T1P3
Poster #: 10

Exploring Mechanisms of Coke Formation and Migration for Increased Catalyst Stability

Joanna M. Rosenberger[1], Vamakshi Yadav[1], Brandon K. Bolton[2],
Rajamani Gounder[2], Christina W. Li[1]
[1]Department of Chemistry, Purdue University
[2]Davidson School of Chemical Engineering, Purdue University

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Transformation of Alkane Resources

GOALS

Bimetallic $PtIn_2$ catalysts exhibit >99% selectivity towards ethylene in ethane dehydrogenation at 600°C. However, these catalysts quickly deactivate due to coking. We are interested in utilizing non-reducible metal-oxide shells to stabilize $PtIn_2$/SiO_2 catalysts.

1.) Understand the effect of Ca doping on reducing deactivation of $PtIn_2$/SiO_2 catalysts

Deactivation Pathways
Sintering
Coking
Stability improves by 10x
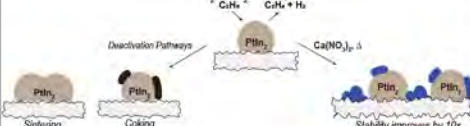
Relatively little is known about the mechanisms of coke formation. Understanding coke formation in different reaction conditions could assist in new catalyst design strategies.
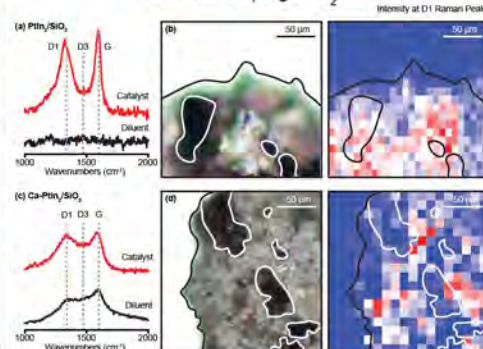
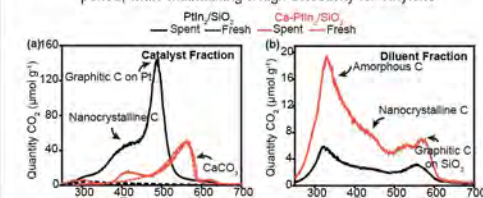2.) Use acetylene oligomerization as a model reaction to probe initial differences in the mechanims of coke formation
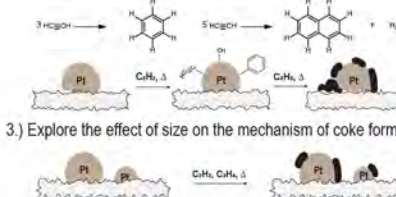
3.) Explore the effect of size on the mechanism of coke formation

MAIN FINDINGS

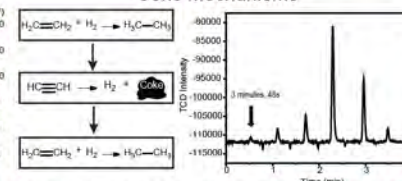### Calcium Doping $PtIn_2$

Ca doping into $PtIn_2$/SiO_2 inhibits catalyst deactivation over 10x over 24 hour period, while maintaining a high selectivity for ethylene.
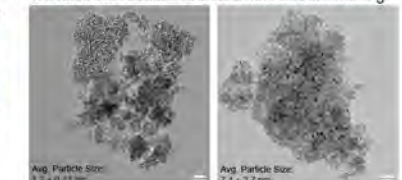

300-400C: amorphous carbon deposits on silica
400-550C: carbonaceous species on the metal and its vicinity
550-700C: graphitized carbon, difficult to oxidize

Coke Mechanisms

Dehydrogenating acetylene results in the production of hydrogen gas. Pairing this method with ethylene hydrogenation can measure available active sites before and after coking.


A variety of differently sized Pt nanoparticle catalysts can be synthesized via incipient wentess impregnation.

Sample	Weight Percent Pt	Calcination Temperature	Dispersion	Average Particle Size
iwi-250	0.5%	250C	24.6%	3.3nm
iwi-300	2%	300C	23.5%	1.9nm
iwi-600	2%	600C	10.8%	5.2nm
iwi-Large	5%	600C	7.7%	7.4nm

OUTCOMES

Ca-$PtIn_2$/SiO_2 reduces the inherent EDH deactivation rate of $PtIn_2$ nanoparticles by 8-fold and maintains >99% selectivity towards ethylene.
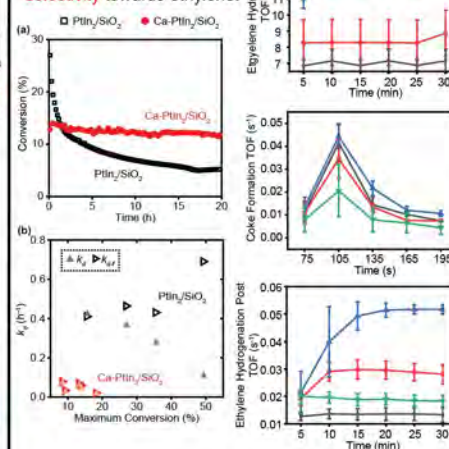

Catalyst size has little effect on coke formation rate or mechanism. Future systems of interest are PtM_x alloys, different substrates, and Ca-doped catalysts.
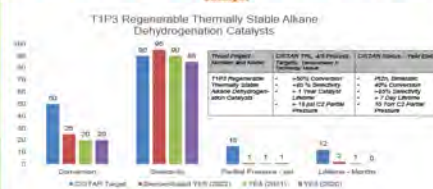
IP & INNOVATION

Understanding coke formation during early reaction stages is severely limited due to its rapid nature. Utilizing acetylene as a model dehydrogenation compound has not been studied before.

SYSTEM DESIGN & BENCHMARKS
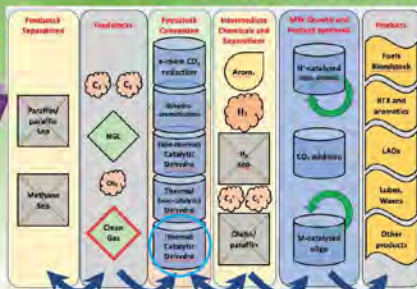
Progress Toward CISTAR Target Catalyst
T1P3 Regenerable Thermally Stable Alkane Dehydrogenation Catalysts

IMPACT & FUTURE

1. Ca doping strategy could easily be expanded to other catalysts of interest (PtSn)
2. Detailed characterization of coked catalyst samples will allow us to probe small molecules involved in coke formation
3. Understanding the differences in coke formation on differnent catalysts could assist in the design of more stable systems

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T1P3
Poster #: 11

Synthesis of Colloidal Platinum Alloys for Stable Alkane Dehydrogenation

Nkem Azuka[1], Joanna Rosenberger[1], Christina Li[1]
[1]Department of Chemistry, Purdue University

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GOALS

- Develop syntheses for colloidal PtM (M = Co, Fe, Mn) alloys

100 C, Ligand
200 C, LiEt₃H,
Reflux for 20 min.
purify

Pt precursor
Metal salt (metal = Fe, Co, Mn)
Phenyl Ether
ROH

PtM (M=Fe, Mn, Co)
Nanoparticles suspended in solution
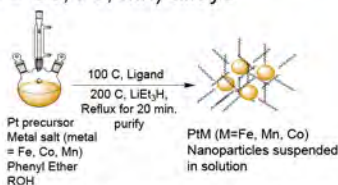
- Utilize colloidal alloys as catalysts instead of impregnated alloys for more stable ethane dehydrogenation

Co wt. loading

Legend: Pt PtCo PtCo

Supported Colloidal
Uniform Alloy
Stable Catalysis

$C_2H_6 \rightarrow C_2H_4 + H_2$ $\geq 600\ °C,\ H_2$

Impregnation
Partial Alloy
Multiple Phases

Sun, S., Anders, S., Thomson, T., Baglin, J. E. E., Toney, M. F., Hamann, H. F., Murray, C. B., & Terris, B. D. (2003). Controlled Synthesis and Assembly of FePt Nanoparticles. *The Journal of Physical Chemistry B*, 107(23), 5419–5425. https://doi.org/10.1021/jp0273419

Cesar, L. G., Yang, C., Lu, Z., Ren, Y., Zhang, G., & Miller, J. T. (2019). Identification of a PtₓCo Surface Intermetallic Alloy in Pt–Co Propane Dehydrogenation Catalysts. *ACS Catalysis*, 9(6), 5231–5244. https://doi.org/10.1021/acscatal.9b00543

Escorcia, N. J., LiBretto, N. J., Miller, J. T., & Li, C. W. (2020). Colloidal Synthesis of Well-Defined Bimetallic Nanoparticles for Nonoxidative Alkane Dehydrogenation. *ACS Catalysis*, 10(17), 9813–9823. https://doi.org/10.1021/acscatal.0c01554
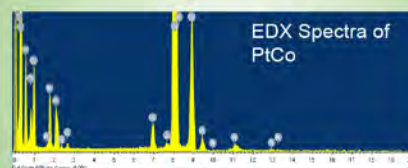
MAIN FINDINGS

Platinum core, iron shell nanoparticles were synthesized. A low weight loading PtCo catalyst was synthesized.
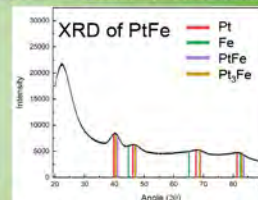
TEM Images
Left: PtCo
Right: PtFe
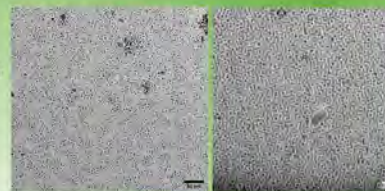
EDX reflects the entire particle. It is taken on a copper grid, hence the high signal among other contaminants, but the relative peak heights of Pt and Co corresponds well to the atomic percent.

EDX Spectra of PtCo

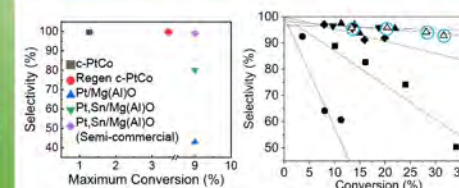XRD of PtFe
— Pt
— Fe
— PtFe
— Pt₃Fe

Intensity
Angle (2θ)

The XRD Spectra closely resembles Pt, despite the high Fe content. Since XRD does not reflect surface composition, the particle is likely a core-shell.

Compound	Metal	EDX Average Atomic Percent	XRF Average Weight Percent
PtCo	Pt	0.39	0.04
	Co	0.62	0.07
PtFe	Pt	0.39	1.62
	Fe	0.50	0.54

Fe shell, Pt core

OUTCOMES

Selectivity (%)
Maximum Conversion (%)
■ c-PtCo
● Regen c-PtCo
▲ Pt/Mg(Al)O
▽ Pt,Sn/Mg(Al)O
◇ Pt,Sn/Mg(Al)O (Semi-commercial)

Selectivity (%)
Conversion (%)
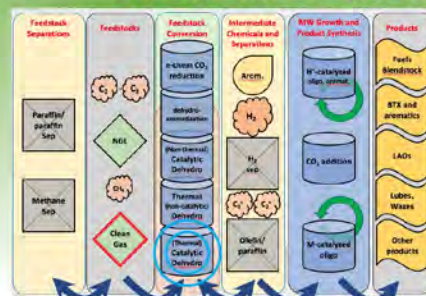■ 3Pt ● 10Co ▲ 2Pt0.6Co ▼ 2PtCo
△ 2Pt2Co ◆ 2Pt4Co

- Colloidal PtCo shows low conversion to ethylene that slightly improves after a regeneration.

- Likely due to remaining ligand migrating to the surface

- Selectivity remains high at 99%

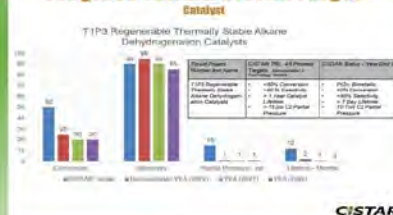- Better than more commercial Pt,Sn catalysts and impregnation PtCo (right, encircled in blue)

Virnovskaia, A., Morandi, S., Rytter, E., Ghiotti, G., & Olsbye, U. (2007). Characterization of Pt,Sn/Mg(Al)O Catalysts for Light Alkane Dehydrogenation by FT-IR Spectroscopy and Catalytic Measurements. *The Journal of Physical Chemistry C*, 111(40), 14732–14742. https://doi.org/10.1021/jp074686u

IP & INNOVATION

- Colloidal PtMn has not been synthesized. These methods will lead towards c-PtMn for ethane dehydrogenation

SYSTEM DESIGN & BENCHMARKS

Feedstock Separations | Feedstocks | Feedstock Conversion | Intermediate Chemicals and Separations | MW Growth and Product Synthesis | Products

Progress Toward CISTAR Target
T1P3 Regenerable Thermally Stable Alkane Dehydrogenation Catalysts

IMPACT & FUTURE

- c-PtCo's high selectivity is promising for future colloidal catalysts

- Remove surface ligands for better conversions

- Synthesize homogeneous alloys of PtCo, PtFe and PtMn

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T1P3
Poster #: 12

Strategies to Mitigate Coke Formation and Buildup with Soft Oxidants *in situ* During PDH

Ryan Alcala[1], Shan Jiang[2], Stephen Porter[1], Brandon Burnside[1], Jeffrey T. Miller[2], Abhaya K. Datye[1]

[1]Department of Chemical and Biological Engineering, University of New Mexico
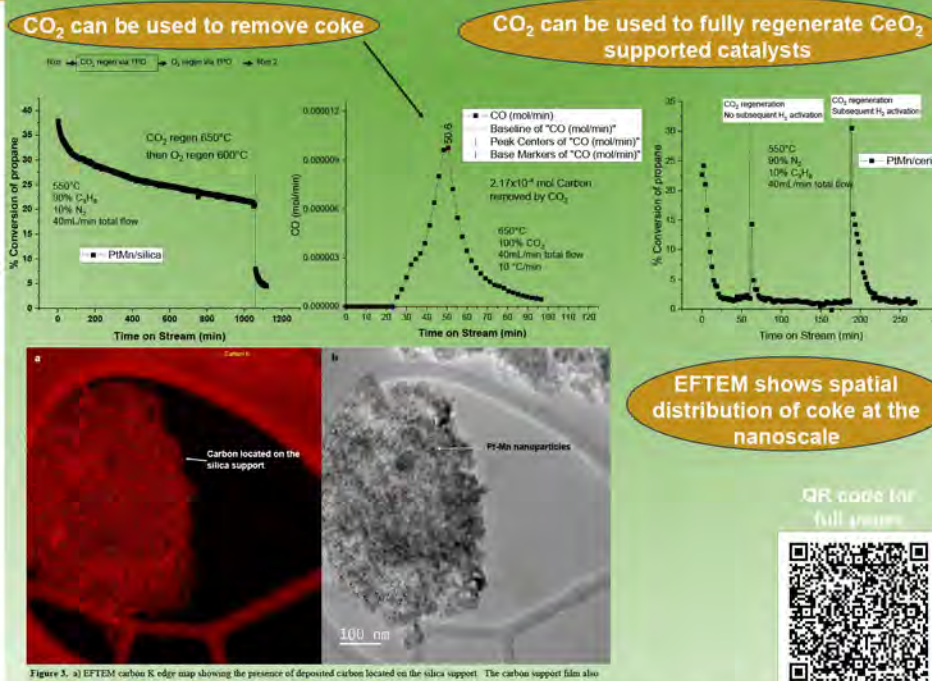[2]Davidson School of Engineering, Purdue University

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GOALS

- Investigate how soft oxidants can assist in regeneration and/or coke mitigation
- Develop procedures for effective regeneration of catalysts and in situ mitigation of coke
- Investigate the role of support on coke formation and its influence on catalyst deactivation

H_2 CO_2 or H_2O cofed or fed in pulses → Gas phase products or migration

Silica or ceria support
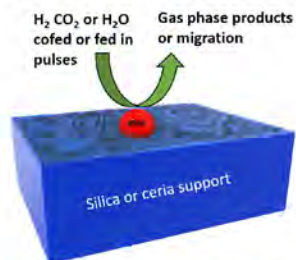
Can support interaction engineering provide novel regeneration strategies?

MAIN FINDINGS

CO$_2$ can be used to remove coke

CO$_2$ can be used to fully regenerate CeO$_2$ supported catalysts

EFTEM shows spatial distribution of coke at the nanoscale

QR code for full poster

Figure 3. a) EFTEM carbon K edge map showing the presence of deposited carbon located on the silica support. The carbon support film also shows up as red in this image. b) TEM image of Pt-Mn/SiO$_2$ showing nanoparticles (small black dots) on the silica support.

OUTCOMES

- Mars-Van Krevelen like coke combustion may be responsible for ceria regenerability in CO_2

- Suggests in situ coke mitigation via reverse Boudouard reaction is possible

- Current studies are focused on CO_2 cofeed experiments

$$(1)\ C_3H_8(g) \rightarrow C_3H_6(g) + H_2(g)$$
$$(2)\ C_3H_6(g) \rightarrow 3C(s) + 3H_2(g)$$
$$(3)\ CO_2(g) + C(s) \rightarrow 2CO(g)$$

Hypotheses:

1. Ceria-metal interface allows for facile combustion of adjacent coke via Mars Van Krevelen mechanism
- allows catalyst to remain intact after oxidation
2. CO_2 can remove coke from silica supported catalyst, but results in catalyst deactivation
- Either coke is only removed from support or CO formed at temp accelerates sintering of the catalyst
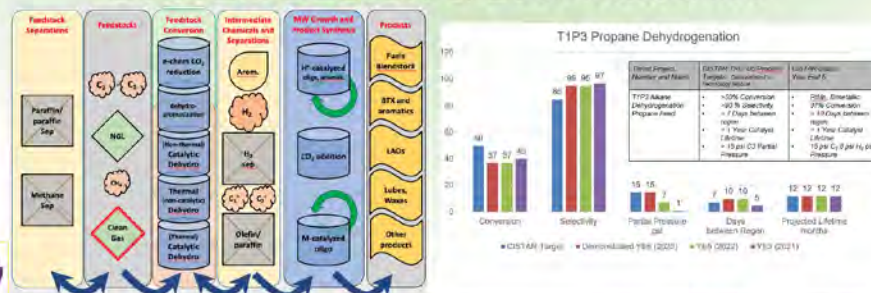
IP & INNOVATION

- Establishes a wide array of strategies to mitigate coke formation/accumulation
- Demonstrates support is effective at modifying the catalysis
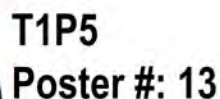- IP to be filed

SYSTEM DESIGN & BENCHMARKS

IMPACT & FUTURE

- Allows for several strategies to be used for regeneration and/or coke mitigation making operation at the well-head possible
- H_2O gasification of coke in situ is next

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T1P5
Poster #: 13

Kinetics and Speciation of Ethane Decomposition in a Nonthermal Plasma

Denver Haycock, Russell Clarke, Jason Hicks, William Schneider
Department of Chemical and Biomolecular Engineering, University of Notre Dame

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GOALS

Demonstrate kinetic modeling possibilities for nonthermal plasma

INPUTS
• Species, reactions, processes
• Rate constant information (Arrhenius or swarm)
• Reactor conditions (T, P, N_{dr}, E/N)

OUTPUTS
Temporally resolved:
• Species densities with
• Reaction rates
• Reactor conditions (T, P, N_{dr}, E/N)

Kinetic modeling software ZDPlasKin

$$\frac{d[N_i]}{dt} = \sum_{j=1}^{j_{max}} Q_{i,j}(t)$$

Plasma Catalysis supports CISTAR's **decarbonization** and **electrification** goals

Steam Cracking – current industry standard
• High temperatures
• High pressure
• Non-selective

$C_2H_6 \rightarrow C_2H_4 + H_2$

Plasma Catalysis – TRL 1-2
• Ambient temperatures
• Ambient pressure
• High selectivity potential
• Electrically powered
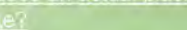
MAIN FINDINGS

We modeled ethane at 1 bar in a homogeneous, low-power-density, nonthermal plasma.

initial ethane density — t < 0
plasma ignites, electrons introduced — t = 0
speciation tracked over time — t > 0

Our model solves for the low-carbon-number species evolution following plasma ignition. It keeps temperature, pressure, and electron density constant.

What does an actual plasma reactor look like?
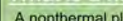
These are photos of plasma and plasma catalytic reactors in use at the University of Notre Dame for CISTAR projects.

Various parameters–including reactor temperature, flow rates, solid packing, and electric power–can be manipulated and tested.
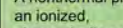
What is a nonthermal plasma, why do we use it?

A nonthermal plasma is an ionized, electronically-conductive gas
• Relatively high density of free, hot electrons, ions, and radicals
• Electrically driven energy input
• Bulk gas temperature remains low

Go, D. B. 2022, IOP Publishing

Enables electrified reactor processes

Nonthermal chemistry allows for less extreme process conditions

Industrially used for ozone production.

OUTCOMES

Time dependent speciation

• Semi stationary state reached within 10 milliseconds
• Very low conversion at these conditions

• This plot shows the major molecule products
• High selectivity towards C_2H_4 at these conditions

Scan for an example from the literature showing kinetic modeling results for an ethane + CO_2 nonthermal plasma

IP & INNOVATION

DEHYDROGENATION — OLIGOMERIZATION — CH₄ ACTIVATION — SEPARATIONS
INTEGRATED PROCESS SYNTHESIS
ENABLING TECHNOLOGIES
Laboratory Scale Modules

This project is TRL 1-2, fundamental research

SYSTEM DESIGN & BENCHMARKS

T1P5 Nonthermal Plasma-Assisted Alkane Dehydrogenation and Coupling

IMPACT & FUTURE

Opportunities and limits of plasma-only ethane activation
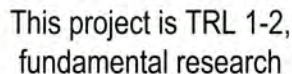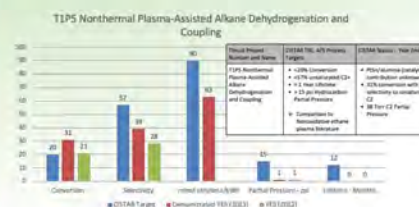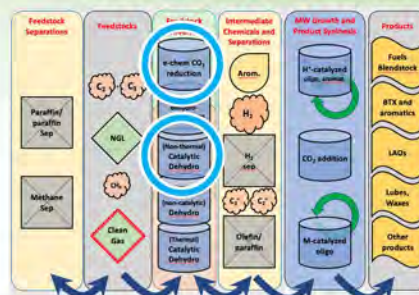
Test sensitivity to:
• Plasma conditions (E/N, N_e)
• Gas compositions (T, diluent)
• Time scales
• Initial conditions
• Reactor configuration

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T1P5
Poster #: 14

Low-Temperature Olefin/Liquid Production and Coke Suppression in Light Alkane Plasmas

Russell J. Clarke[1] and Jason C. Hicks[1*]
[1]Department of Chemical and Biomolecular Engineering, University of Notre Dame

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GOALS

Plasma Forms Reactive Species and Lowers Dissociation Barrier

Mehta, P., et al. *Nat. Catal.* 2018

Y5 Goal: Develop a Spectroscopic Tool to Observe Plasma-Surface Interactions

Full Paper
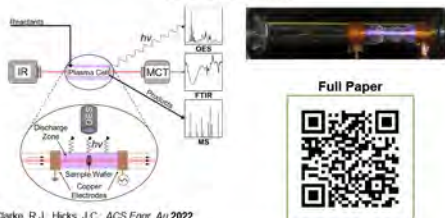
Clarke, R.J.; Hicks, J.C.; *ACS Engr. Au* 2022

Y6-7 Goal: Determine Drivers of Selectivity and Stability to Inform Catalyst Selection

- Plasma-catalyst system is complex
- Desired role of catalyst, if any, is not yet clear

> Initial focus on plasma-only chemistry will help advise catalyst selection
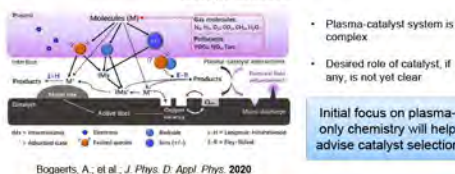
Bogaerts, A.; et al. *J. Phys. D: Appl. Phys.* 2020

MAIN FINDINGS

Insight into coking process in alkane plasmas led to control over carbon formation and enhanced stability

Ethane Dehydrogenation and Coupling Below 298 K
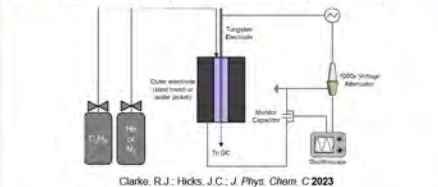
Clarke, R.J.; Hicks, J.C.; *J. Phys. Chem. C* 2023
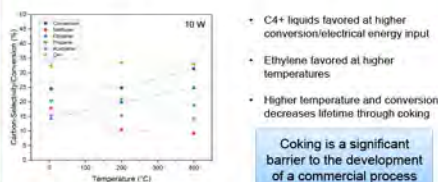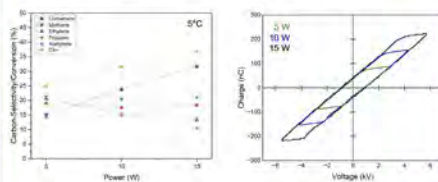
- C4+ liquids favored at higher conversion/electrical energy input
- Ethylene favored at higher temperatures
- Higher temperature and conversion decreases lifetime through coking

> Coking is a significant barrier to the development of a commercial process

Synthesis Patterns of Diamond-Like Carbon Microrods (Coke)
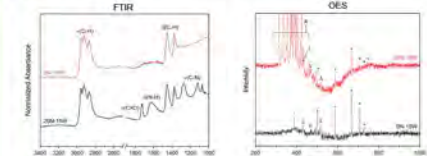
Clarke, R.J.; Hicks, J.C.; *J. Phys. Chem. C* 2023
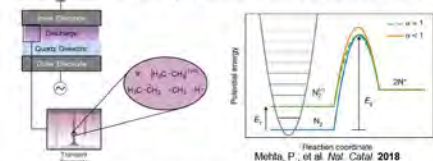
- Microrods have little aromaticity and high sp³ bonding (diamond-like)
- Growth spacing from electrode to dielectric dictated by microdischarge pattern

Full Paper

> Carbon formation can be controlled through adjustments to plasma properties

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OUTCOMES

Carbon Growth Spacing Can Be Controlled by Tuning Plasma Properties
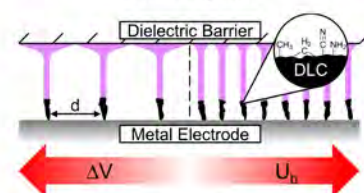
Clarke, R.J.; Hicks, J.C.; *J. Phys. Chem. C* 2023

Carbon Growth Can Be Slowed or Inhibited Through Minor Changes to the Plasma/Reaction Conditions

Normal Conditions — **Coke Suppressing Conditions**

IP & INNOVATION

FUNDAMENTAL KNOWLEDGE

- Developed technique for suppressing coke in alkane plasmas
- Understand catalyst role in plasma-assisted alkane dehydrogenation

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SYSTEM DESIGN & BENCHMARKS
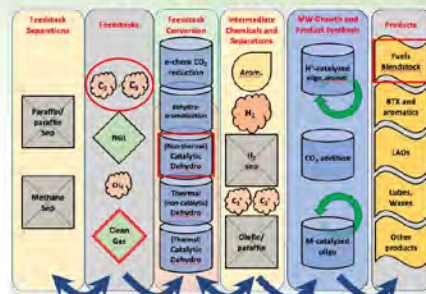
T1P5 Nonthermal Plasma-Assisted Alkane Dehydrogenation and Coupling

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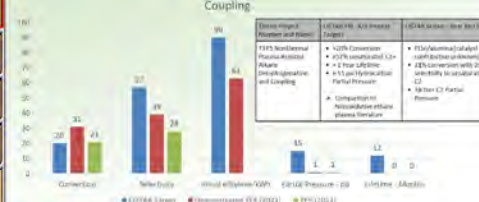
IMPACT & FUTURE

Nanosecond Pulsed Power for More Efficient Power Delivery

Malik et al. Plasma Chem. Plasma Process. 2017
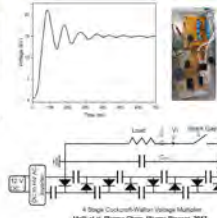
Catalyst Characterization Post-Reaction and/or Post-Regeneration with Plasma

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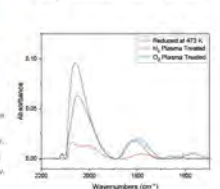
T2P1
Poster #: 15

Isolating Kinetic Effects of Void Environment in MFI Zeolites on Transport-Limited Propene Oligomerization

Lauren Kilburn[1], Diamarys Salomé Rivera[1], David Hibbits[1], Rajamani Gounder
[1]Davidson School of Chemical Engineering, Purdue University
[2] Department of Chemical Engineering, University of Florida

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GOALS

- *H-MFI zeolite catalyzed propene oligomerization reaction*

Heavy products become occluded in MFI pores and inhibit intrazeolite diffusion

Higher C_3H_6 Pressure → Heavier Products ($\geq C_9$)

Dimerization is the entry step of the complex propene oligomerization reaction network

Challenge: Propene oligomerization kinetics in MFI zeolites are coupled with transport limitation effects

Al location is a tunable property in MFI zeolites that may influence reaction kinetics

Str/Sin ~ 4.5 Å diam
↑ van der Waals
↑ steric hindrance

Int ~ 6.4 Å diam
↓ van der Waals
↓ steric hindrance

6.4 Å Intersection
4.5 Å Sinusoidal
4.5 Å Straight

Goals:
- Combine a computational and experimental approach to study the independent effect of Al location in propene oligomerization rates, selectivity and deactivation behavior.
- Identify promising samples for the oligomerization Testbed

MAIN FINDINGS

Al location in MFI can influence dimerization kinetics during propene oligomerization

Al atoms site at 12 crystallographically unique tetrahedral sites (T-sites) in MFI

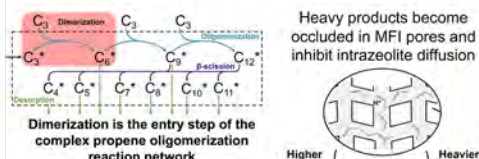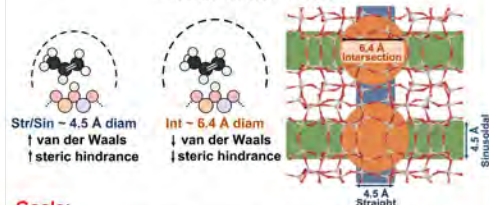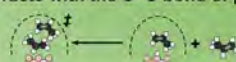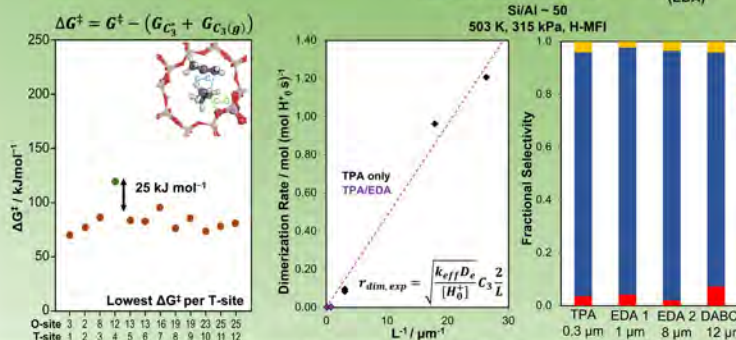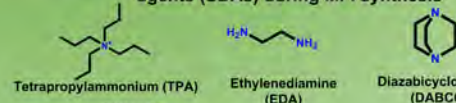| T-site:	1	2	3	4	5	6	7	8	9	10	11	12
Int:	X	X			X	X	X	X	X	X	X	X
Sin:	X	X	X	X	X	X			X		X	
Str:	X	X		X	X		X					X

Propene dimerization transition state involves the formation of a carbocation that interacts with the C=C bond of propene
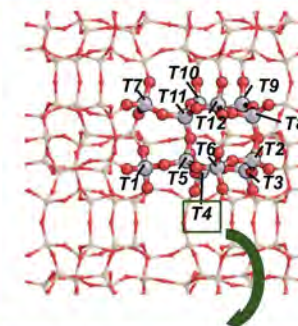
Al location can be varied using structure directing agents (SDAs) during MFI synthesis

Tetrapropylammonium (TPA)
Ethylenediamine (EDA)
Diazabicyclooctane (DABCO)

$$\Delta G^{\ddagger} = G^{\ddagger} - (G_{C_3^=} + G_{C_{3(g)}})$$

25 kJ mol⁻¹

Lowest ΔG‡ per T-site

O-site 3 2 8 12 13 16 19 20 25 25
T-site 1 2 3 4 5 6 7 8 9 10 11 12

Si/Al ~ 50
503 K, 315 kPa, H-MFI

TPA only
TPA/EDA

$$r_{dim, exp} = \sqrt{\frac{k_{eff}D_e}{[H_0^+]}} C_3 \frac{2}{L}$$

QR Code for Full Poster

C_9
C_6
C_β

TPA — 0.3 μm
EDA 1 — 1 μm
EDA 2 — 8 μm
DABCO — 12 μm
X ~ 0.1%

Black data from Bickel, E. et al., ACS Catal. **2023**, *13*, 1257–1269

OUTCOMES

T7 T10 T9 T11 T12 T8 T6 T2 T5 T3 T4 T1

T4–the only T-site without access to the intersection–has the highest ΔG‡ of the 12 T-sites by 25 kJ mol⁻¹

- DFT suggest dimerization rates will decrease if an SDA preferentially sites Al at T4

- Void environment weakly influences the stability of C_3 and C_6 adsorbates across T-sites (ΔG_{Ads} range of ~20 kJ mol⁻¹) when only the most favorable species are considered

- Preliminary selectivity data shows similar product distribution for samples synthesized with different SDAs

IP & INNOVATION

- Identify and optimize catalyst properties that result in high yields and selectivity to higher molecular weight olefins under testbed conditions

- Provisional patent application for:
Stable Product Oligomer Selectivity From Olefin Oligomerization on ZSM5-5 Zeolites and Zeotypes. Rajamani Gounder, Elizabeth Bickel, Songhyun Lee, Evan Sowinski U. S. Patent Application No.63/445,206 (2023)

SYSTEM DESIGN & BENCHMARKS

Feedstock Separation
Feedstocks
Feedstock Conversion
Intermediate Chemicals and Separations
MW Growth and Product Synthesis
Products

T5P2: Oligomerization Technology Module

Conversion: 98, 38, 34, 27
Selectivity: 55, 82, 92, 94
Partial Pressure - psi: 35, 24, 24, 36
Lifetime - Months: 12, 2, 1, 0.5

■ CISTAR Target ■ Demonstrated YE6 (2023)
■ YE5 (2022) ■ YE4 (2021)

IMPACT & FUTURE

- Provide mechanistic explanations for differences in dimerization rates and selectivity during propene oligomerization as catalyst properties (e.g., Al location in MFI) are varied.

- This study provides fundamental insights that can guide catalyst design for upgrading hydrocarbons.

- Future work will involve further experimental measurements on MFI samples synthesized with different SDAs. Observed trends will be compared to DFT-predicted results to assess the influence of transport effects
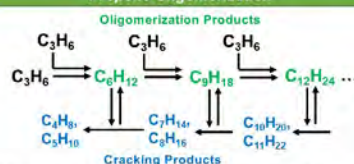
Experimental ↔ DFT

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T2P1
Poster #: 17

Heterogeneous distribution of acid-site regulates diffusional constraints governing propene oligomerization deactivation

Ricem Diaz Arroyo[1], Elizabeth Bickel[1], Rajamani Gounder[1]
[1]Department of Chemical Engineering, Purdue University

C⭒STAR
NSF Engineering Research Center
Center for Innovative and Strategic Transformation of Alkane Resources

GOALS

Propene Oligomerization
Oligomerization Products

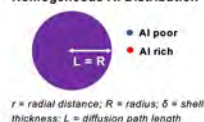**Cracking Products**

- Crystallite-scale Al distribution (external sites, zoning) also affects rates, selectivity, and deactivation during olefin oligomerization.

Homogeneous Al Distribution

- Al poor
- Al rich

$L = R$

$$\text{Thiele Modulus} = \frac{\text{Reaction Rate}}{\text{Diffusion Rate}}$$

$$\text{Catalyst properties} \quad \text{Active site property}$$

$$= \frac{[H^+] L^2}{De} \times k$$

$$\text{Diffusion parameter} = [H^+] L^2$$

r = radial distance; R = radius; δ = shell thickness; L = diffusion path length

Challenge: No well-defined boundary of spatial Al distribution.

Heterogeneous (zoned) Al Distribution

$Al_{surface} > Al_{center}$ | $Al_{center} > Al_{surface}$
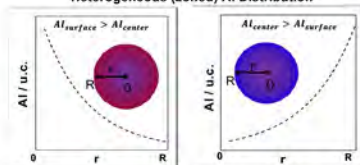
Objective: Tune the diffusion path length by biasing the spatial Al distribution using core@shell synthesis methods to influence olefin oligomerization rates and product selectivity.

MAIN FINDINGS

Crystallite-scale Al distribution influences the selectivity and deactivation profile during propene oligomerization.

Al-MFI@Si-MFI **Al-MFI** **Si-MFI@Al-MFI** **Al-MFI**

190 nm Si/Al 75 | 150 nm Si/Al 40 | 150 nm Si/Al 50 | 50 nm Si/Al 50

QR Code for Full Paper

OUTCOMES

Al-MFI@Si-MFI Synthesis
TEM-EDX Mapping: Al-MFI@Si-MFI
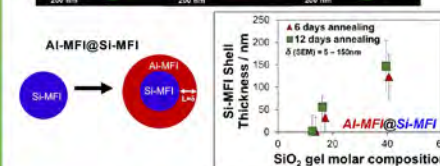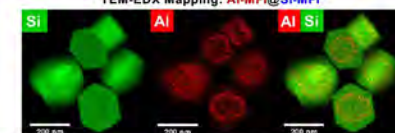
Si-MFI → Al-MFI@Si-MFI

Si-MFI@Al-MFI Synthesis
TEM-EDX Mapping: Si-MFI@Al-MFI

Si-MFI@Al-MFI

IP & INNOVATION

- Develop core@shell zeolite synthesis methods to bias Al spatial distribution toward or away from external crystallite surfaces, to alter the effects of coupled reaction-diffusion phenomena and pathways that cause deactivation
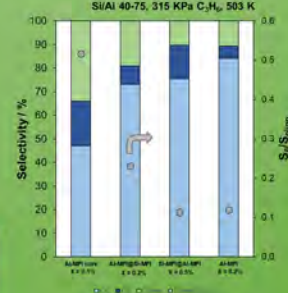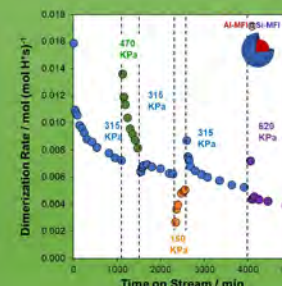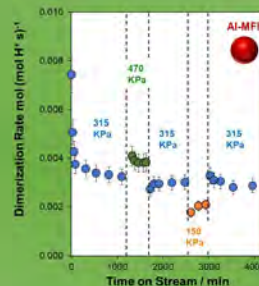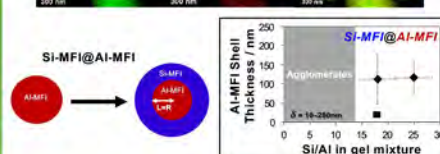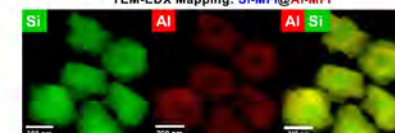
SYSTEM DESIGN & BENCHMARKS
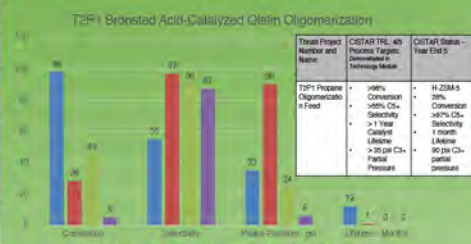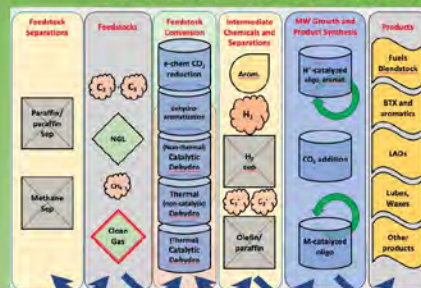
IMPACT & FUTURE

- Identify effects of solid material properties such as Al spatial zoning, crystallite size and diffusion parameter on olefin oligomerization rate, product selectivity and deactivation behavior.

- **Future:** Assess the influence of crystallite-scale Al distribution on diffusion limitations through transient changes in observed rates upon step changes of reactant pressure.

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T2P4
Poster #: 18

Effects of Ethene Pressure on the Deactivation of Nickel Active Sites Exchanged on Porous Aluminosilicate Materials During Ethene Oligomerization

Richard Caulkins[1], Christian Borrero Villabol[1], Fabio Ribeiro[1], Rajamani Gounder[1]
[1] Davidson School of Chemical Engineering, Purdue University

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

GOALS

- Ni-exchanged zeolites catalyze alkene oligomerization at low temperatures but rapidly deactivate.
- This work is motivated by the need to develop catalysts and/or reaction conditions which can achieve CISTAR stability target
- Several mechanisms explain this deactivation; some pathways can be eliminated via synthetic approaches, while other deactivation pathways are better handled through choosing appropriate reaction conditions.

Sequential Ni-catalyzed oligomerization
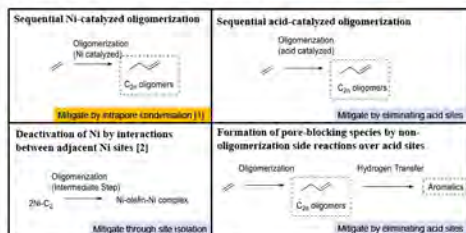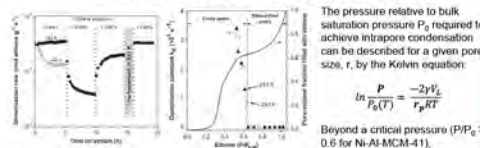Oligomerization (Ni catalyzed) → C_{2n} oligomers
Mitigate by intrapore condensation [1]

Sequential acid-catalyzed oligomerization
Oligomerization (acid catalyzed) → C_{2n} oligomers
Mitigate by eliminating acid sites

Deactivation of Ni by interactions between adjacent Ni sites [2]
Oligomerization (Intermediate Step) $2Ni-C_2$ → Ni-olefin-Ni complex
Mitigate through site isolation

Formation of pore-blocking species by non-oligomerization side reactions over acid sites
Oligomerization → C_{2n} oligomers → Hydrogen Transfer → Aromatics
Mitigate by eliminating acid sites

Intrapore condensation (i.e., when confinement effects within mesoporous and microporous materials cause a fluid to form a liquid-like phase within a pore at pressures below bulk saturation pressures) significantly reduces deactivation in Ni-Al-MCM-41 during ethene oligomerization. [1]
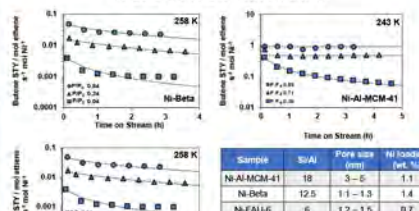
The pressure relative to bulk saturation pressure P_0 required to achieve intrapore condensation can be described for a given pore size, r, by the Kelvin equation:

$$\ln \frac{P}{P_0(T)} = \frac{-2\gamma V_L}{r_p RT}$$

Beyond a critical pressure ($P/P_0 > 0.6$ for Ni-Al-MCM-41), deactivation becomes undetectable during ethene oligomerization.

[1] Agirrezabal-Tellena and Iglesia, J. Catal. **352** (2017) 505-514
[2] A Milnar et al., J. Catal. **296** (2012) 156-164

Deactivation via formation of heavy oligomers over Ni sites can be mitigated in Ni-Al-MCM-41 by operating under capillary condensation conditions; can this principle be generalized to CISTAR Ni-exchanged zeolites?

MAIN FINDINGS

Deactivation is mitigated under capillary condensation conditions in (mesoporous) Ni-Al-MCM-41 but not in Ni-exchanged (microporous) zeolites at conditions that should lead to capillary condensation

A series of Ni-exchanged aluminosilicates (zeolites and mesoporous Al-MCM-41) with varying pore diameters were prepared:
Ni-Beta < Ni-FAU-6 < Ni-Al-MCM-41

(plots: Butene STY / mol ethene s^{-1} mol Ni^{-1} vs Time on Stream (h), labeled Ni-Beta 258 K, Ni-Al-MCM-41 243 K, Ni-FAU-6 258 K)

Sample	Si/Al	Pore size (nm)	Ni loading (wt. %)
Ni-Al-MCM-41	18	3 – 5	1.1
Ni-Beta	12.5	1.1 – 1.3	1.4
Ni-FAU-6	6	1.2 – 1.5	0.7

*H2 was co-fed (1% of total flow) during Ni-FAU experiments
**Dashed lines represent fits of deactivation models.

Sample	P/P_0	k_d	n
Ni-Al-MCM-41	0.36	3.15	1.9 (± 0.3)
Ni-Al-MCM-41	0.71	0	0
Ni-Al-MCM-41	0.89	0	0
Ni-Beta	0.04	6.07×10^{-3}	2*
Ni-Beta	0.24	8.49×10^{-3}	1.8 (± 1.1)
Ni-Beta	0.84	3.90×10^{-3}	2.2 (± 1.7)
Ni-FAU-6	0.04	3.04×10^{2}	1.8 (± 1.6)
Ni-FAU-6	0.36	2.13×10^{3}	1.8 (± 0.3)
Ni-FAU-6	0.84	1.52×10^{3}	1.8 (± 0.9)

*Fitting to the generalized deactivation model could not be achieved within specified limits (n < 2.3, standard error < 0.65) and data was thus fit to either n = 1 or n = 2 power law models.

Deactivation orders and constants can be calculated for each catalyst and pressure [3]:

$$r = \frac{r_0}{\left(1 + (n-1) k_d r_0^{n-1} t\right)^{\frac{1}{n-1}}}$$

Solvation of products mediated by an intrapore condensed phase is demonstrated by an abrupt drop in deactivation constant in Ni-Al-MCM-41, but this drop is not observed in Ni-exchanged zeolites.

Ni site density needs to be evaluated to confirm that capillary condensation has no effect on deactivation in Ni-exchanged microporous zeolites.

Decreasing site density reveals a transition in deactivation order in Ni-FAU-40 (Si/Al = 40) as a function of ethene pressure

Sample	Pore diameter (nm)	Ni loading (wt. %)	Ni site density (Ni/nm²)	Avg. Ni-Ni distance (nm)
Ni-FAU-6	1.2 – 1.5	0.7	0.33	1.3
Ni-FAU-40	1.4 – 1.7	0.3	0.12	2.6

(plot: Butene STY / mol ethene s^{-1} mol Ni^{-1} vs Time on Stream (h), Ni-FAU-40 258 K)

Sample	P/P_0	k_d	n [a]
Ni-FAU-40	0.04	0.741	1.6 (1.3)
Ni-FAU-40	0.36	9.98×10^{-1}	1.1 (0.1)
Ni-FAU-40	0.84	16.1	1.9 (0.02)

Ni sites in Ni-FAU-40 are more isolated than Ni sites in Ni-FAU-6, as shown by estimated Ni-Ni site distances.
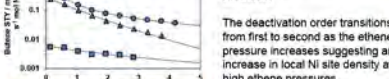
The deactivation order transitions from first to second as the ethene pressure increases suggesting an increase in local Ni site density at high ethene pressures.

Ni-FAU-40 deactivates regardless of the conditions studied indicating capillary condensation conditions do not influence the deactivation behavior.
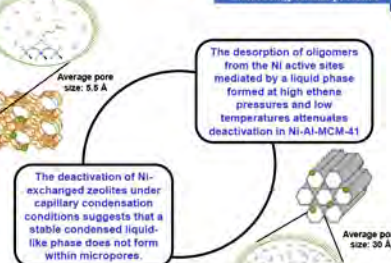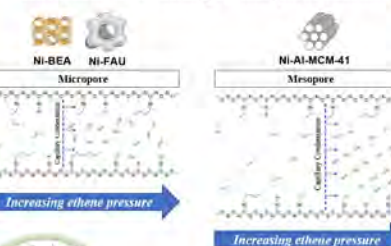
The transition from a first-order to a second-order deactivation behavior with increasing ethene pressure could be a combined effect of increased generation of active Ni(II)-alkyl sites [4] influenced by initial density and by the mobilization of Ni sites under high ethene pressures [5].

[3] J. Butt, Activation, Deactivation, and Poisoning of Catalysts, Elsevier, San Diego, 2012
[4] Saxena et al., ACS Eng. Au (2021).
[5] Brogaard et al., ACS Catal. **9** (2019) 5645-5650.

OUTCOMES

Capillary condensation does not attenuate deactivation in Ni-exchanged microporous zeolites

Ni-BEA, Ni-FAU — Micropore; Ni-Al-MCM-41 — Mesopore

Increasing ethene pressure

Average pore size: 5.5 Å
Average pore size: 30 Å

The desorption of oligomers from the Ni active sites mediated by a liquid phase formed at high ethene pressures and low temperatures attenuates deactivation in Ni-Al-MCM-41

The deactivation of Ni-exchanged zeolites under capillary condensation conditions suggests that a stable condensed liquid-like phase does not form within micropores.

The results from this work motivate efforts to develop synthetic methods and establish reaction conditions at which Ni-exchanged catalysts are stable and industrially viable.
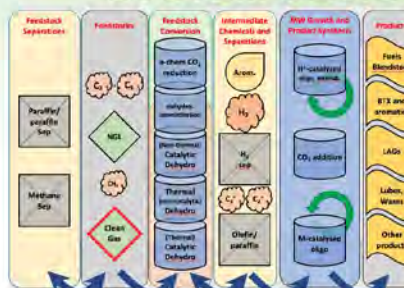
IP & INNOVATION

- Current efforts seek to develop materials that show behaviors (during alkene oligomerization) that are different to those already reported in literature and that are industrially applicable.

- Intellectual property documentation will be filed upon the design of a material relevant to CISTAR's main goals.
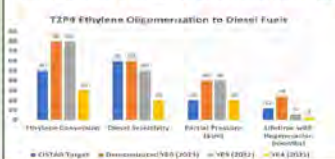
QR Code for Full Paper

SYSTEM DESIGN & BENCHMARKS

Progress Toward CISTAR Target
T2P4 Ethylene Oligomerization to Diesel Fuels

Thrust Project Name and Name	CISTAR TRL 4/5 Process Targets: Demonstrated in Technology Module	CISTAR Status: Year Ending 2022
T2P4 Oligomerization Catalyzed by Transition Metals Based on Non-Zeolites	>50% C_2 Conversion; >90% Selectivity to C_2^+ olefin products; >50% Selectivity to C_{12}^+; > 20 atm C_2^+ Partial Pressure; 1-year life with regeneration	>75% C_2^+ Conversion; >90% Selectivity to C_2^+ olefin products; >65% Selectivity to C_{12}^+; 10-15 atm C_2^+ Partial Pressure; 2+ year life with regeneration

IMPACT & FUTURE

Ni-Al-MCM-41 exhibits stable behavior during ethene oligomerization due to capillary condensation.

Capillary condensation does not attenuate deactivation in Ni-exchanged microporous zeolites, suggesting that only mesoporous materials have pores sufficiently large to support a solvating phase of ethene.

High ethene pressures result in a shift in deactivation mechanism in microporous Ni zeolites from a first-order mechanism, where heavy molecular weight species form over single Ni sites, to a second-order mechanism, where a bridging alkyl species forms between two proximal Ni sites.

These results generate new research questions regarding mesoporous materials. Can other mesoporous Ni catalysts be stabilized under condensation conditions? Could the capillary condensation regime be altered in Ni-Al-MCM-41 by functionalizing these materials?

Future work will focus on mesoporous catalysts such as Ni-POM materials dispersed within mesoporous SBA-15 and functionalized Ni-Al-MCM-41 developed in collaboration with colleagues at Notre Dame and Northwestern University.

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T2P4
Poster #: 20

Computational Exploration of the Catalytic Activity of Single Site Polyoxometalates for Oligomerization Reactions

Michael Appoh[1], William Schneider[1,2]
[1]Department of Chemistry and Biochemistry, University of Notre Dame
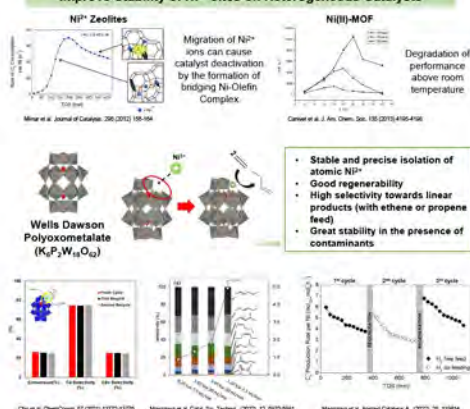[2]Department of Chemical Engineering, University of Notre Dame

C★STAR
NSF Engineering Research Center
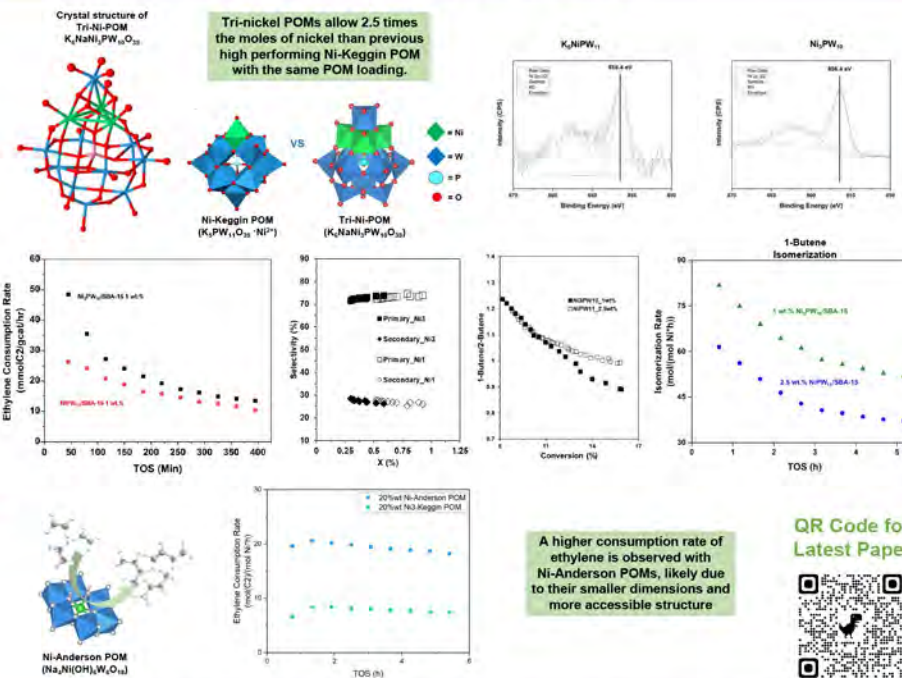Center for Innovative and Strategic Transformation of Alkane Resources
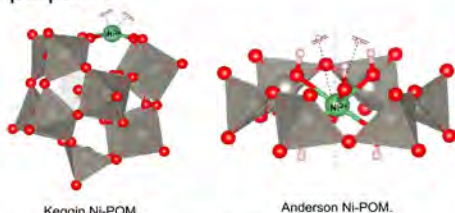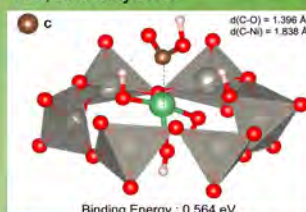
GOALS

- 'Heterogeneous' single site catalysts shows promising route to controllable to practical ethylene oligomerization reaction.

- POM provides a tunable and heterogenizable platform for such purpose.
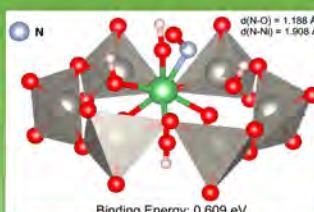

Keggin Ni-POM.

Anderson Ni-POM.

- Explore the structure of the two polyoxometalate and their accessibility, particularly, their affinity with target adsorbate using Density Functional Theory (DFT).
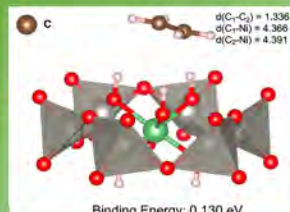
MAIN FINDINGS

- To test our model and provide insight into the performance of these single site catalyst, we explored two polyoxometalate classes, Anderson and Keggin, focusing on their interactions with target adsorbates: CO, NO, and ethylene.
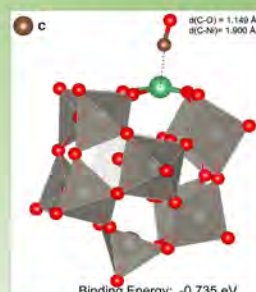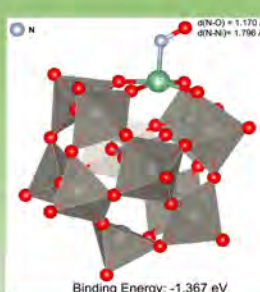

d(C-O) = 1.396 Å
d(C-Ni) = 1.838 Å

Binding Energy : 0.564 eV
CO Anderson Ni-POM.

d(N-O) = 1.188 Å
d(N-Ni) = 1.908 Å

Binding Energy: 0.609 eV
NO on Anderson Ni-POM.

d(C_1-C_2) = 1.336 Å
d(C_1-Ni) = 4.366 Å
d(C_2-Ni) = 4.391 Å

Binding Energy: 0.130 eV
Ethylene on Anderson Ni-POM.

d(C-O) = 1.149 Å
d(C-Ni) = 1.900 Å

Binding Energy: -0.735 eV
CO on Keggin Ni-POM.

d(N-O) = 1.170 Å
d(N-Ni) = 1.796 Å

Binding Energy: -1.367 eV
NO on Keggin Ni-POM.

d(C_1-C_2) = 1.356 Å
d(C_1-Ni) = 2.294 Å
d(C_2-Ni) = 2.288 Å

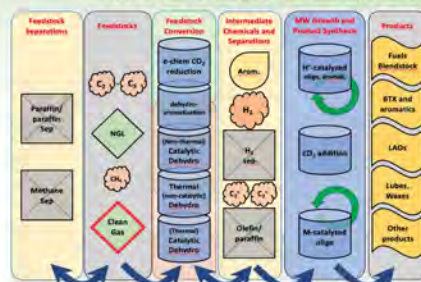Binding Energy: -0.458 eV
Ethylene on Keggin Ni-POM.

OUTCOMES

- Adsorption energies suggest weak Anderson POM-target adsorbate interaction, as the target adsorbates easily desorbs from the active site.

- Binding energy calculations reveal highly endothermic adsorption.

- Moreover, for CO adsorption, CO prefers to bind with OH to form COOH.

- Keggin Polyoxometalates exhibit promising interactions with target adsorbates.

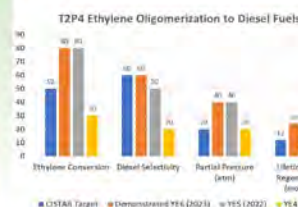- The interaction with the adsorbate is highly exothermic.

IP & INNOVATION

DEHYDROGENATION | OLIGOMERIZATION | CH₄ ACTIVATION | SEPARATIONS
ENABLING TECHNOLOGIES

Highly selective catalysis at high conversions | High efficiency separations of like molecules | Catalyst durability under extreme conditions | Integrated aromatic environmental & technical design
FUNDAMENTAL KNOWLEDGE

SYSTEM DESIGN & BENCHMARKS

Progress Toward CISTAR Target

T2P4 Ethylene Oligomerization to Diesel Fuels

IMPACT & FUTURE

- Establish the reaction pathway by determining the elementary steps between reactants and products.

- Use these models to guide material and system design

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