHC-DHA Screening: Report 3 or more physical mixtures (or composite) catalysts with > 20% single pass aromatics yield.	BP2-Q5	Report reaction data in Q-Report
3.2.	***Go/No-go:*** *Report DHA-SHC composite with > 800 g/kgCat-hr aromatics productivity at < 700 °C.*	BP1-Q6	Report reaction data in Q-Report
5.1	Core-shell Synthesis/Screening: Report three or more SHC@DHA (or composite) catalysts with > 30% single pass aromatics yield.	BP2-Q8	Report reaction data in Q-Report
6.1	Modular test unit commissioning: Report >50 ml/day aromatic productivity using >10 g physically mixed DHA-SHC catalyst bed at < 700 °C	BP2-Q9	Report reaction data in Q-Report
5.2	Catalyst synthesis scale-up: Prepare 20+ gram batch of DHA@SCH core-shall (or composite) catalyst for long-term testing	BP2-Q10	Report activity data of large batch catalyst
6.2	***Long-Term OAS Testing:*** Report selected SHC-DHA catalyst for 100 hours of continuous operation with >40% single pass aromatics yield and <5% deactivation, showing >200 ml/day aromatics productivity at 650 °C.	BP2-Q11	Report reaction data in Q-Report
6.3	Post testing characterization: Determine phase and surface properties of the catalyst after the long-term stability test.	BP2-Q12	Report Characterization in final report
7.0	***Final TEA:*** Confirm 90% overall aromatics yield and 25% return on investment using refined process model. Develop commercialization roadmap with TEA and LCA for the OAS system.	BP2-Q12	Report final TEA at end of project

Backup

Summary of Project Progress – DHA + SHC Composite Bed

0.7 g 3% Mo/HZSM-5 + 0.1 g $Na_2WO_4/CaMnO_3$



- DHA bed starts to work only when the SHC bed is fully consumed of active lattice oxygen.

Other Configurations:

Composition	Result
Pre-carburized DHA + NW/CMO	Failed.
DHA+NW/CMO (partially oxidized)	Failed.
Pre-carburized DHA + NW/CMO (partially oxidized)	Failed.

- **Water concentration in our study = ~6.2 Vol.%**
- **Water concentration in Chem. Comm. paper on Mo/ZSM5+CGO < 2.7 Vol.%**
  - **Note also that CGO has poorer H_2 conversion ability than $Na_2WO_4/CaMnO_3$**

In-situ synthesis of Ga-ZSM-5 in Microwave

- We adapted the conventional hydrothermal in-situ synthesis of Ga-ZSM-5 (Si/Ga 30) catalysts to be applicable to the microwave synthesizer unit [1]
- Preparation of the precursor solutions for both the conventional and microwave synthesis was the same
- However, the synthesis temperature and time were different:
  - **Conventional hydrothermal synthesis:** 170°C for 72 hours
  - **Microwave synthesis:** 220°C for 30 mins (a lot less time consuming)
- Finally, each sample was then dried at 100°C for 12 hrs, calcined at 550°C for 6 hrs, and treated with an ammonium nitrate solution 3x times 90mins each and calcined again.
- Both conventional and microwave synthesized samples show a similar crystal size and uniformity in shape.

[1] Y. Zhou, H. Thirumalai, S. K. Smith, K. H. Whitmire, J. Liu, A. I. Frenkel, L. C. Grabow, J. D. Rimer, Angew. Chem. Int. Ed. 2020, 59, 19592.

Screening of each Ga-ZSM-5

- Each prepared Ga-ZSM-5 microwave synthesized catalyst is screened via
  - SEM, TEM, XRD, and catalytic DHA performance tests
- Catalytic testing:
  - 1) 10% Ethane (total flow 30 mL/min), 700°C, 60 mins
  - 2) 10% Ethylene (total flow 30 mL/min), 700°C, 60 mins
  - 3) 10% Each (10% Ethane & 10% Ethylene) , 700°C, 60 mins
- GC-MS Analysis to help close carbon balance – being calibrated now
  - Following reactor during the reaction a cold trap was placed in-line
  - After each reaction, the trap was then washed with chloroform and analyzed

Reaction [Temp] (Syn. Batch)						
	10%Ethane [700C] (B9-30)	10%Ethane [700C] (B10-30)	10%Ethane [700C] (B11-30)	10%Ethane [700C] (B12-30)	10%Ethylene [700C] (B5-30)	10%Each [700C] (B5-30)
C2H6 Conv.	75.1 %	79.0 %	77.3 %	76.9 %	-	73 %
C2H4 Conv.	-	-	-	-	95 %	71 %
C2H4 Sel.	32.3 %	31.0 %	33.1 %	32.4%	-	-
C2H6 Sel.	-	-	-	-	0.78 %	-
CH4 Sel.	11.8 %	11.2 %	11.1 %	11.0 %	9.3 %	11 %
C3H8 Sel.	1.0 %	1.0 %	0.9 %	0.9 %	0.2 %	0.5 %
C6H6 Sel.	25.0 %	31.0 %	28.0 %	28.3 %	18 %	18.3 %
C7H8 Sel.	2.3 %	7.15 %	6.68 %	6.20 %	1.2 %	0.9 %
Stream Carbon Balance (Missing)	66.1 % (33.9 %)	70.0 % (30.0 %)	68.2 % (31.8 %)	68.7 % (31.3 %)	37.3 % (62.7 %)	50 % (50 %)
TGA Carbon Balance (Missing)	69.8 % (30.2 %)	73.0 % (27.0 %)	70.2 % (29.8 %)	71.4 % (28.6 %)	43.8 % (56.2 %)	60 % (40 %)

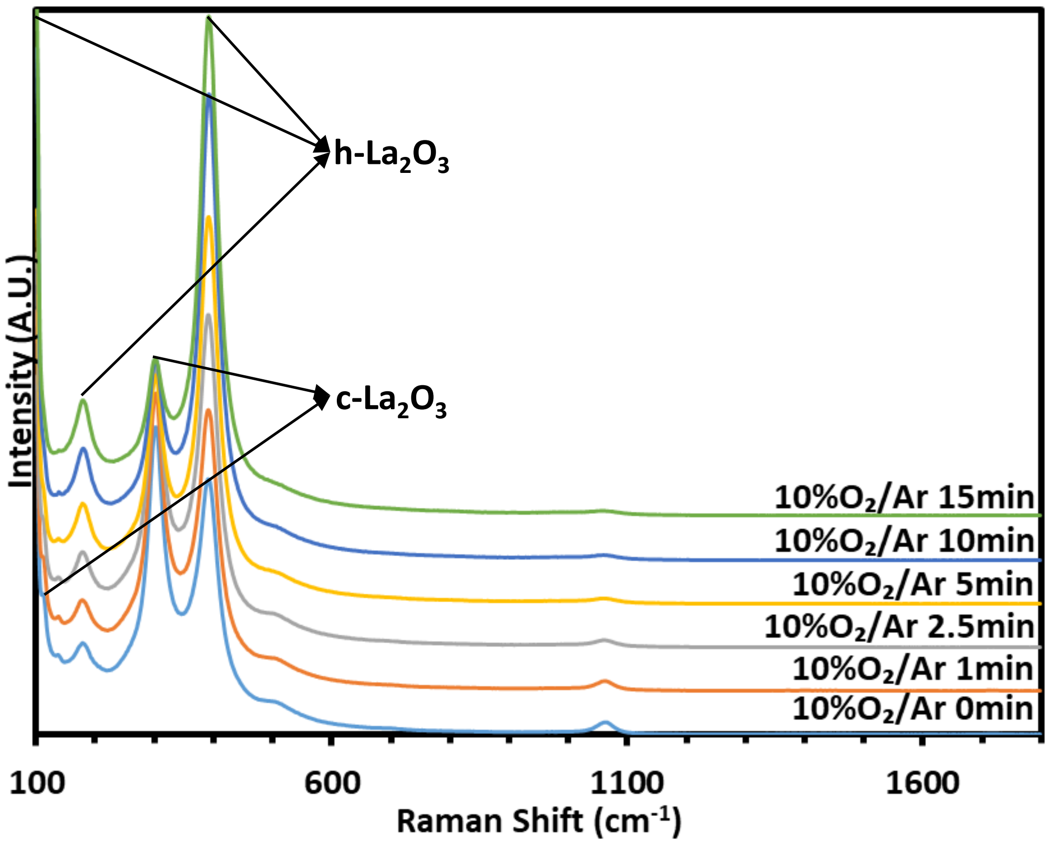
**GC-MS qualitative data from trap -> next slide

In Situ Raman Characterization of OCM Catalysts

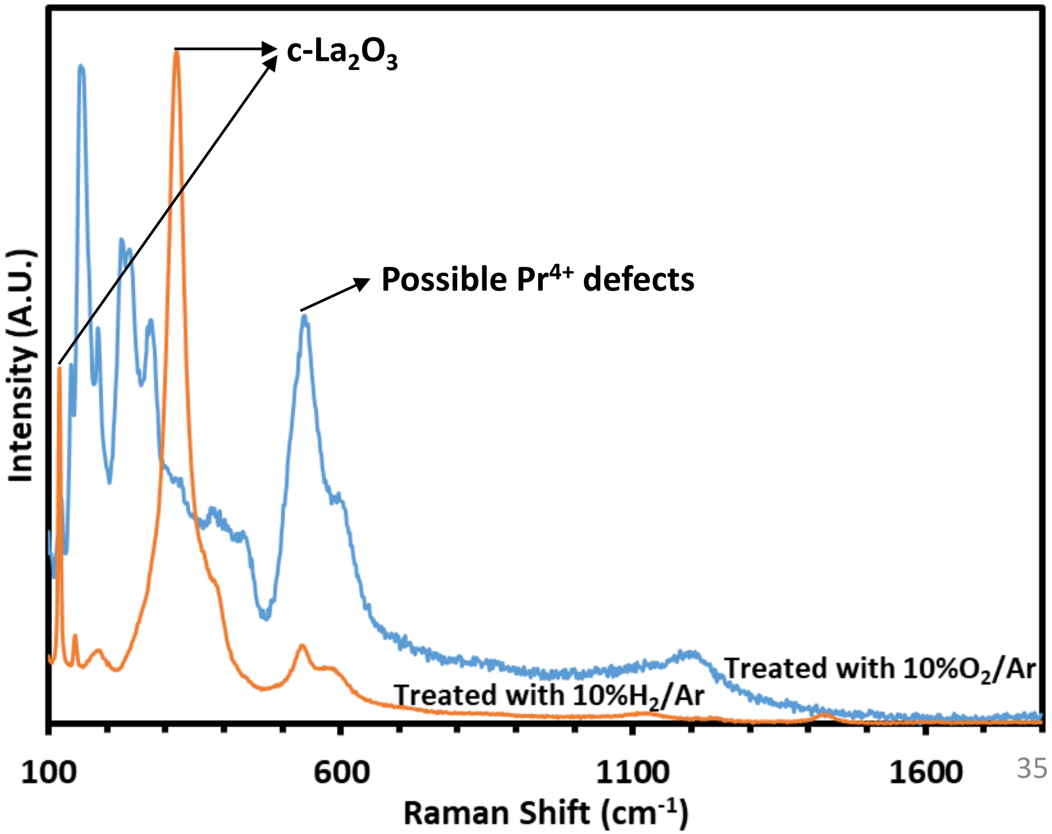
Metal Oxide Support Reference Materials

- The spectra of a bulk lanthanum oxide acquired under *in situ* oxidizing conditions at 700°C (**left figure**) reveals the progressive formation of a hexagonal La_2O_3 phase from a cubic La_2O_3 phase, each with distinct Raman vibrations.
- A Pr_6O_{11} sample that was dehydrated and then exposed *in situ* to either oxidizing (10%O_2/Ar) or reducing (10%H_2/Ar) conditions at 700°C **(right figure)** demonstrated the formation of a Pr^{4+} defect rich structure or a cubic Pr_2O_3 phase respectively.

La_2O_3 at 700°C under 10%O_2/Ar



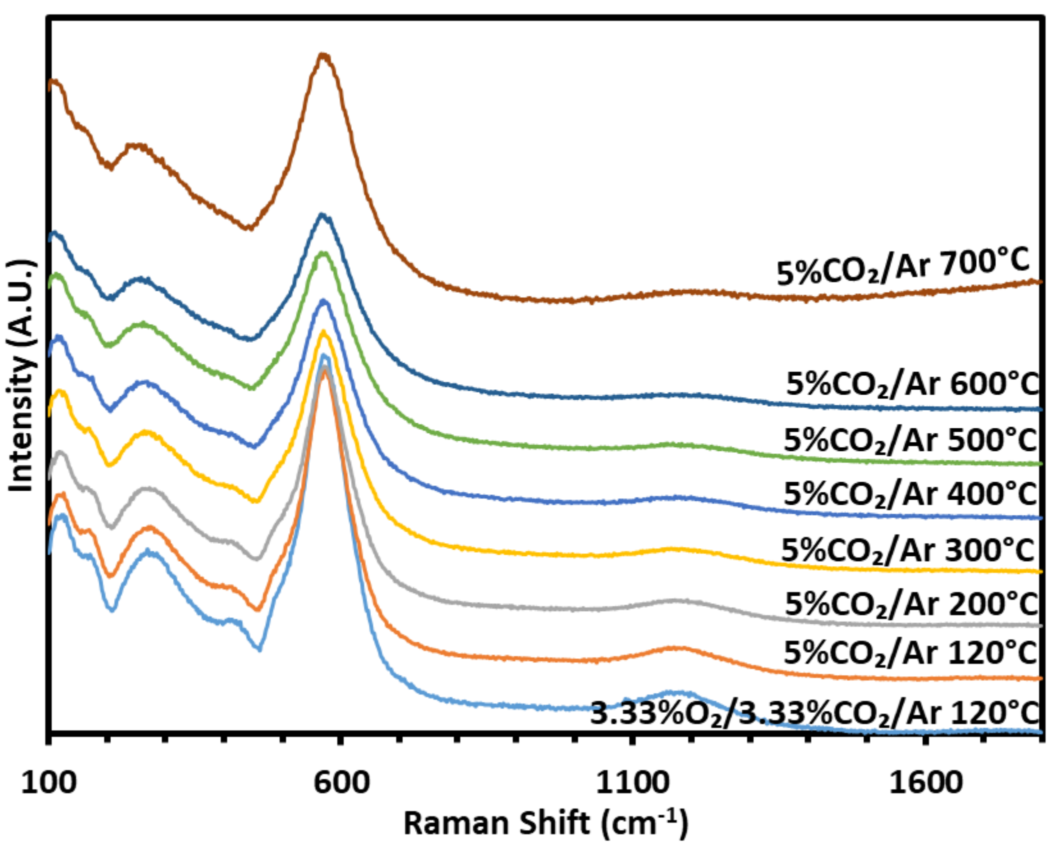
Dehydrated PrO_x at 100°C after treatement at 700°C



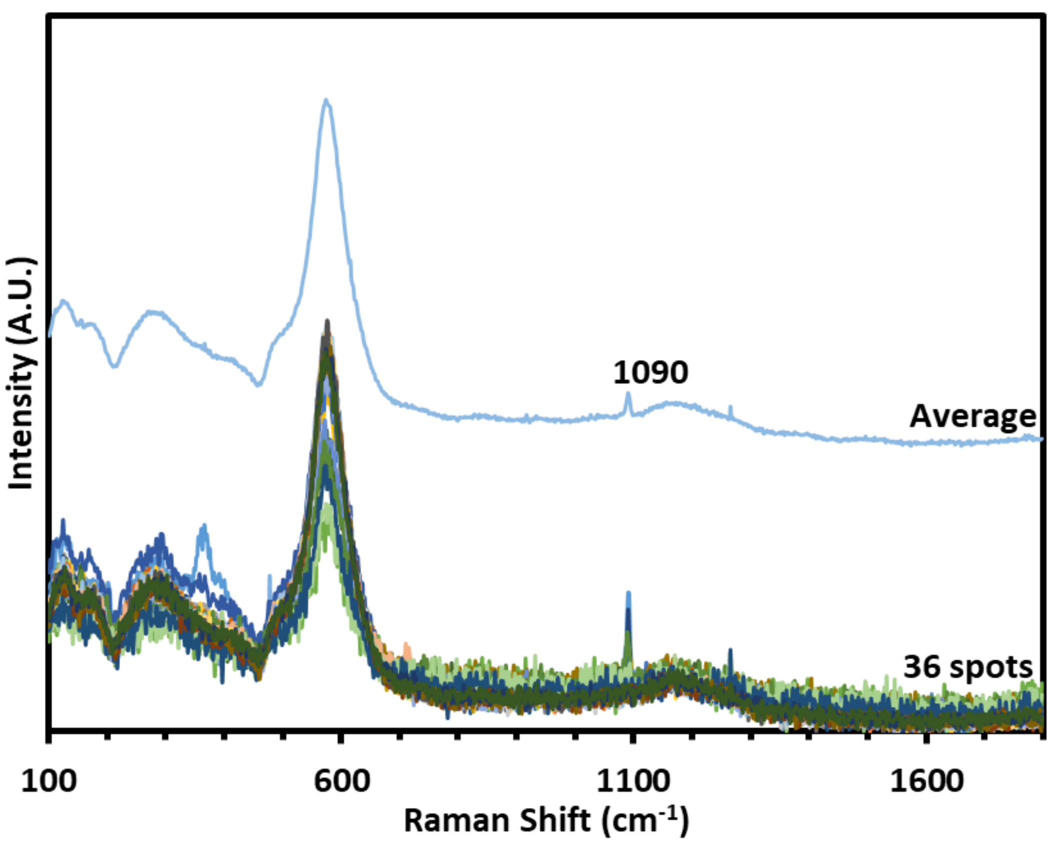
In Situ Raman Characterization of OCM Catalysts

Carbonate distribution on the mixed oxide support

- No crystalline Li_2CO_3 species (~1010 cm^{-1}) were detected when the oxidatively dehydrated $Li_2CO_3/LaPrO_3$ catalyst was exposed to a flow of mildly oxidizing 5%CO_2/Ar flow at progressively higher temperatures (**left figure**).
- The CO_2 treated catalyst was also mapped over 36 distinct spatial locations after cooling to 120°C under the 5%CO_2/Ar flow (**right figure**), demonstrating that while crystalline Li_2CO_3 is present, it is inhomogenously distributed on the $LaPrO_3$ surface, suggesting that most of the Li_2CO_3 is present in an amorphous surface phase.

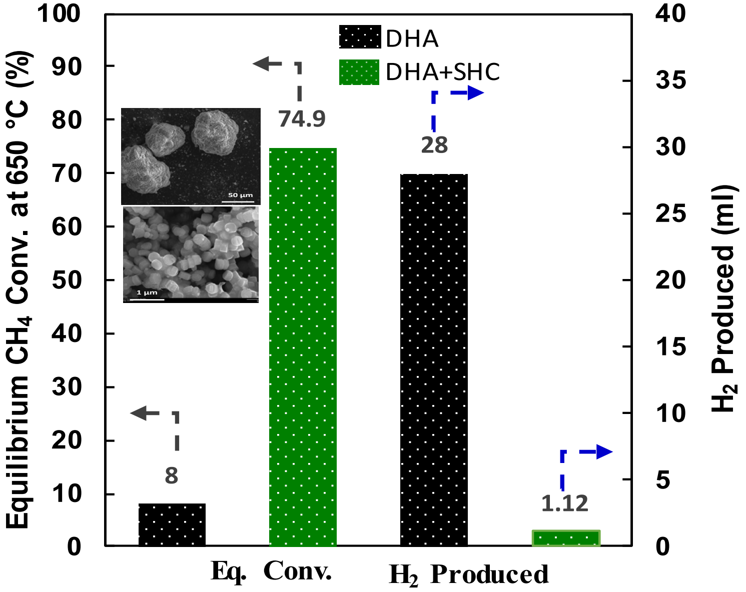


Dehydrated $Li_2CO_3/LaPrO_3$ under 5%CO_2/Ar

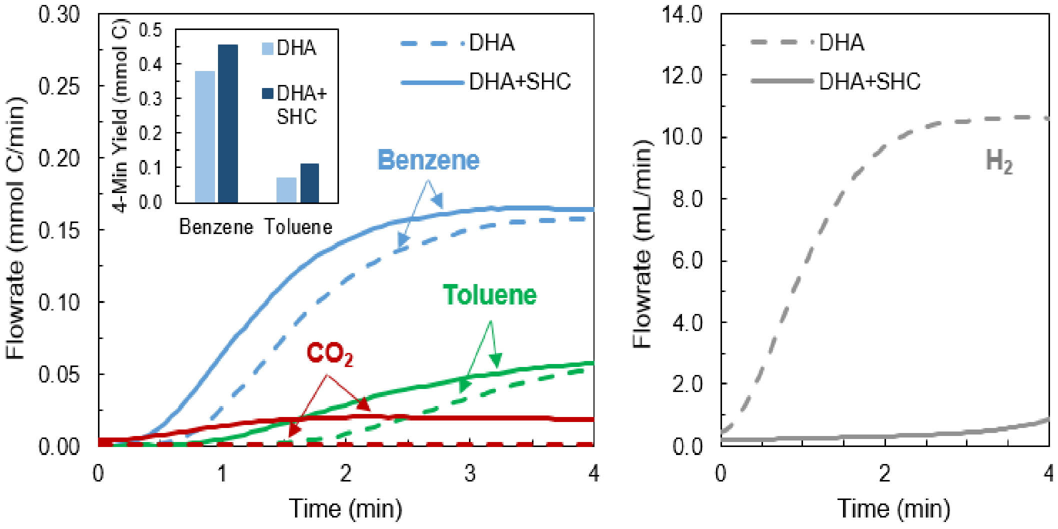


5%CO_2/Ar treated $Li_2CO_3/LaPrO_3$ at 120°C

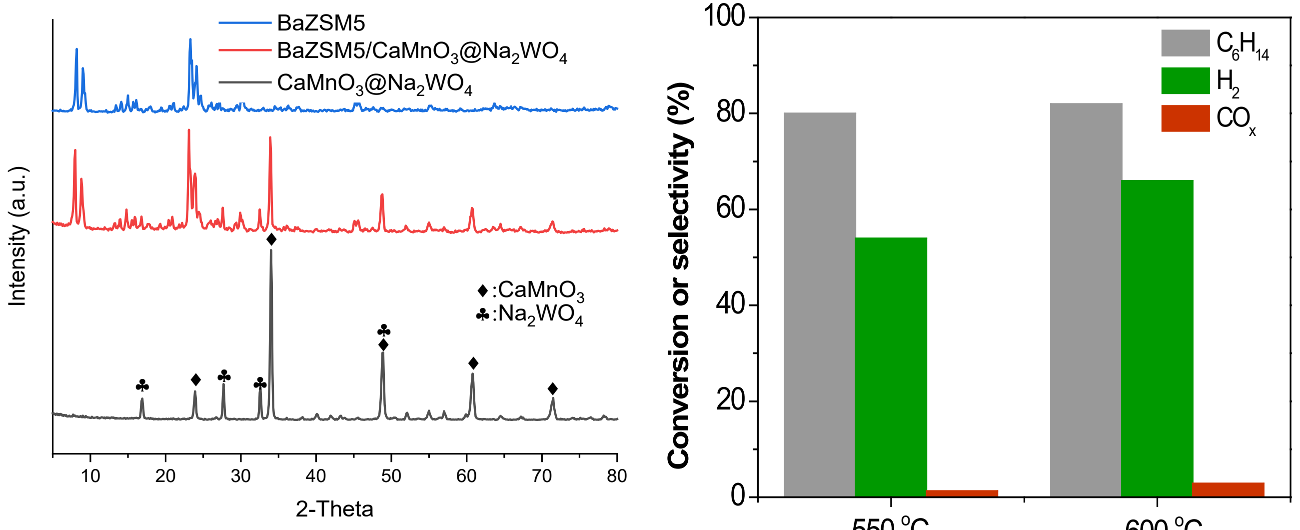
Preliminary Data for the OAS Concept



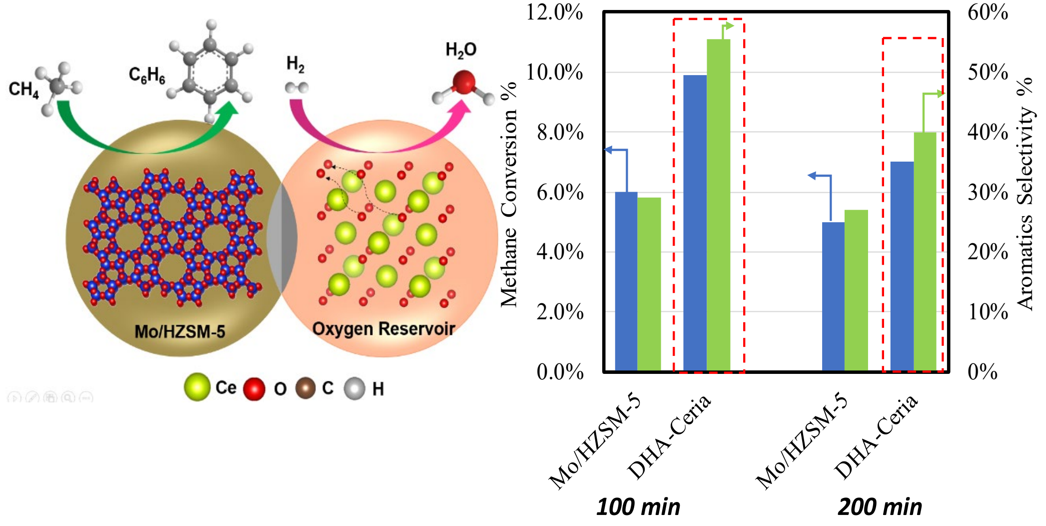
H_2 combustion can lead to 10-fold increase in equilibrium aromatic yield.



Effect of SHC redox catalyst on DHA in a sequential bed configuration



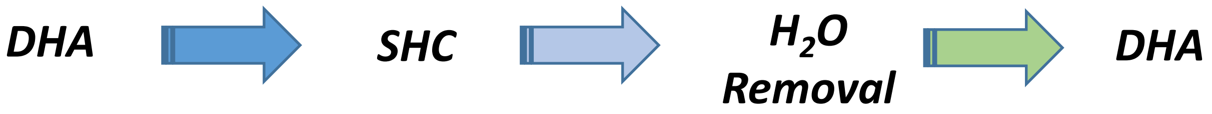
Composite ZSM-5 and SHC Catalyst for n-hexane cracking



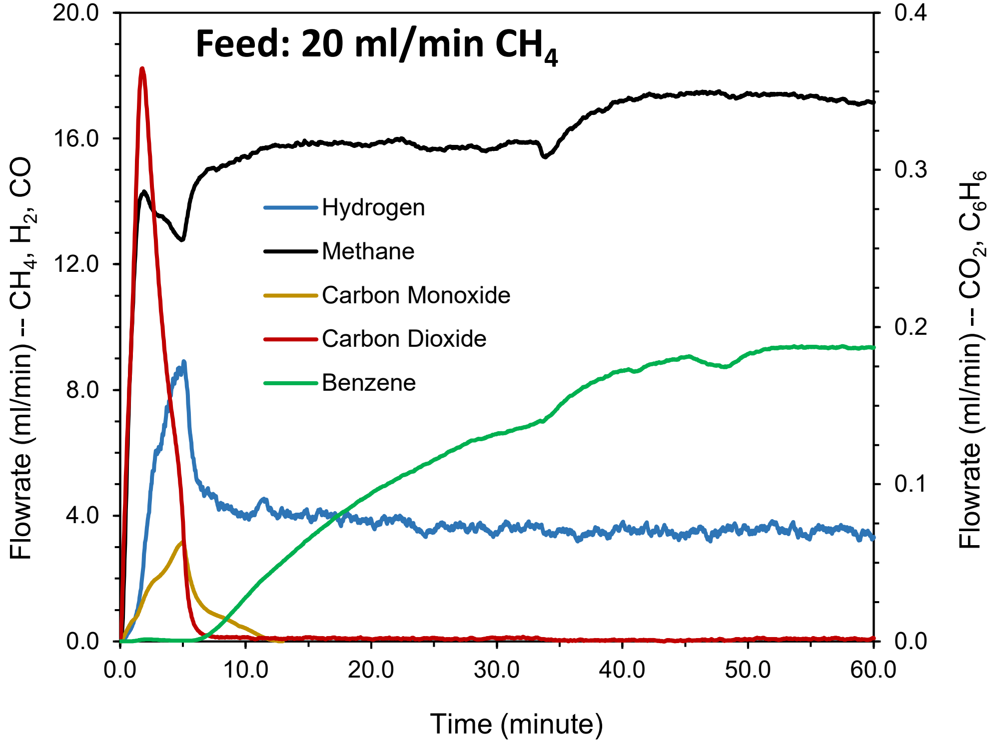
Dudek, et al. AIChE Journal, 2018. 64(8): 3141-3150

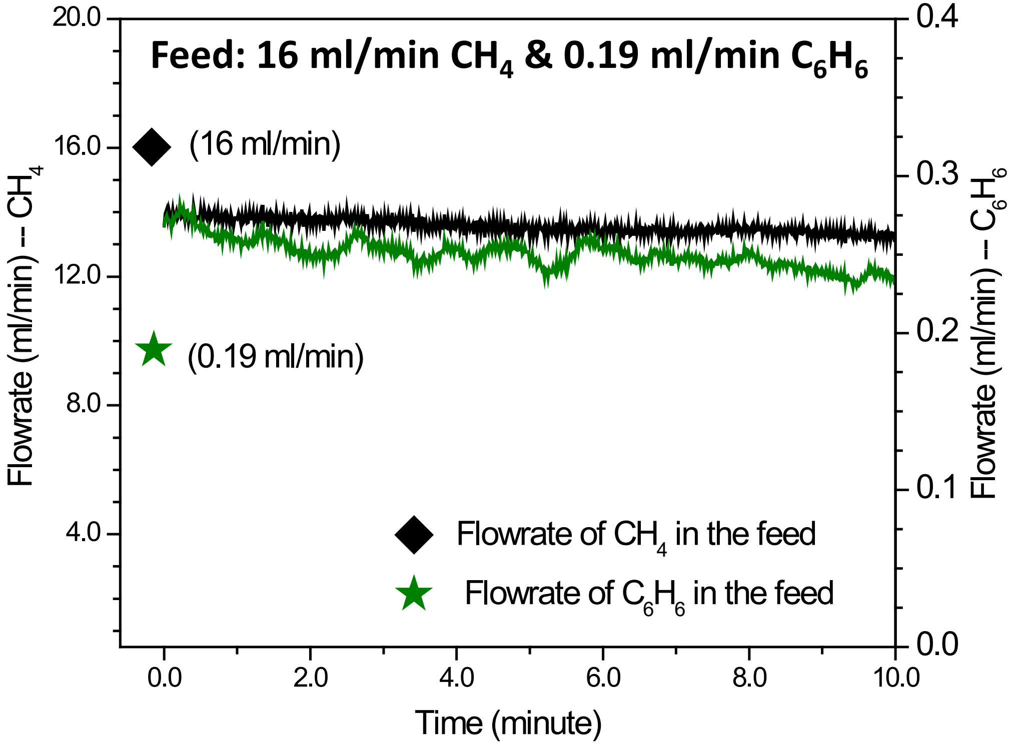
Zhang and Jiang, Chemical Communications 2018, 54(73): 10343-10346

Summary of Project Progress – Simulant Benzene+CH_4 feed



DHA → ***SHC*** → ***H_2O Removal*** → ***DHA***

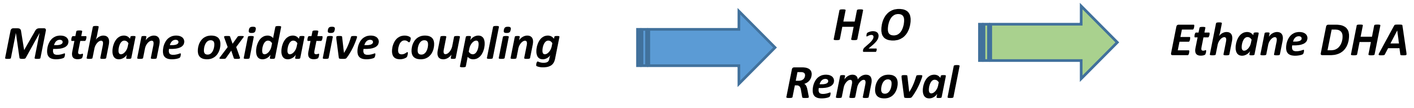




- Gas mixture simulating the product after H_2O removal was used as the feed for a second DHA step.
- Equivalently, the benzene yield in the alternative approach was ~40% more than a single DHA step.

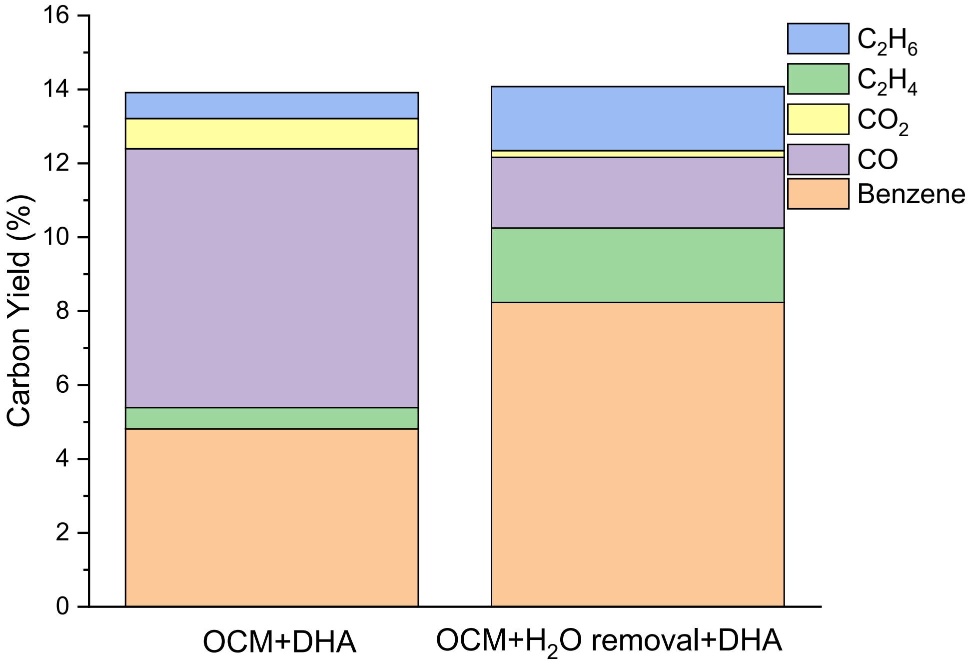
Summary of Project Progress – Alternative approach OCM + H_2O removal+ DHA

Alternative approach flow diagram:



Methane oxidative coupling → *H_2O Removal* → *Ethane DHA*

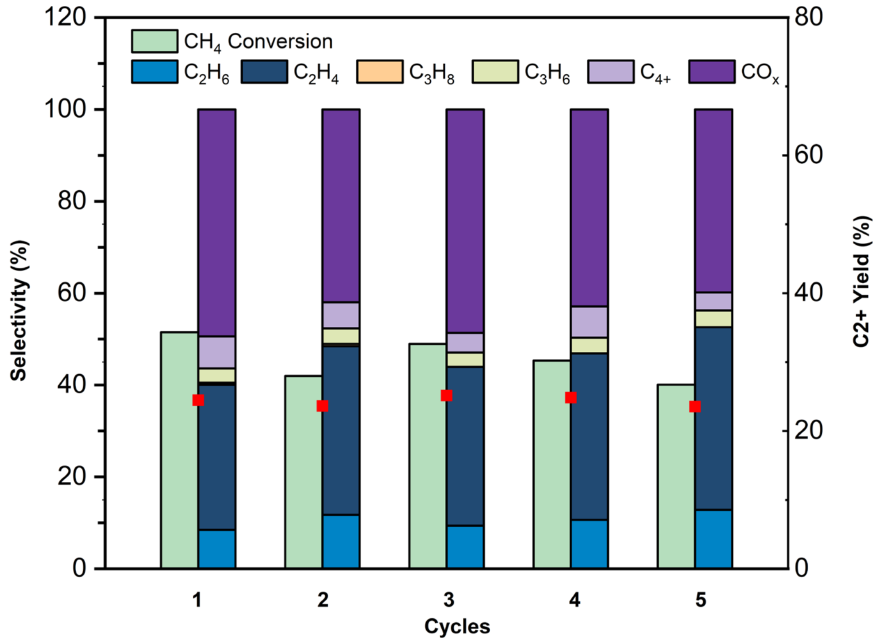
Ethane DHA catalyst: GaPt/ZSM5

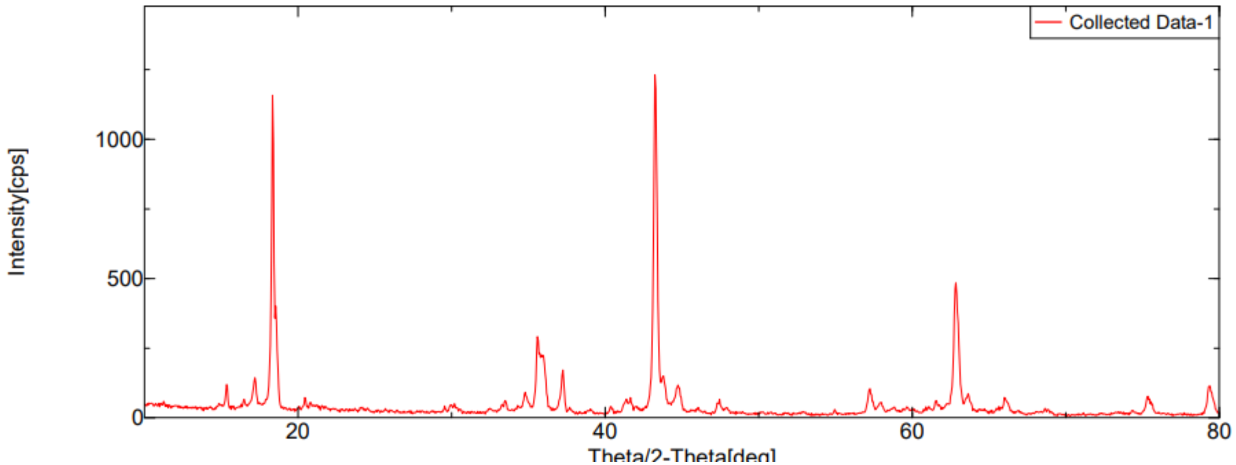


- This approach could achieve benzene yield ~8.2% at 700°C (total B+T up to 11%).
- H_2O and CO_2 leads to reforming reaction, forming CO.

Ongoing work and anticipated accomplishments

Task 6.2 : Development of new borate-based OCM catalyst

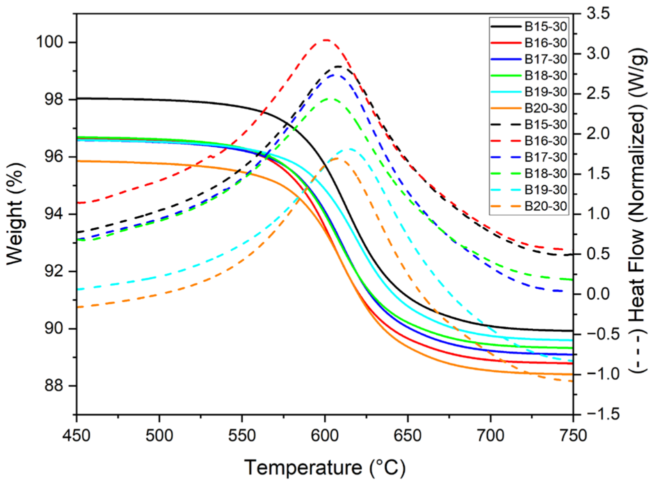




- OCM catalyst enabled 25.2% C2+ yield and 51.5% methane conversion.
- Higher C_2H_4/C_2H_6 ratio at ~3.9 will produce more aromatic.

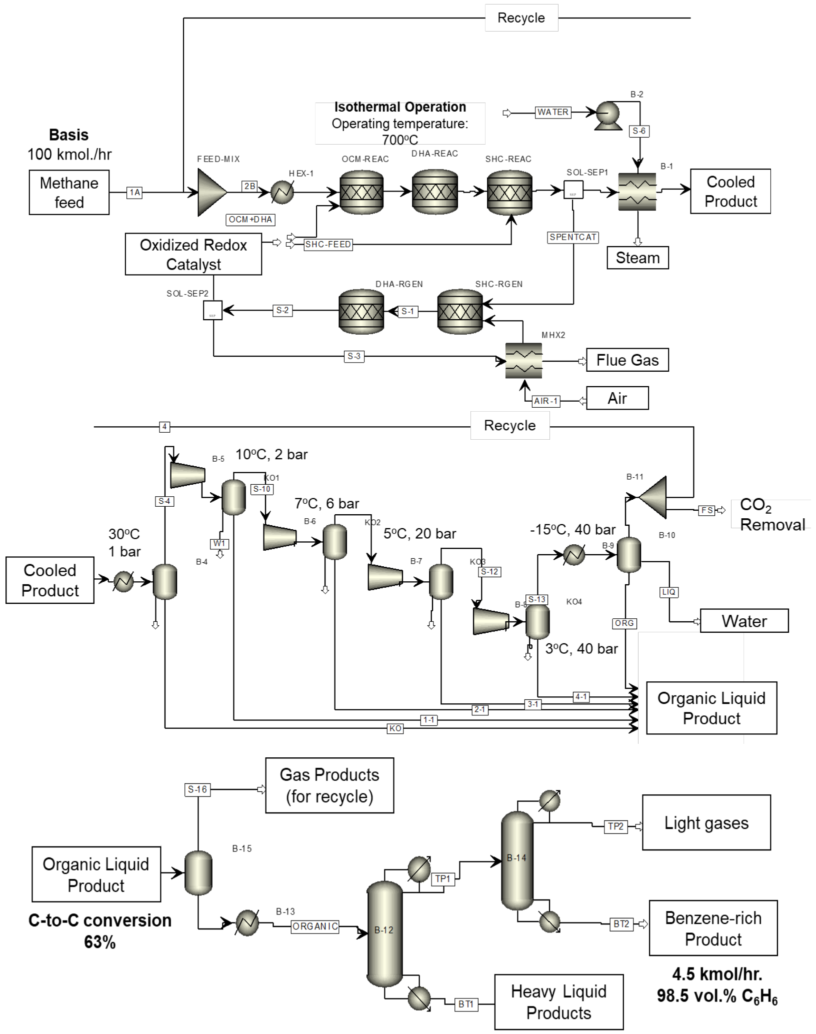
Ongoing work and anticipated accomplishments

Task 6.3 : Post testing characterizations were conducted.



- TGA was conducted to investigate the surface coking and bulk element behavior for >40 samples.
- NMR and TPD were conducted to investigate the effect of treatment during regeneration for the Ga-H.
- Mechanistic understanding or performance will be further developed for optimizing the material in the next 6 months.

Task 7: Aspen Plus™ process models was established.



- Aspen Plus™ process models was established based on previous experiment product distribution with ~43% net energy reduction.
- More detailed TEA and LCA will be performed.