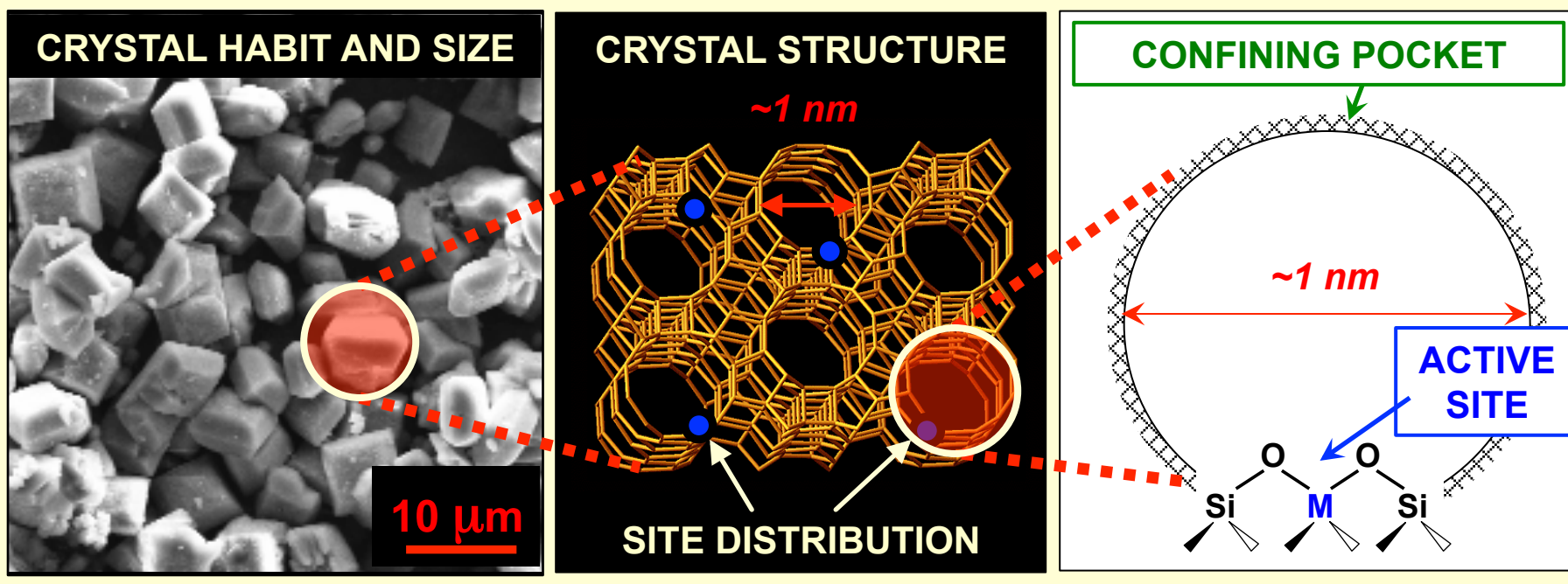


Gounder Research Laboratory: Chemistry and Catalysis of Nanoscale Materials

Nanoscale catalysts with tunable site and structural properties



Rajamani Gounder

rgounder@purdue.edu

Larry and Virginia Faith Associate Professor of Chemical Engineering, Purdue University

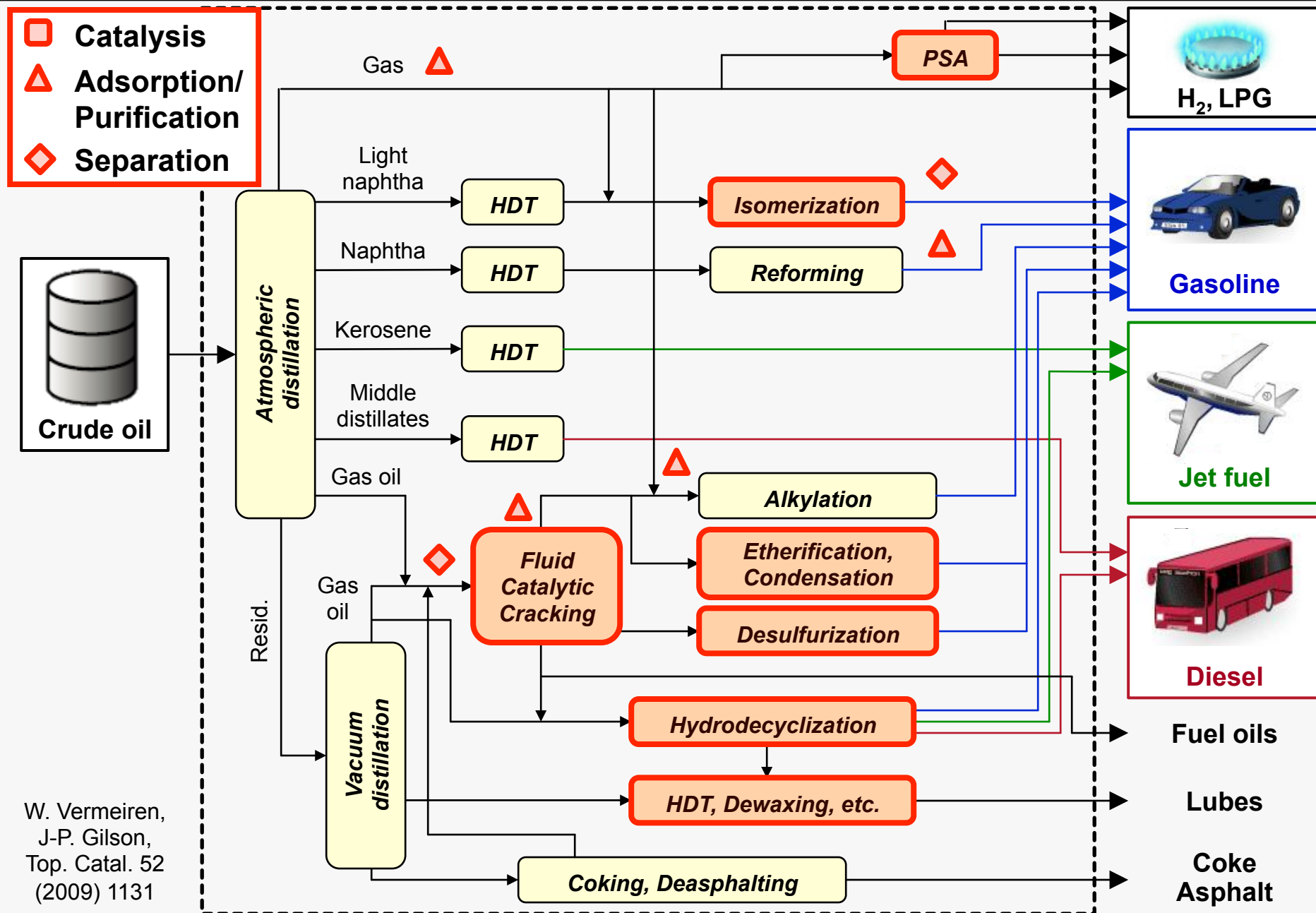
Purdue Process Safety and Assurance Center (P2SAC) Meeting

May 17, 2021 – West Lafayette, IN

Overview of today's presentation

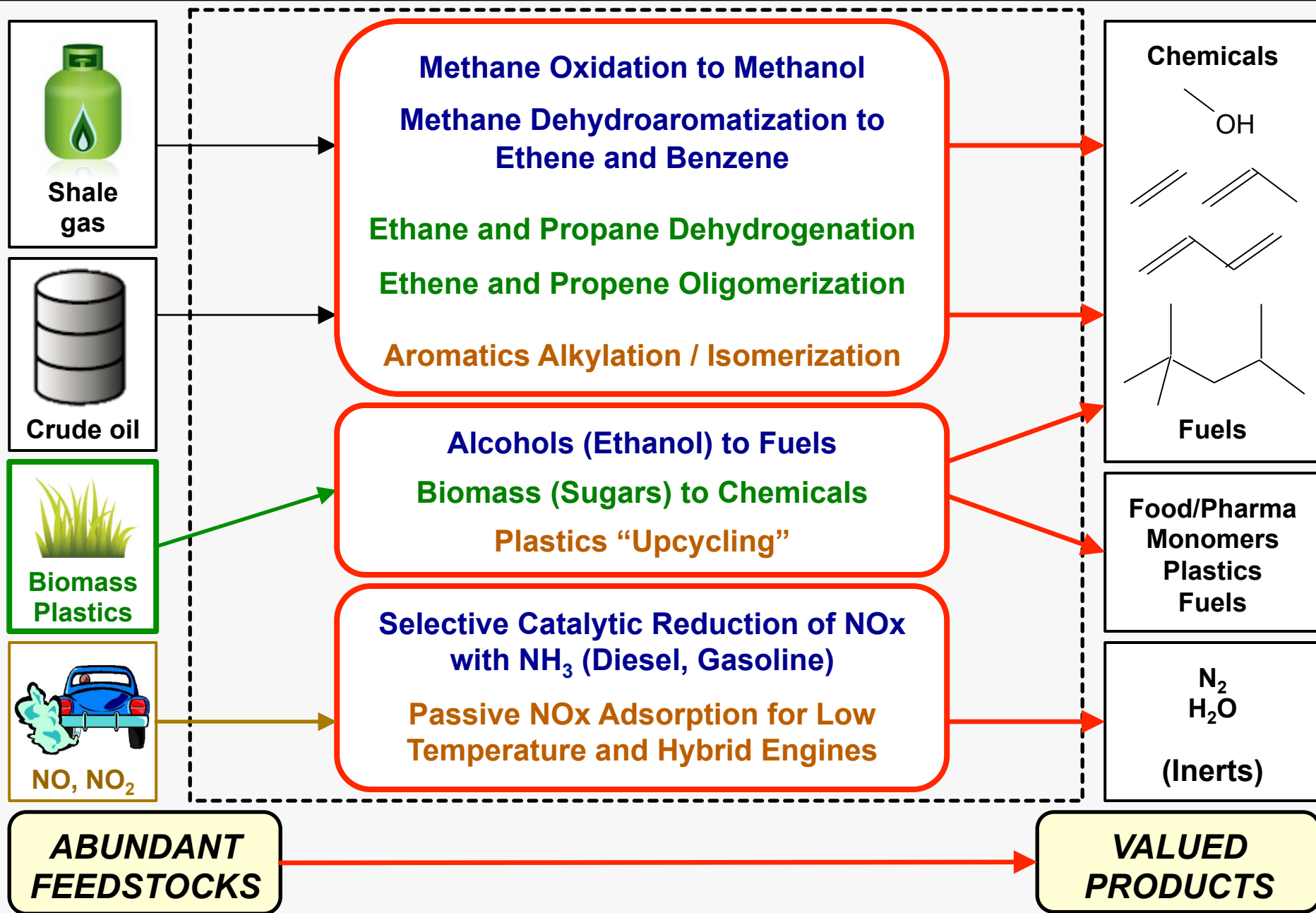
- Overview of research group, interests and capabilities, collaborations
 - Overall project vision: Prevention through design (PTD) concepts in catalysis and reaction engineering (CRE)
 - Brief summary of first project in P2SAC (safer (ep)oxidation catalysis)
-
- Current project in P2SAC: solid acid alternatives to alkylation (motivation, goals)
 - Catalytic chemistry: complementarity of alkylation and oligomerization catalysis
 - Olefin chain-growth (e.g., oligomerization) is a coupled reaction-diffusion process
 - Technical progress:
 - Synthetic methods to influence catalyst properties
 - Data on oligomerization at low conversion (fundamental studies)
 - Data on oligomerization at high conversion (process feasibility data)
-
- Current workplan for CY 2021, future ideas in CRE/PTD

Petrochemical refining is driven by zeolite-based technologies



W. Vermeiren,
J-P. Gilson,
Top. Catal. 52
(2009) 1131

Energy and environmental applications driven by **zeolite catalysis**



P2SAC Project: Prevention through catalyst design for applications in the petrochemical industry (*PI: Raj Gounder*)

LONG-TERM GOAL: A collaborative project that can leverage the expertise of more than 1 faculty in Purdue ChE

PhD-level projects



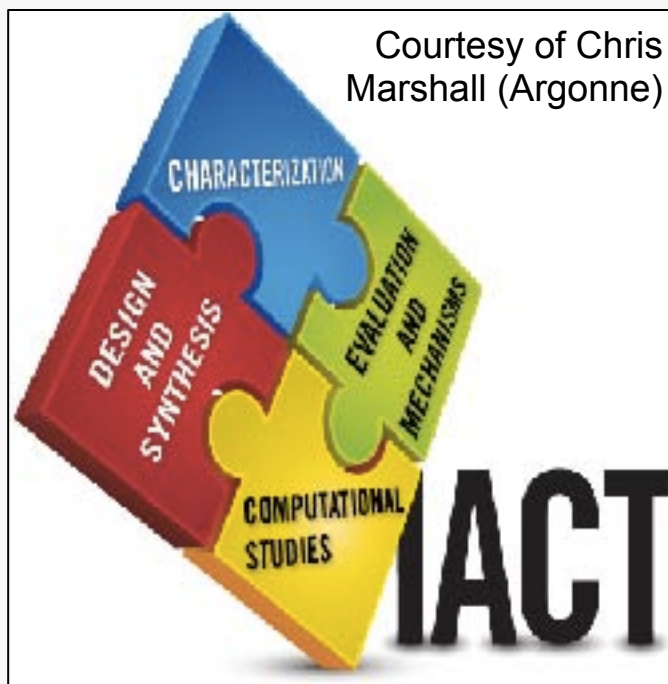
Raj Gounder



Fabio Ribeiro



Brian Tackett
(new assistant professor joining fall 2021)
electrochemistry/catalysis, CO₂ reduction



Jeff Greeley



Jeff Miller

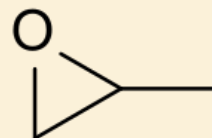
P2SAC Project: Prevention through catalyst design for applications in the petrochemical industry (*PI: Raj Gounder*)

VISION: Prevention through catalyst design. Design catalysts to allow practicing safer industrial processes, and eliminating safety/occupational hazards.

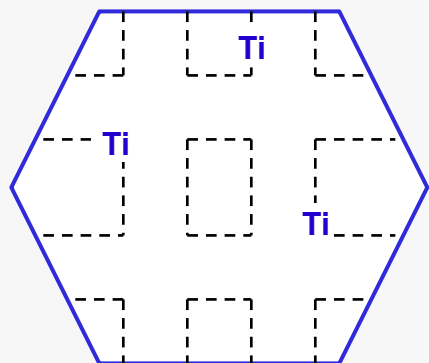
CHEMICALS: Synthesis of solid Lewis acids for safer catalytic oxidation reactions

Example: Propylene oxide (PO) monomers

- 7.7 million tons/yr produced worldwide in 2012 (9.5/yr in 2016)
- BASF/Dow Chemical make PO using Ti-zeolites (HPPO process)

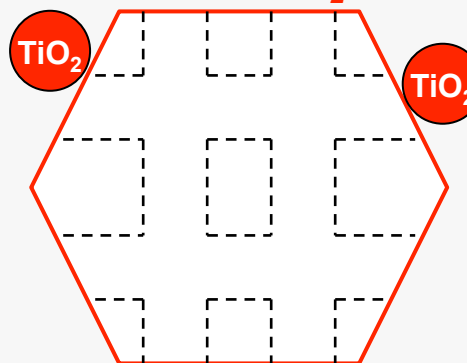


framework Ti desired



Propylene epoxidation occurs on isolated Lewis acidic Ti centers in zeolites

non-framework TiO₂ undesired



Unwanted H₂O₂ decomposition to O₂ occurs on non-framework TiO₂ sites, potential overpressures / explosions

P2SAC Project: Prevention through catalyst design for applications in the petrochemical industry (*PI: Raj Gounder*)

VISION: Prevention through catalyst design. Design catalysts to allow practicing safer industrial processes, and eliminating safety/occupational hazards.

CHEMICALS: Synthesis of solid Lewis acids for safer catalytic oxidation reactions

Major accomplishments of this project

Research Products

- Publications (10)
- Presentations (67)
- U. S. Patents (1 issued, 1 patent pending)

Mentoring / Education Outcomes

- Postdoctoral scholars (1)
- PhD students (4) -> 1 faculty, 3 postdocs (1 NL, 2 academia)
- PhD student (1) affiliated with project and engaged with P2SAC
- Undergraduate students (5) -> 2 are now PhD students

Other Outcomes

- Internal (Purdue) and External Research Collaborations
- Laboratory/Instrumentation Safety (Publications, and Instrument Design Adopted at Other Universities)

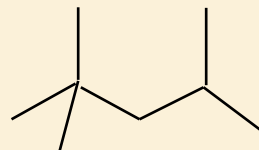
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VISION: Prevention through catalyst design. Design catalysts to allow practicing safer industrial processes, and eliminating safety/occupational hazards.

REFINING: Synthesis of solid Brønsted acids to practice carbon chain growth chemistry

Example: Alkylation for high-octane gasoline

- 2 million barrels/day produced worldwide in 2016
- Several refiners make alkylate using H_2SO_4 or HF liquid acids
- Last major refinery/petrochemical process using strong liquid acids



- **Numerous well-documented process safety incidents with HF acid handling, storage/release, usage that motivate a PTD approach**
- **Some potential alternatives are emerging:**
 - Solid Lewis-Brønsted superacids
 - AlkyClean® (Albermarle, CB&I, Neste Oil): 2700 barrels/day
 - ISOALKY (Chevron -> Honeywell UOP): ionic liquids

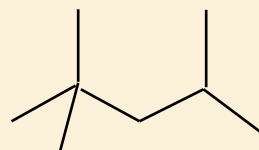
P2SAC Project: Prevention through catalyst design for applications in the petrochemical industry (*PI: Raj Gounder*)

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Example: Alkylation for high-octane gasoline

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- **Project Goals: Basic research on solid acid hydrocarbon chain-growth catalysts**
 - Research needs: Synthesis methods and structure-property relations to design catalysts with higher stability (lifetime) and selectivity
 - Minimize coke precursors (deactivation)
 - Improve hydride transfer selectivity (toward alkylate)
 - Track 1: Design of solid Brønsted acid catalysts (zeolites, oxides)
 - Controlled local active site distributions (proximity) and densities (Si/Al)
 - Controlled diffusion properties (crystallite size, Thiele moduli, ...)
 - Track 2: Catalyst Testing (low conversion for fundamental work, high conversion for feasibility)

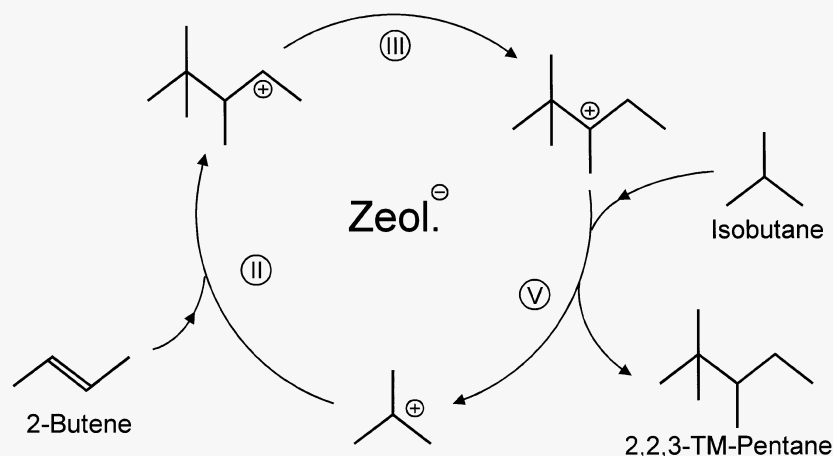
Alkylation Catalysis: Background and Motivation

- **Reaction:**

- Alkylation of isobutane with light (C_3 - C_5) olefins to make multiply-branched C_7 - C_9 alkanes with high octane number (gasoline)

- **Alkylation Mechanism (simplified):**

Weitkamp and Traa, Catal. Today 49 (1999) 193-199



Propagated by intermolecular hydride transfer reactions

Promoted by stronger acids, higher acid site densities

- **Catalyst deactivation: loss in conversion / selectivity to alkylate (and formation of oligomers)**

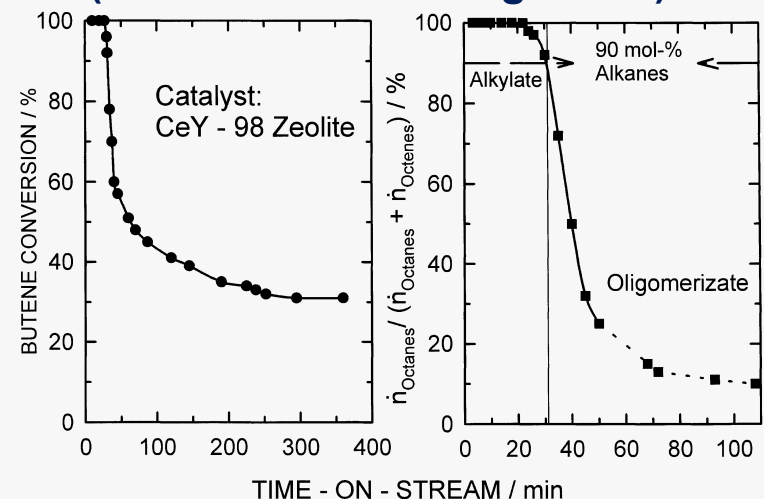
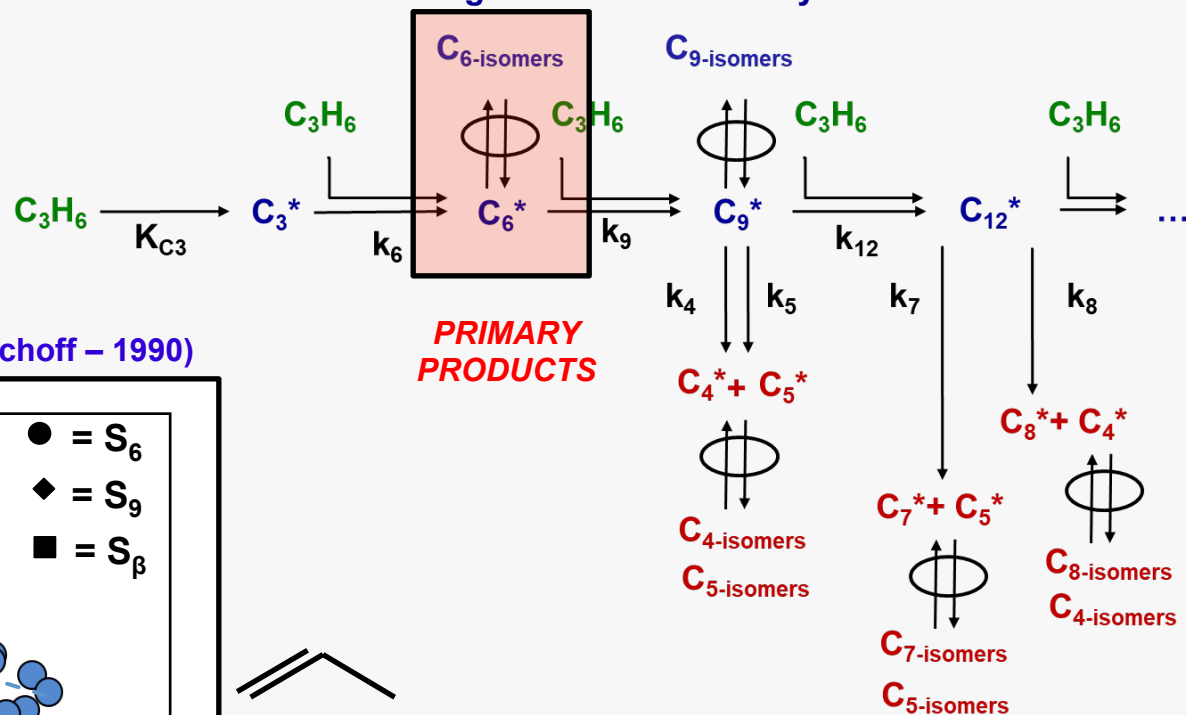


Fig. 2. Conversion of a liquid isobutane/1-butene mixture on a CeY-98 zeolite in a fixed-bed reactor ($T=80^\circ\text{C}$, $p=31$ bar, liquid feed rate= $7.5\text{ cm}^3/\text{h}$, mass of catalyst= 1.4 g , $\dot{n}_{\text{isobutane}}/\dot{n}_{1\text{-butene}} = 11 : 1$), after [13-15].

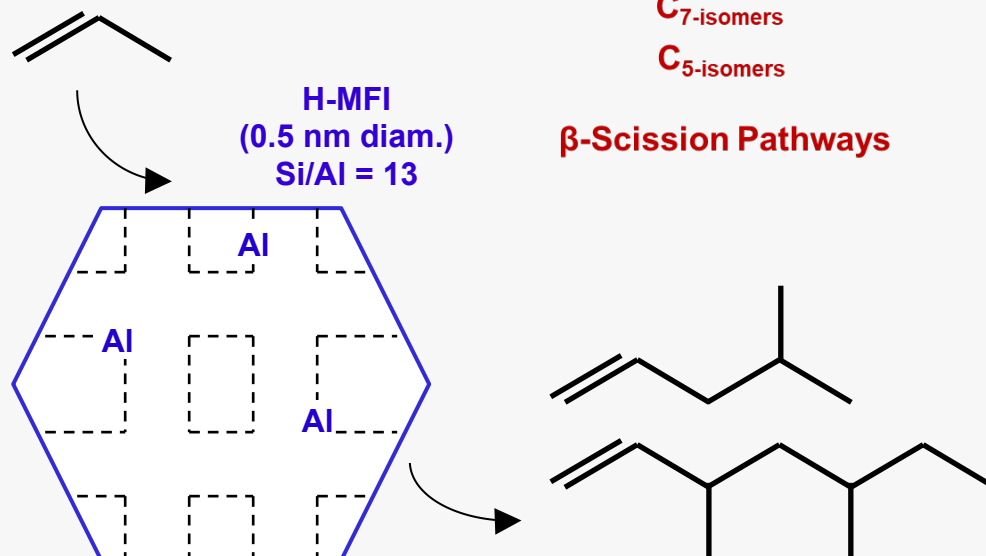
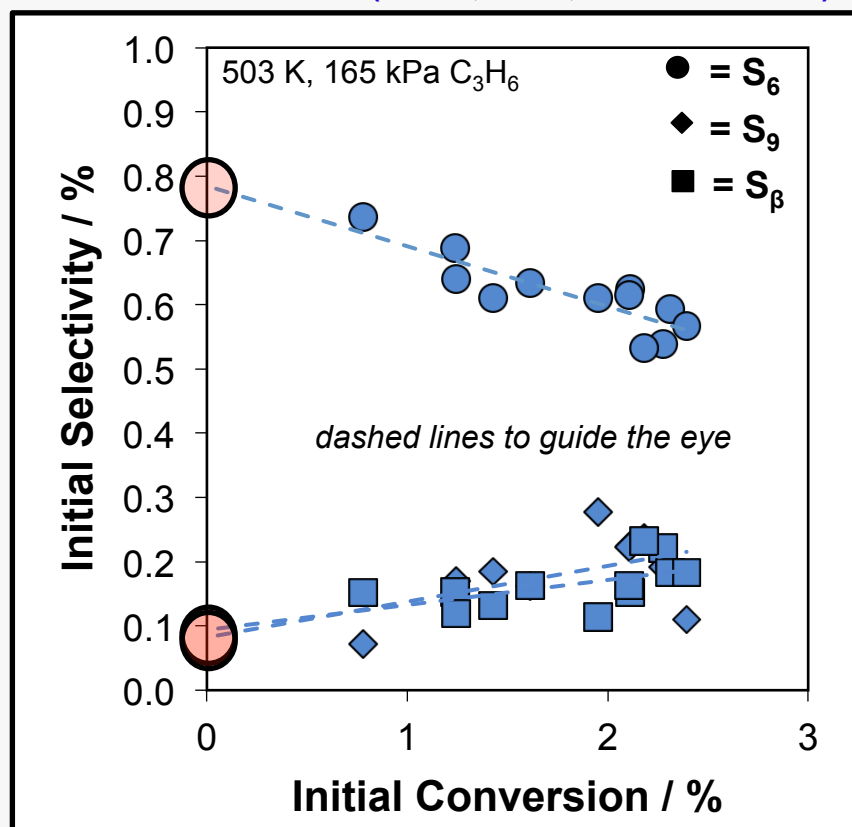
Complementarity between alkylation/oligomerization reactions: connections in fundamental knowledge (kinetics/mechanisms, site requirements, etc.)

Olefin oligomerization (and chain-growth processes) in acid zeolites are inherently a coupled reaction-diffusion process

Oligomerization Pathway



PRIMARY DELPLOT (Bhore, Klein, Bischoff – 1990)



Fundamental experimental investigations of coupled reaction-diffusion phenomena in zeolites

Crystallite length, active site density influence diffusion

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

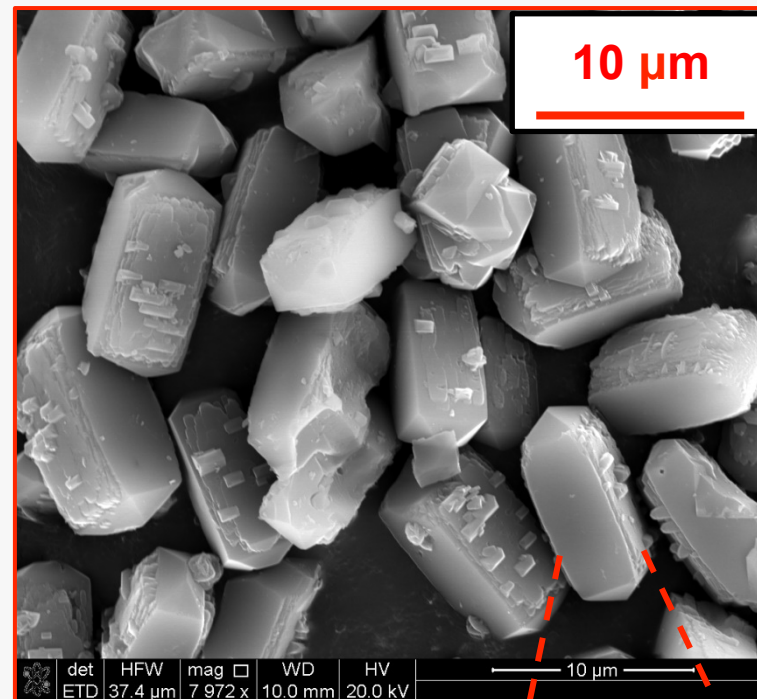
$$\Phi^2 = \frac{\text{Catalyst properties}}{\text{Reaction property}} \times k$$

$$(n = 1) \quad \frac{[H^+] L^2}{D_e} \times k$$

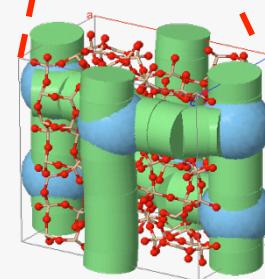
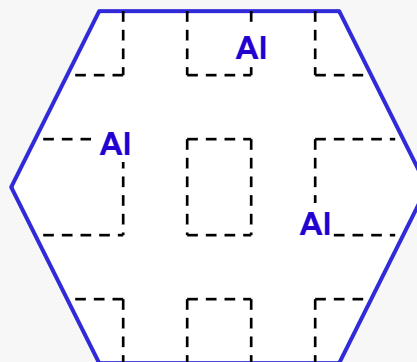
$$\text{Material "Diffusion Parameter"} = [H^+] L^2$$

Materials design approaches:

- Vary crystallite size
- Al spatial distribution (toward crystallite exterior)



H-MFI
(0.5 nm diam.)
Si/Al = 13



MFI
12 unique T-Sites
10-MR channels (~0.55 nm)
Intersections (~0.70 nm)

Current progress to date: Installation and safety / performance validation of a high pressure/conversion reactor in FlexLab

Micromeritics Microactivity
Effi Reactor



- **Status update**

- Installed and validated a benchtop-scale reactor (1-10 gram catalyst scale) to perform hydrocarbon reactions at industrial conditions and high conversions
- Housed in FlexLab, primarily designed for olefin oligomerization (CISTAR)
- Also capable of other hydrocarbon chemistries

- **Goals**

- Assess the practical functionality (and generate data for patents) of Purdue-developed catalysts for hydrocarbon reactions
- Characterize the product slate from catalysts at high conversions
- Evaluate long-term (eg, days-to-weeks) catalyst behavior (deactivation, time-on-stream product profiles) and regeneration

Current progress to date: Installation and safety / performance validation of a high pressure/conversion reactor in FlexLab

Micromeritics Microactivity
Effi Reactor



• Operational Features

- Automated and programmable for long-term unintended operation
- Max P: 100 bar, Max T: 800 °C
- Heated enclosure and transfer lines to prevent liquid condensation and send effluent to GC-MS (online analysis)
- Gas-liquid-liquid separator capable of separating two immiscible liquids (offline analysis)

• Safety Features (will automatically shut-off temperature / flow)

- Flammable gas detectors (2 for H₂, 2 for hydrocarbons) to identify leaks inside and outside the heated box
- Loss of air-flow in lab room and exhaust/ventilation system
- Over-temperature and over-pressure alarms and safety shut-offs

Acknowledgements



(Oxidation project) (Other P2SAC research)

- **Jason Bates (alumni)**
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- **YoonRae Cho (UG alumni)**
- Yury Zvinevich



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