

T3P5 - POSTER #21



T3P5
Poster #: 21



Converting Ethane to Aromatics by Bifunctional Catalysts

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GOALS

• Background:

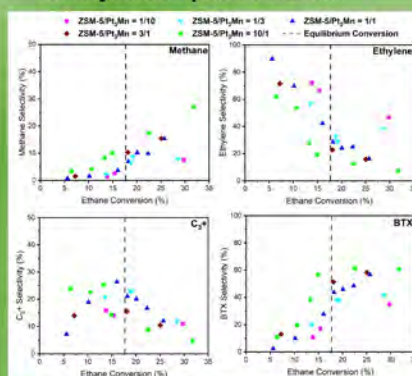
- Ethane conversion is limited by low product yield and high by-product selectivity
- Multi-stage reactor required for ethane conversion

• Goals:

- Convert ethane to aromatics in a single reaction by using bifunctional catalysts
- Improve the product yield by reducing the by-product formation
- Investigate the primary methane formation pathway in the reaction network

MAIN FINDINGS

Catalytic Composition Effect



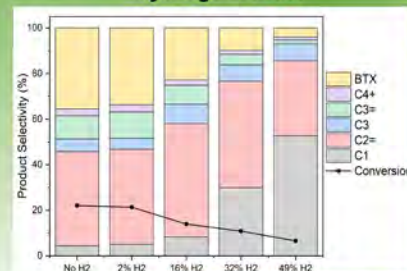
Reaction condition: cat. 0.2-0.8 g, temperature 600°C; pressure 135 kPa; 99.99% C₂H₆

Cat. Composition	Ave. Product Selectivity
ZSM-5/Pt ₃ Mn = 1/10	86%
ZSM-5/Pt ₃ Mn = 1/3	85%
ZSM-5/Pt ₃ Mn = 1/1	82%
ZSM-5/Pt ₃ Mn = 3/1	84%
ZSM-5/Pt ₃ Mn = 10/1	70%

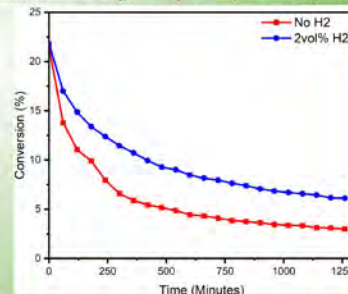
$$S_{\text{product}} = \frac{S_{\text{BTX}}}{S_{\text{BTX}} + S_{\text{C}_1}}$$

- Catalytic composition affects product distributions and activity

Hydrogen Effect



Reaction condition: cat. 0.6 g, ZSM-5/Pt₃Mn=1; temperature 600°C; pressure 135 kPa



Reaction condition: cat. 0.1-0.6 g, ZSM-5/Pt₃Mn=1; temperature 600°C; pressure 135 kPa

- Low H₂ partial pressure mitigated coke and didn't affect the product distribution

OUTCOMES

• Main Conclusions:

- Tuning the catalyst compositions improves the product distributions
- Industrial product selectivity and conversion approach 85% and 30%, separately
- High content H₂ decreases the conversion and increases by-product formation; low H₂ content reduce deactivation

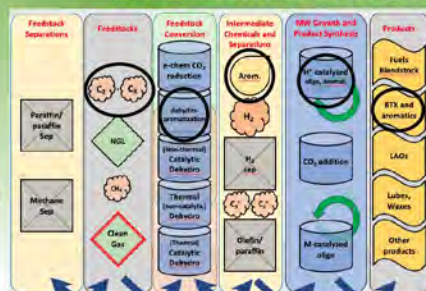


IP & INNOVATION

- Unconventional bifunctional catalyst for ethane conversion



SYSTEM DESIGN & BENCHMARKS



Progress Toward CISTAR Target



IMPACT & FUTURE

- Investigate methane formation pathway
- Catalytic stability and regeneration study
- Economic analysis

T3P6 - POSTER #22



T3P6
Poster #: 22



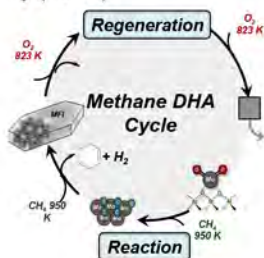
Consequences of the Structural Evolution of Mo-Zeolites for Methane DHA Reaction-Regeneration Cycles

Ángel Santiago-Colón, Rajamani Gounder
Davidson School of Chemical Engineering, Purdue University

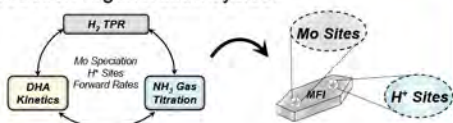
CISTAR
NSF Engineering Research Center
Center for Innovative and Strategic
Transformation of Alkane Resources

GOALS

- Mo-MFI catalyzes methane DHA to near-equilibrium conversion with high aromatics selectivity (~80%).



Challenge: Catalyst stability for successive reaction-regeneration cycles.

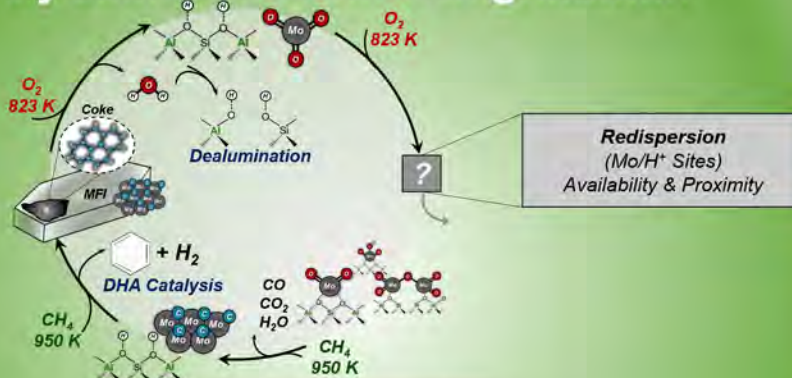


Objective:

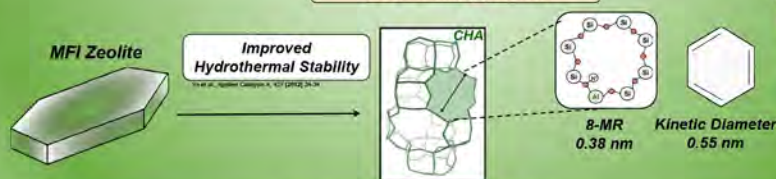
Monitor structural changes of Mo sites and H⁺ sites during cycles.
Design Mo-Zeolites for methane DHA cycles

MAIN FINDINGS

Catalyst lifetime and stability is influenced by zeolite structural degradation



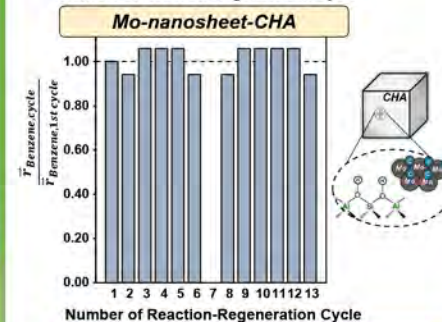
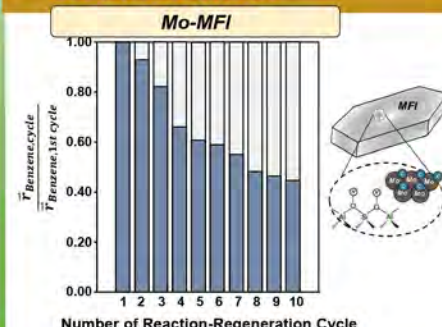
Research Approach



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OUTCOMES



Challenge: Mo-nanosheet-CHA shows rates 6x lower than Mo-MFI

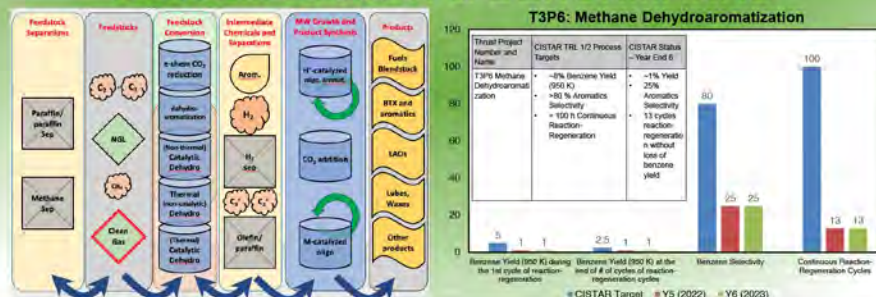
IP & INNOVATION

- Developed tools to assess catalysts structural changes for methane DHA cycles.

Patent Applications

- Gounder R., Santiago-Colón, A. 2023. "Process for Extending Mo-Zeolite Catalyst Lifetime During Methane Dehydroaromatization." US Provisional Patent Application No. 63/521,517
- Gounder R., Santiago-Colón, A., Lee, S. 2023. "Method for Making CHA Zeolites and Zeotypes." US Provisional Patent Application No. 63/529,264
- Gounder R., Santiago-Colón, A. 2023. "Preparation of Nanosheet Zeolites and Applications for Methane Dehydroaromatization." US Provisional Patent Application No. 63/529,189

SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

- Identified key parameters that influence catalyst stability for methane DHA cycles.
- Future:** Optimizing Mo-CHA synthesis for improved benzene selectivity

T3P6 - POSTER #23



T3P6
Poster #: 23



Overcoated Mo-Catalysts under Methane Dehydroaromatization(MDA) conditions

Jordy Ramos-Yataco¹, Justin M. Notestein^{1,2}

¹Department of Chemical and Biological Engineering, Northwestern University

²Center for Catalysis and Surface Science, Northwestern University

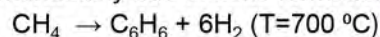


Center for Innovative and Strategic Transformation of Alkane Resources

GOALS

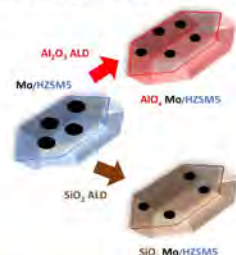
Background

Mo/HZSM-5 is a benchmark catalysts for CH₄ transformation to liquid aromatics under non-oxidative conditions. However, it deactivates continuously due to coke formation



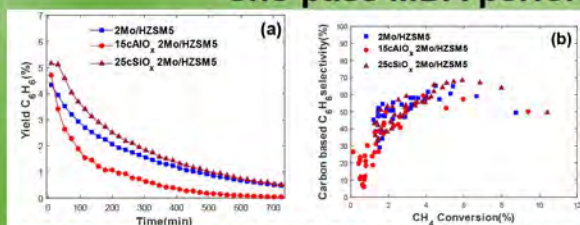
Goal

Modify Mo/HZSM-5 external surface area to reduce coke formation by partially SiO₂ and Al₂O₃ overcoats via atomic layer deposition (ALD)



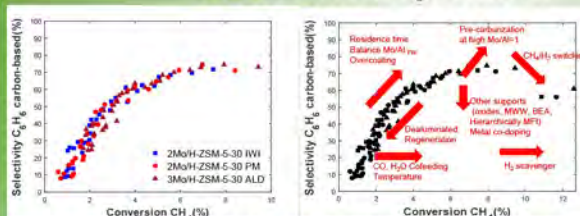
MAIN FINDINGS

SiO₂ and Al₂O₃ overcoats on Mo/HZSM5 impact one-pass MDA performance



Effect of SiO₂ and Al₂O₃ overcoat on 2wt% Mo/HZSM5 (a) C₆H₆ yield over time on stream (b) Carbon-based selectivity of benzene as a function of methane conversion. Reaction conditions 700 °C, 1atm, WHSV 2.7 h⁻¹

Mo/HZSM5 shows a non-selective deactivation process



Carbon-based selectivity of C₆H₆ as a function of methane conversion (a) Various methods and loadings (b) Overview of MDA literature approaches on increasing catalysts performance. Reaction conditions 700 °C, 1atm, WHSV 2.7 h⁻¹

Overcoating Mo/HZSM5:

- Doesn't impact textural properties
- Redistribute MoO_x centers
- After isothermal regeneration, all formulations behave similarly

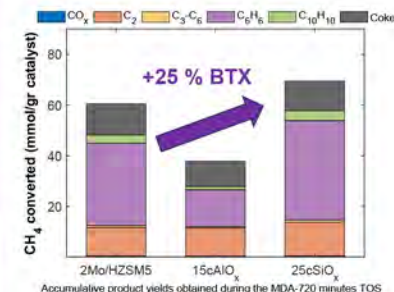


QR Code for Full Paper

60 papers on MDA were evaluated showing modifications on deactivation profiles

OUTCOMES

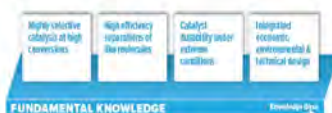
- SiO₂-overcoated Mo/HZSM5 has better C₆H₆ yields under one-pass evaluation. In addition, this modification does not impact the intrinsic nature of active site.
- Deactivation profiles tend to be universal on Mo/HZSM5, providing an excellent mode to identify outlier behavior, either positive or negative.



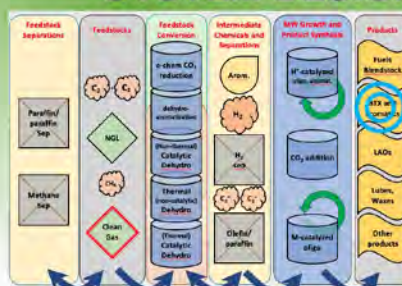
Accumulative product yields obtained during the MDA-720 minutes TOS

IP & INNOVATION

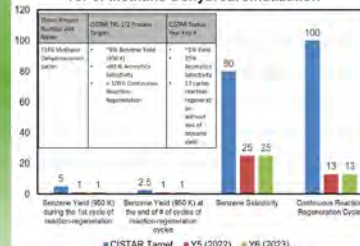
- Improve MDA benchmark catalysts performance
- Evaluate MDA catalysts regeneration



SYSTEM DESIGN & BENCHMARKS



T3P6: Methane Dehydroaromatization



IMPACT & FUTURE

- Evaluate MoO_x supported on overcoated oxides such as catalysts resistance to oxidative regeneration.
- In C2C collaboration, we will assess tandem conversion of NGL and CO₂ as coupling CH₄-MDA and CO₂ reverse water shift.

T3P6 - POSTER #24



T3P6
Poster #: 24

N



One-pot Construction of Fe-ZSM-5 Zeolites with High MDA Activity and No Induction Period

Xinrui Zhang¹, Jordy Ramos², Selim Alayoglu², Tobin Marks³ and Justin Notestein²

¹Department of Materials Science and Engineering, Northwestern University

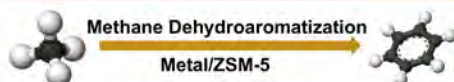
²Department of Chemical Engineering, Northwestern University

³Department of Chemistry, Northwestern University

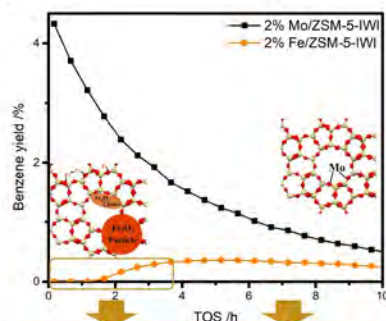
CISTAR
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GOALS



Methane dehydroaromatization directly converts methane, the main component of natural gas, into transportable and value-added liquid hydrocarbons without CO₂ emission.



Lengthy induction period Inferior benzene yield

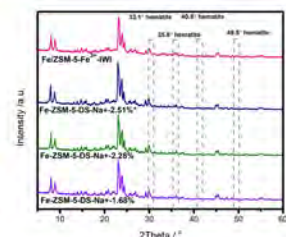
- ❖ Synthesize Fe-ZSM-5 catalysts with highly dispersed Fe sites (framework Fe sites) by one-pot construction
- ❖ Minimize Fe dislodgment and aggregation
- ❖ Study the active sites in isomorphous substituted Fe-ZSM-5 catalysts

MAIN FINDINGS

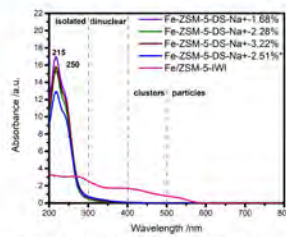
Synthesis Strategy: Fe-EDTA Provides Fe Source and Stabilizes Fe³⁺



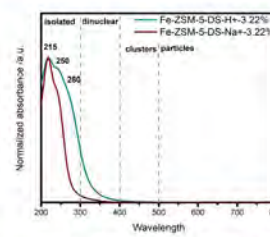
Synthesized Catalysts: Exhibit Uniformly and Stably Isolated Fe Sites



MFI structure with high crystallinity

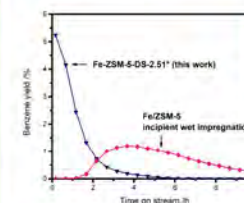


No Fe dislodgment and aggregation after template removal



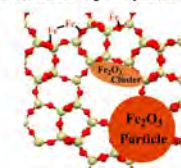
No Fe aggregation after ammonium exchange

OUTCOMES

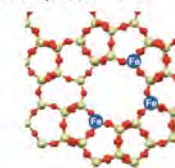


Sample loading, %	Maximum Benzene Yield, %
1.68	2.05
2.28	4.94
3.22	4.23
2.51*	5.24
IWI	1.20

Condition: 300 mg catalysts, 27 sccm 95%CH₄ flow, 730 °C



Fe/ZSM-5 prepared by incipient wet impregnation



Fe-ZSM-5 prepared by one-pot construction

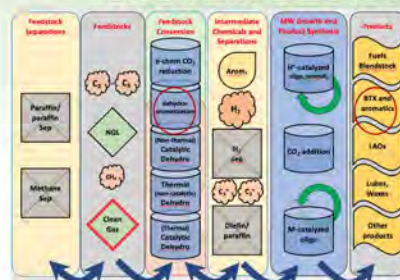
- ❖ Synthesized isomorphous substituted Fe-ZSM-5 catalysts using Fe-EDTA as Fe source and SDA
- ❖ No Fe dislodgment and aggregation was observed during crystallization and template removal
- ❖ Fe-ZSM-5 catalysts exhibit a high maximum benzene yield with no induction period

IP & INNOVATION

- Employed Fe-EDTA as both iron source and structure directing agent; Minimized iron dislodgment and aggregation during crystallization and template removal



SYSTEM DESIGN & BENCHMARKS



Thrust Project Number and Name	CISTAR TRL % Process Targets	CISTAR Status Year End 6
T3P6 Methane dehydroaromatization	<ul style="list-style-type: none"> ~8% Benzene Yield (950 K) > 80% Aromatic Selectivity > 100h Continuous Reaction/Regeneration 	<ul style="list-style-type: none"> 5% Benzene Yield 50% Benzene Selectivity

IMPACT & FUTURE

- Conduct operando XAS characterization to study the active sites
- Study the Fe/Al ratio on catalytic performance
- Employ the synthesis strategy to prepare metal-zeolite and screen MDA activity



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T3P9 - POSTER #28



T3P9
Poster #: 28

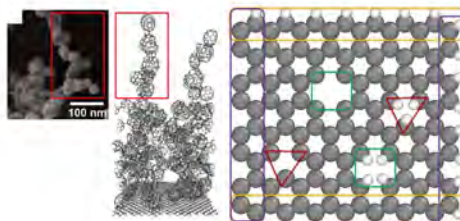
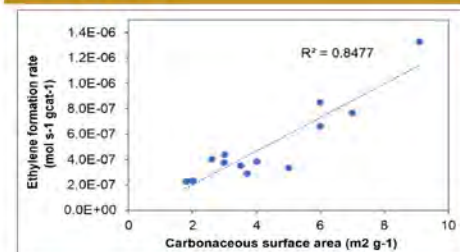


CH₄ Activation over Graphene Defect Models: A First-Principles Analysis

Luke Nunzio Pretzie & Jeffrey Greeley¹
¹Department of Chemical Engineering, Purdue University

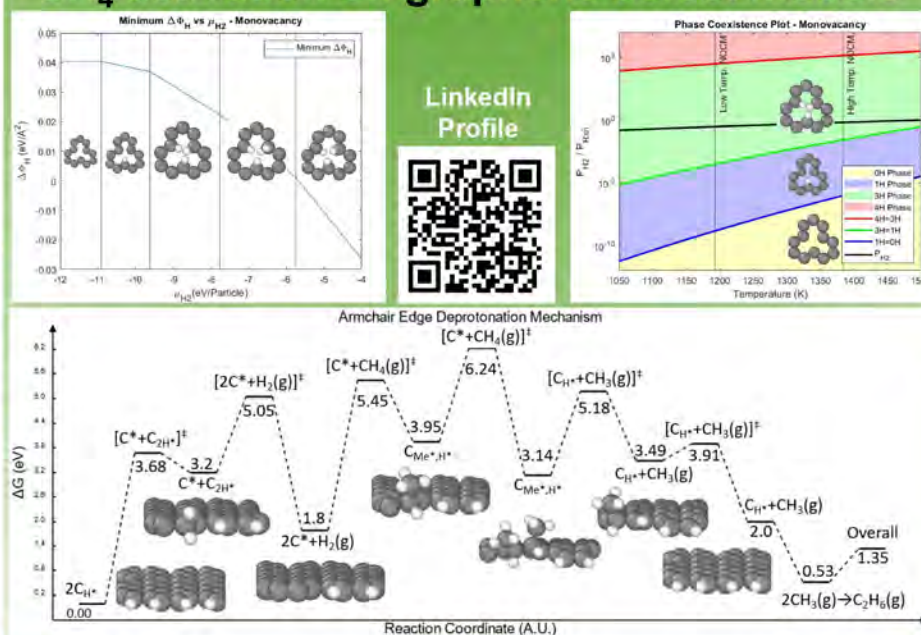


GOALS

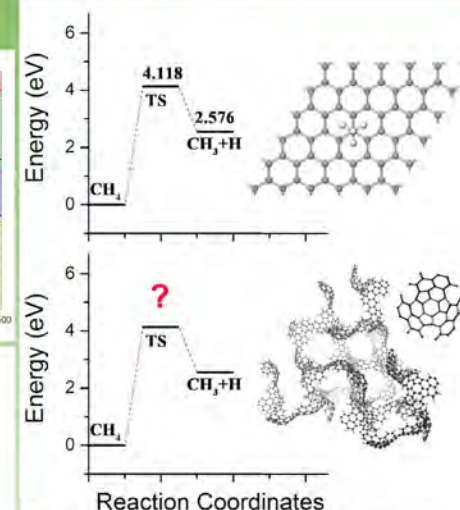


- Evidence of coke having autocatalytic properties in NOCM processes (1)
- Morphological defects credited as possible active sites (2,3,4)
- Thermodynamic stability of model defects studied

Proton diffusion/desorption may facilitate CH₄ activation on graphene defect models



OUTCOMES

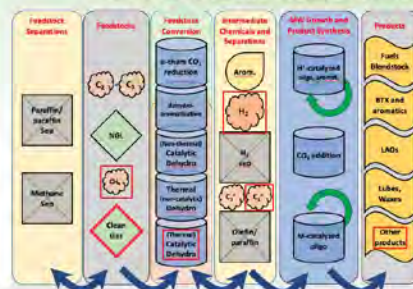


- Defect carbons shown to have lower barriers than non-defect carbons (5)
- Encourages search for alternative carbon defect models (6)

REFERENCES

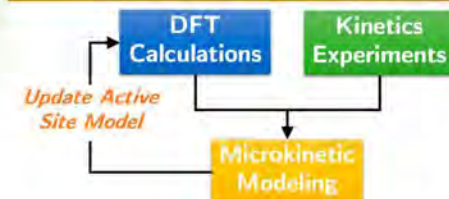
1. Talpade & Ribiero, PhD Thesis, Purdue Univ., 2021
2. Catal. Comms., 2001, 2, 89-94
3. Science, 2011, 335, 67-70
4. Phys. Rev. Lett., 1999, 83, 4
5. Appl. Surf. Sci., 2018, 459, 30, 693-699
6. Chem. Comms., 2018, 54, 5648
7. Accts. Of Chem. Res., 53 (9), 1893-1904

SYSTEM DESIGN & BENCHMARKS



• System Design & Benchmarks will be developed in the near future

IMPACT & FUTURE



- Microkinetic modeling to better understand the active site & reaction mechanism (7)

T3P9 - POSTER #29



T3P9
Poster #: 29



Evaluating Carbon-Based Catalysts for the Non-Oxidative Coupling of Methane

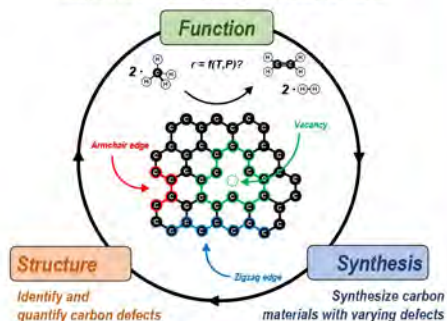
Justin Rosa Rojas¹, Abhijit Talpade¹, Fabio Ribeiro¹, Rajamani Gounder¹
¹Department of Chemical Engineering, Purdue University



GOALS

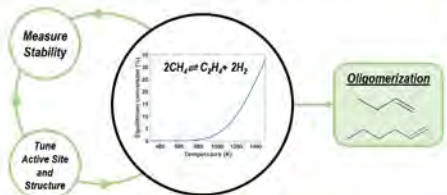
Determine Structure-Function Relations

Elucidate the kinetics and mechanisms of the non-oxidative coupling of methane (NOCM) to heavier hydrocarbons (e.g., C_2H_4) on carbon surfaces



[1] Huang, L. et al. *J. Chem. Phys.* 2008, 128 (21), 214702.

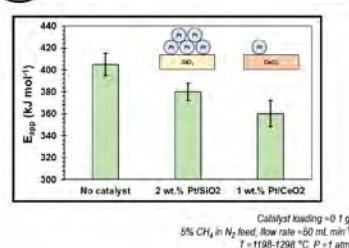
Design Carbon Surfaces with Tuned Active Sites



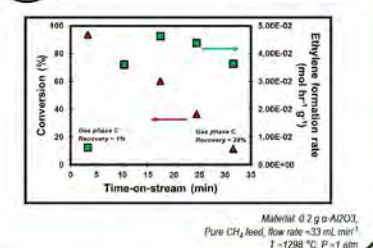
MAIN FINDINGS

Carbon Contributes to Ethylene Formation during the Non-Oxidative Coupling of Methane

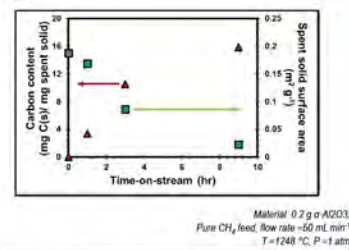
1 Presence and dispersion of Pt do not significantly decrease apparent activation energies



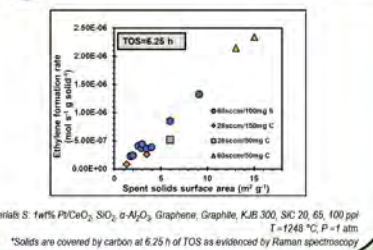
2 Solid carbon may have a role in ethylene formation rates



3 Carbon deposition during NOCM decreases the surface area of solid exposed to methane



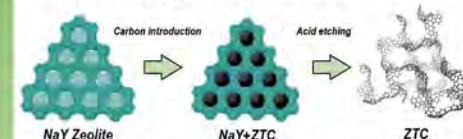
4 Ethylene formation rates scale with exposed carbon



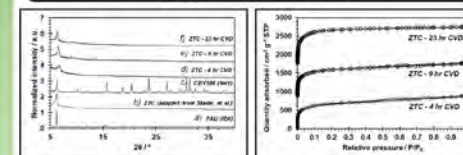
OUTCOMES

Zeolite-Templated Carbon (ZTC) Synthesis

The high surface density of zeolite-templated carbon (ZTC) edges will validate the hypothesis of these defects as active sites.



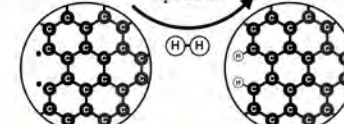
High surface area ZTCs were synthesized by increasing the carbon introduction time via propylene chemical vapor deposition



[2] Taylor, E. et al. *Chem. Mater.* 2020, 32, 2742–2752. [3] Nishihara, H. et al. *Carbon* 2009, 47 (5), 1220–1230. [4] Sladov, et al. *Langmuir* 2012, 28 (26), 10057–10063.

Carbon Edge Site Titration

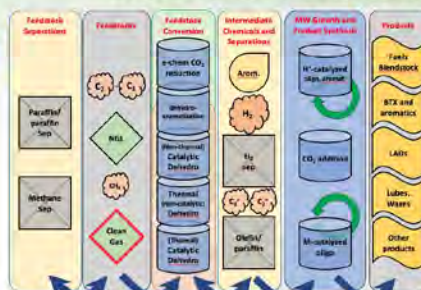
Unpassivated carbon edge sites are proposed to be quantified by H_2 titration.



IP & INNOVATION

- There are no disclosures on the project.
- Novel CISTAR material designs showing different methane NOCM behavior relative to commercially available support materials will be disclosed.

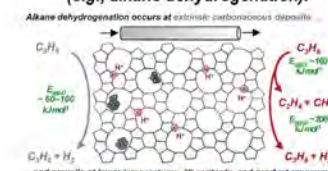
SYSTEM DESIGN & BENCHMARKS



- System Design and Benchmarks will be developed for next year.

IMPACT & FUTURE

Development of carbon-based catalysis quantification methods applied to NOCM and other chemistries impacted by carbon deposition (e.g., alkane dehydrogenation).



[4] Kesler, P. et al. *J. Phys. Chem. C* 2020, 124, 15839–15855.