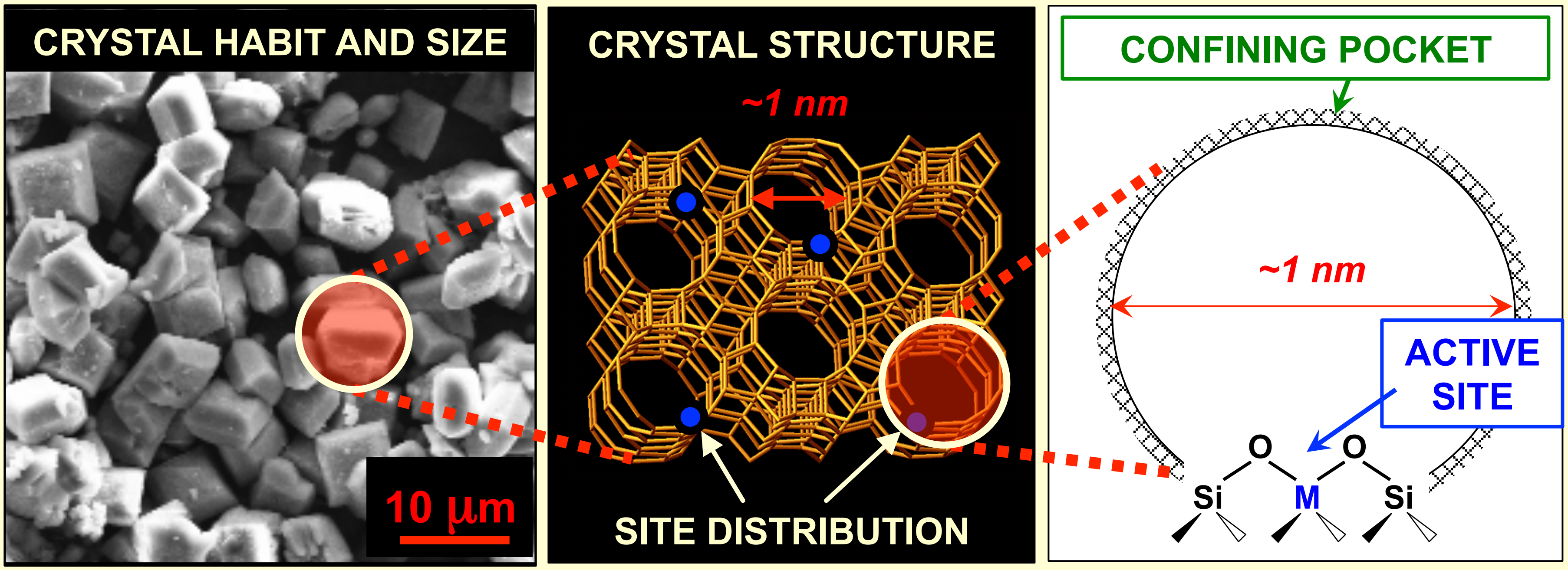
Gounder Research Laboratory: Chemistry and Catalysis of Nanoscale Materials

Nanoscale catalysts with tunable site and structural properties



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Purdue Process Safety and Assurance Center (P2SAC) Meeting
December 12, 2018 – West Lafayette, IN

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 project

Raj Gounder

Fabio Ribeiro

Courtesy of Chris Marshall (ANL)

Jeff Greeley

Jeff Miller

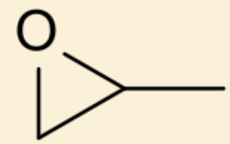
P2SAC Project: Prevention through catalyst design for applications in the petrochemical industry (*PI: Raj Gounder*)

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

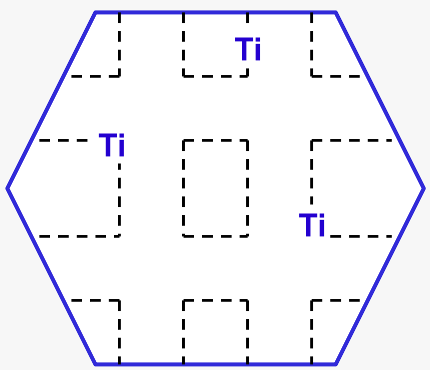
CHEMICALS: Synthesis of solid Lewis acids for safer catalytic oxidation reactions

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)

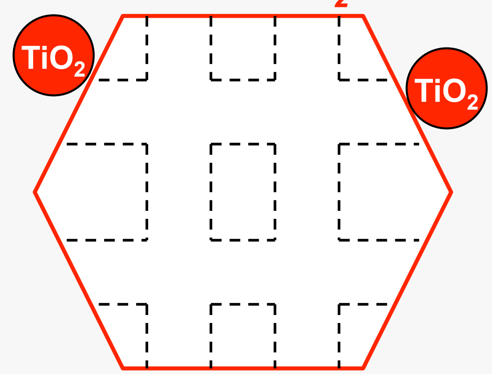


framework Ti desired



Propylene epoxidation occurs on isolated Lewis acidic Ti centers in zeolites

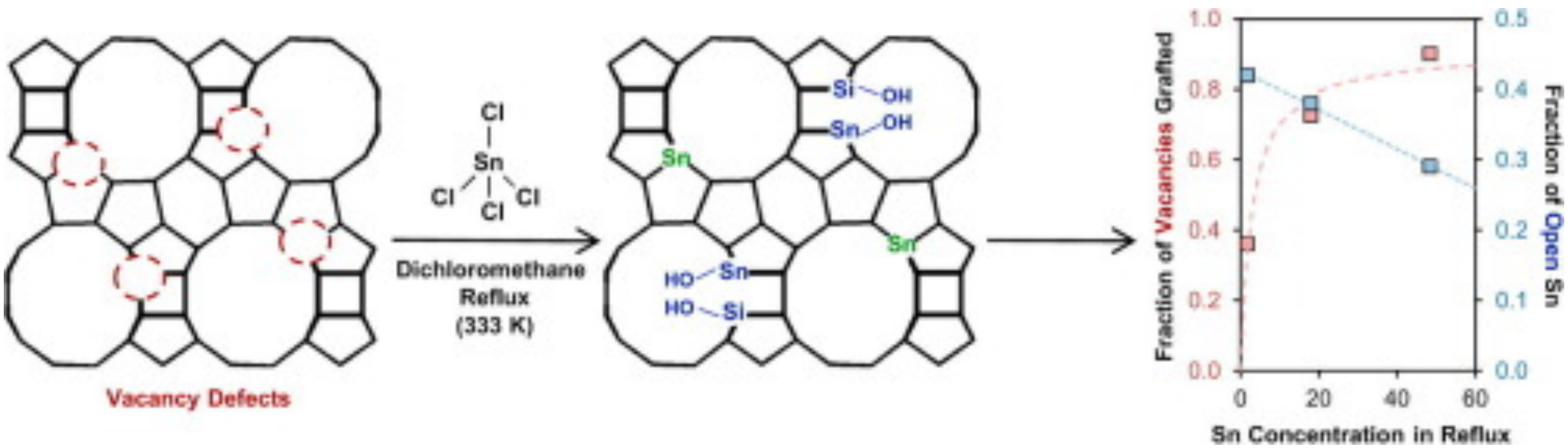
non-framework TiO_2 undesired



Unwanted H_2O_2 decomposition to O_2 occurs on non-framework TiO_2 sites, *potential overpressures / explosions*

Project: Development of Catalysts for Safer Oxidation Reactions

Technical Achievements (to date)



"Controlled Insertion of Tin Atoms into Zeolite Framework Vacancies and Consequences for Glucose Isomerization Catalysis"

J. C. Vega-Vila, J. W. Harris, R. Gounder

Journal of Catalysis, 344 (2016) 108-120

Circumvent HF-assisted synthesis of hydrophobic zeolites

"Methods to Synthesize Stannosilicate Materials with Controlled Tin Coordination"

R. Gounder, J. C. Vega-Vila, J. Harris

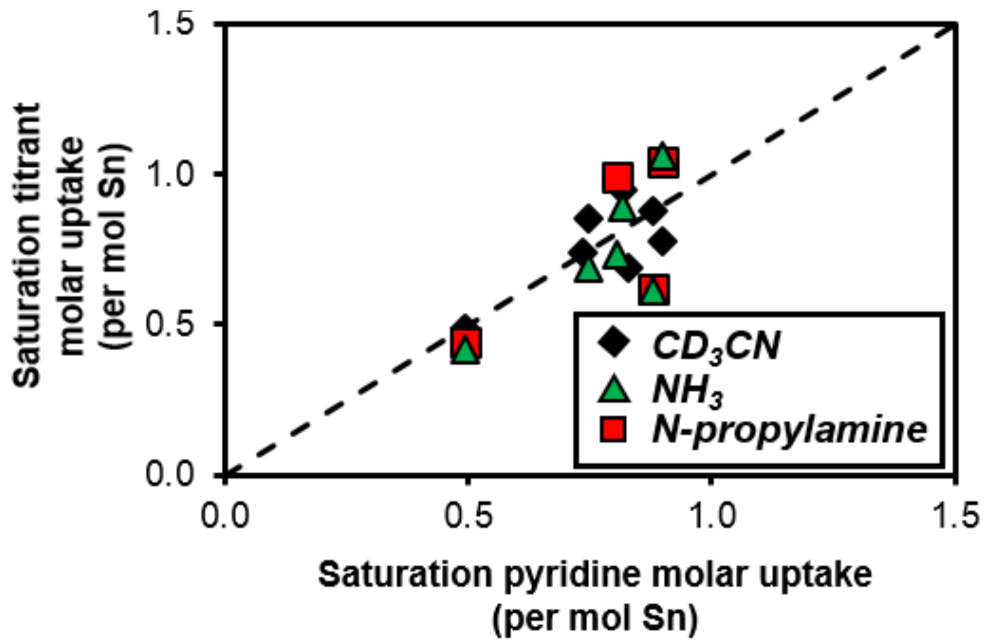
U. S. Patent Application No. 15/686,235

Filed Aug. 2017

Project: Development of Catalysts for Safer Oxidation Reactions

Technical Achievements (to date)

Counting Lewis acidic Sn sites in zeolites using four Lewis base titrants

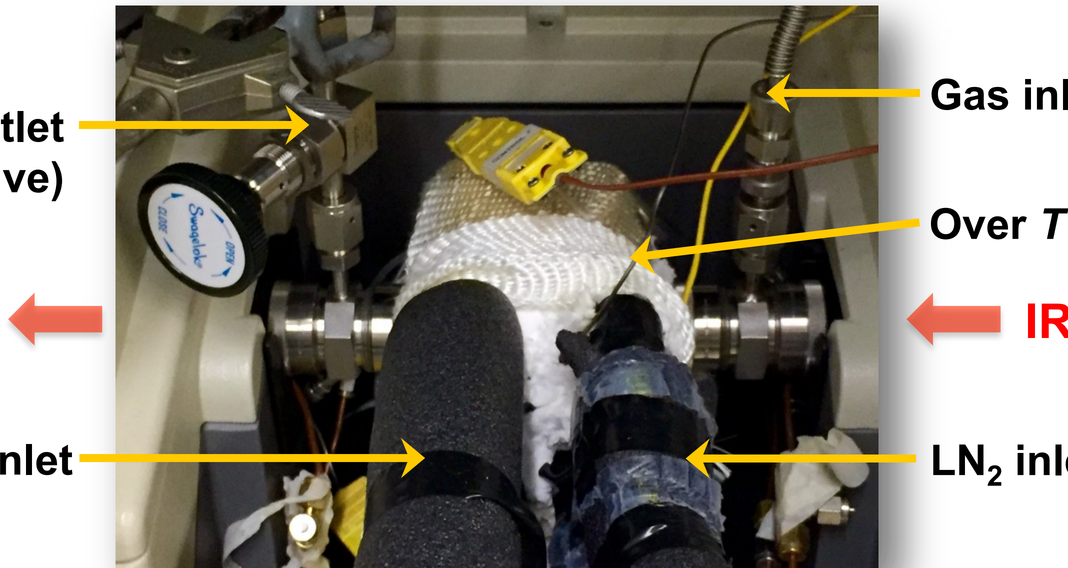


IR and TPD methods for quantifying Lewis acid active sites

"Titration and Quantification of Open and Closed Lewis Acid Sites in Sn-Beta Zeolites that Catalyze Glucose Isomerization"
J. W. Harris, M. J. Cordon, J. R. Di Iorio, J. C. Vega-Vila, F. H. Ribeiro, R. Gounder
Journal of Catalysis 335 (2016) 141-154

Project: Development of Catalysts for Safer Oxidation Reactions

Lab Safety Achievements (to date)



Safer handling of liquid cryogens in the laboratory

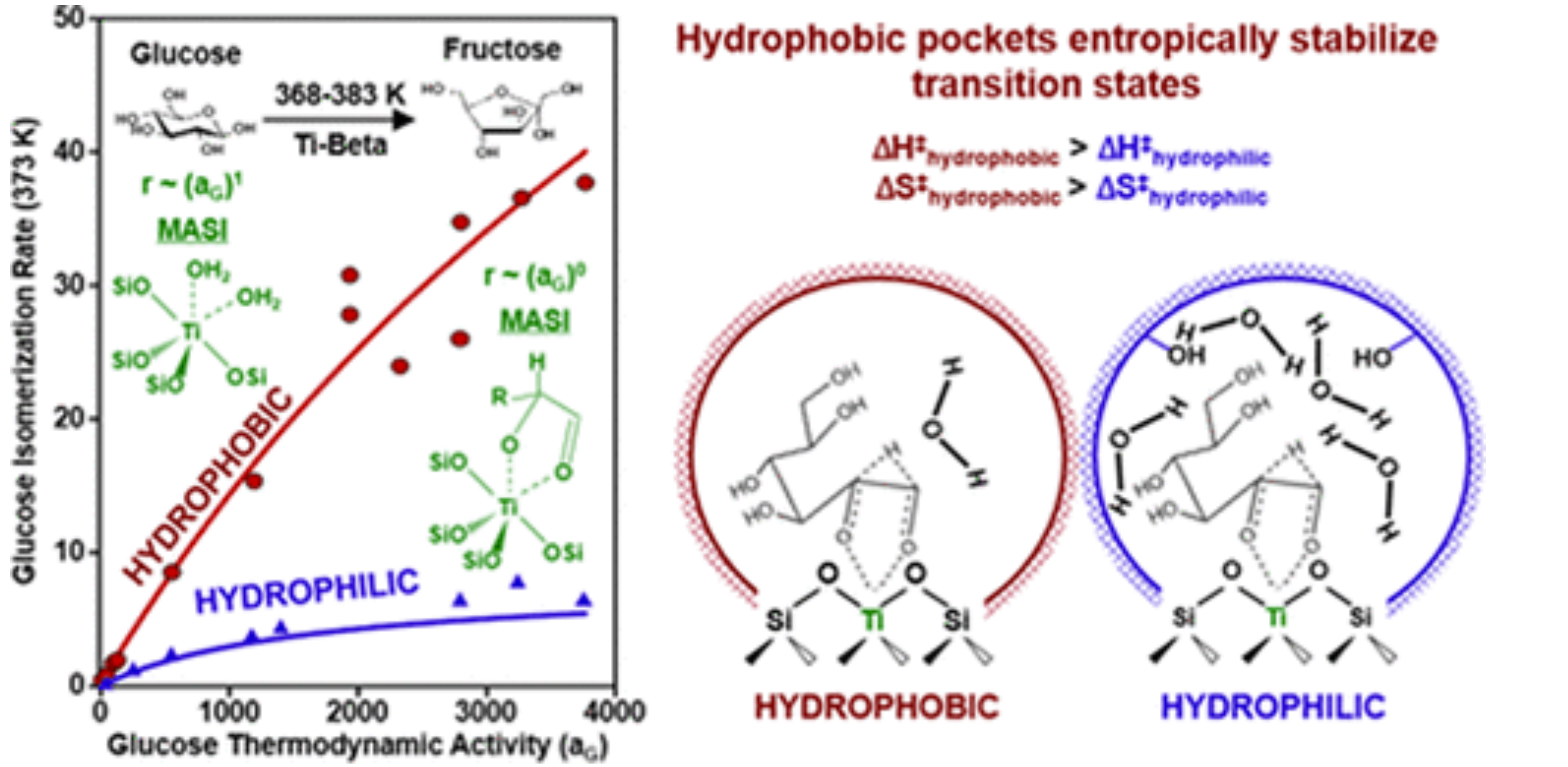
"A Transmission Infrared Cell Design for Temperature-Controlled Adsorption and Reactivity Studies on Heterogeneous Catalysts"

V. J. Cybulskis, J. W. Harris, Y. Zvinevich, F. H. Ribeiro, R. Gounder

Review of Scientific Instruments 87 (2016) 103101

Project: Development of Catalysts for Safer Oxidation Reactions

Technical Achievements (to date)



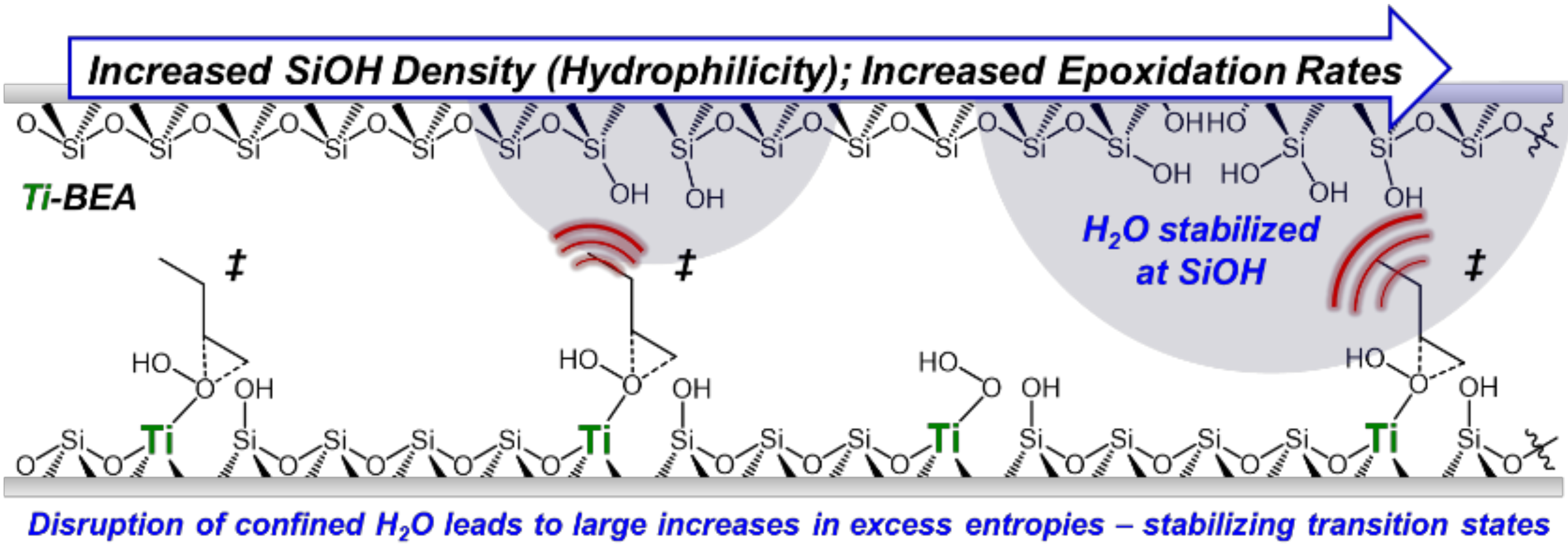
"Dominant Role of Entropy in Stabilizing Sugar Isomerization Transition States within Hydrophobic Zeolite Pores"

M. J. Cordon, J. W. Harris, J. C. Vega-Vila,
J. S. Bates, J. T. Miller, R. Gounder, et al.
JACS, 140 (2018) 14244-14266

Catalytic effects of hydrophilic pores on reaction rates in liquid solvents

Project: Development of Catalysts for Safer Oxidation Reactions

Technical Achievements (to date)



"Cooperative Effects Between Hydrophilic Pores and Solvents: Catalytic Consequences of Hydrogen-Bonding on Alkene Epoxidation in Zeolites"
D. T. Bregante, A. M. Johnson, A, Y. Patel, E. Z. Ayla, M. J. Cordon, B. C. Bukowski, J. Greeley, R. Gounder, D. W. Flaherty, *JACS,* (2018) under review

Catalytic effects of hydrophilic pores on reaction rates in liquid solvents

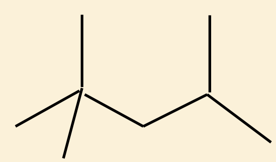
P2SAC Project: Prevention through catalyst design for applications in the petrochemical industry (*PI: Raj Gounder*)

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

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

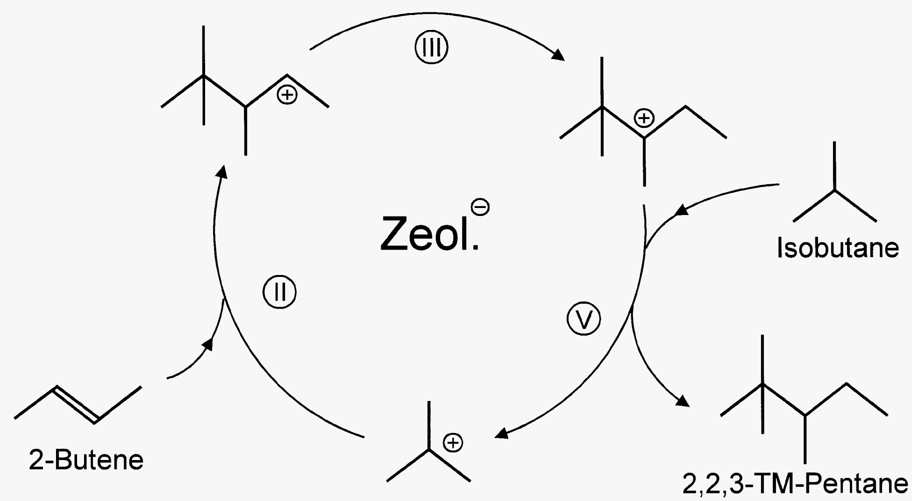


- **Technical challenges with solid catalysts:**
  - Catalyst lifetime (deactivation and fouling) and regeneration

- **Some potential alternatives are emerging:**
  - Solid Lewis-Brønsted superacids
  - AlkyClean® (Albermarle, CB&I, Neste Oil): 2700 barrels/day
  - ISOALKY (Chevron -> Honeywell UOP): ionic liquids

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)
- **Refinery Motivation:**
  - Worldwide capacity: 1.6 million BBL/day
  - Total gasoline demand shrinking, but high octane (and clean) demand increasing
  - Current alkylation units have reached capacity
  - Butanes and pentanes (lighter HCs) are being excluded from the gasoline pool due to Reid Vapor Pressure (RVP) limits
  - New opportunities from increasing supply of light hydrocarbons in shale oil, heavier hydrocarbons are attractive energy carriers
- **Mechanism (simplified):**



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

Intermolecular hydride transfer reactions are critical

Promoted by stronger acids and higher acid site densities

Alkylation catalysis: Background and Motivation

- **Liquid acid catalysts for alkylation:**
  - 1932: Vladimir Ipatieff (UOP): Aluminum Chloride ($AlCl_3$/HCl, BF_3/HF)
  - 1930s (late): Sulfuric acid (H_2SO_4)
  - 1942: Hydrofluoric acid (HF) plants built by Phillips
    - Demand for high-octane aviation gasoline for World War II (5M gallons/day)
  - 1952: Demand increased again during Korean War (14M gallons/day)
  - 1980s: Demand increase due to phase-out of leaded gasoline (50M gallons/day)

- **Several process safety and hazard issues with liquid acid catalysts:**
  - Catalyst consumption (H_2SO_4) is high
  - Catalyst aftertreatment: spent acid contains tarry hydrocarbons and water
  - Alkylate quality is lower from H_2SO_4 catalysts than HF
  - HF is toxic and corrosive, safety hazards with handling and operation
  - 1960s-1986: HF plants >> H_2SO_4 plants

Alkylation catalysis: Background and Motivation

Marathon Refinery, Texas City, TX
October 31, 1987

"On the fateful Friday, October 31, 1987, according to Marathon spokesman William Ryder, refinery workers were using a crane to lift a 40-ton heat exchanger convection section from a hydrofluoric acid heater. At about 5:20 PM, the crane failed and the piece fell. As it fell, and severed a 4″ loading line containing hot acid and a 2″ pressure relief line to an HF alkylation reactor settler drum. Hydrogen fluoride vapors were emitted under pressure for about two hours and the vessel was plugged and drained approximately 44 hours later.

An extensive analysis was conducted to determine the total inventory loss and to model the blowdown process and the concentrations of HF in the plume. **Since the discharge rate was decreasing with time, a peak concentration of HF in the emitted vapors occurred just before the water spray mitigation system became fully operative.** Consequently, the mitigation efforts were more effective late in the response when concentrations were already low."

3000 people evacuated from homes (52-block area)

1000 people treated

Alkylation catalysis: Background and Motivation

ExxonMobil Refinery, Torrance, CA
September 6, 2015 (HF near miss)

Alkylation catalysis: Background and Motivation

Husky Energy Refinery, Superior, WI
April 26, 2018 (HF near miss)

Alkylation catalysis: Background and Motivation

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  - HF is toxic and corrosive, safety hazards with handling and operation
  - 1960s-1986: HF plants >> H_2SO_4 plants
  - 1987: Marathon Texas City accidental HF release, (3000 evacuated, 1000 treated)
  - Extensive mitigation systems required for HF
  - New installations are not even commissioned for HF

- **Can solid acids be developed to avoid the use of liquid acids?**

... a brief history

Alkylation catalysis: Background and Motivation

- **Solid acid catalysts for alkylation:**
  - 1960s: Rare earth-exchanged FAU zeolites (Mobil, Sun Oil)
  - 1974: Pt incorporation into zeolites for regeneration (Union Carbide)
  - 1970s (late): Solid acids and zeolites (J. Weitkamp)
  - Supported liquid acids (triflic acid) on porous solids (Haldor-Topsoe)
  - Sulfated zirconia, heteropolyacids, organic resins
    - Some catalysts themselves also exhibit environmental and health hazards

Faujasite (FAU)

International Zeolite Association Database (iza-online.org)

Alkylation catalysis: Main Challenges with Solid Acid Alkylation

- **Technical challenges with solid catalysts:**
  - Catalyst lifetime (deactivation and fouling)
  - Catalyst regeneration
  - Loss in conversion + loss of selectivity to alkylate (and formation of oligomers)

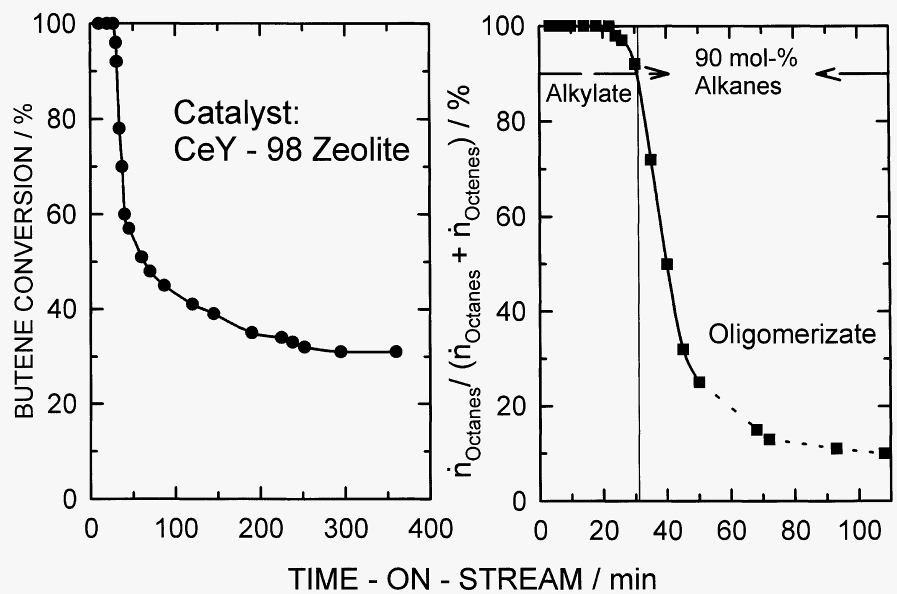


Fig. 2. Conversion of a liquid isobutane/1-butene mixture on a CeY-98 zeolite in a fixed-bed reactor (T=80°C, p=31 bar, liquid feed rate=7.5 cm^3/h, mass of catalyst=1.4 g, $\dot{n}_{isobutane}/\dot{n}_{1-butene}$ = 11 : 1), after [13–15].

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

Alkylation catalysis: Main Challenges with Solid Acid Alkylation

- **Requirements for any solid acid (zeolite) catalyst:**
    - At least as durable as liquid acids
    - Low sensitivity to feedstock composition, impurities
    - Higher quality (octane) alkylate than liquid acids (very evolved/optimized processes)
    - (Regulation / legislation) away from liquid acids
    - **One Breakthrough:** More than 1 paraffin activated per olefin (… or no olefins)

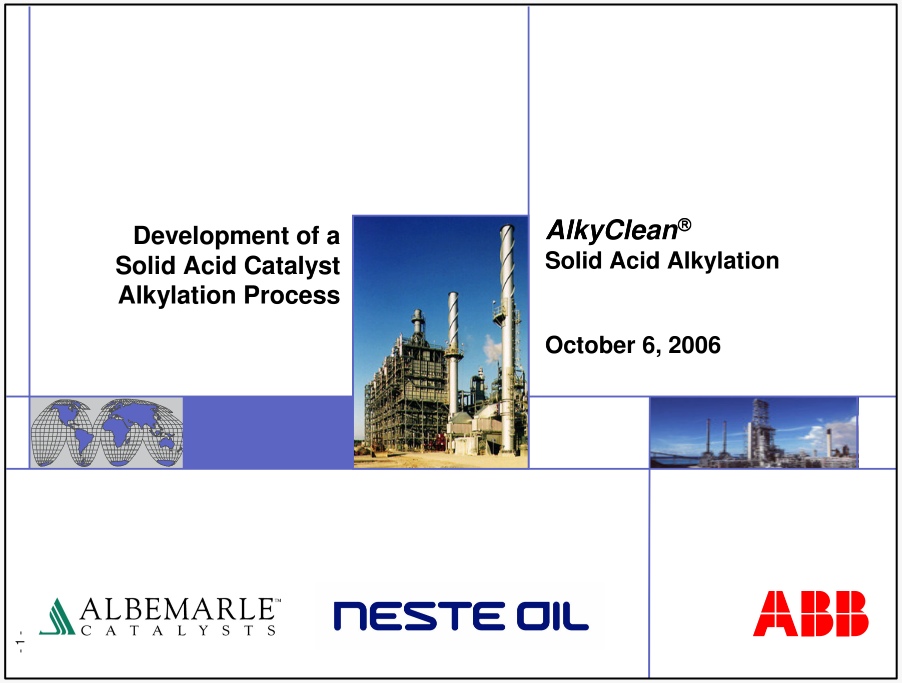
T. F. Degnan, Curr. Opin. In ChE 9 (2015) 75-82

- **Shell strategy (K. P. de Jong), 1990s:**
    - Beta zeolite shows optimal shape selectivity
    - Want lower Si/Al (higher concentrations of acid sites)
        - Gives higher alkylate quality, longer lifetime
        - **<u>Novel synthesis techniques needed</u>**
    - No halogens or other additives

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

- **Albermarle strategy (AlkyStar®), 1990s-present:**
    - Pt/USY

Alkylation catalysis: Main Challenges with Solid Acid Alkylation

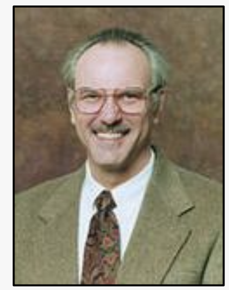


http://crelon-web.eec.wustl.edu/files/CRELMEETINGS/2006/AlkyClean.pdf

- **1994:** ABB Lummus (now CB&I) starts research effort to displace HF and H_2SO_4 using zeolite-catalyzed alkylation
- **1996:** Akzo Nobel (now Albemarle) joins effort to develop catalyst
- **2001:** Neste Oil joins venture to test this
- **2002:** 10 BBL/day demonstration in Neste's Porvoo refinery in Finland
- ……
- **2013:** Shandong Wonfull Petrochemical Group Ltd. (China) licenses this technology
- **2015:** Zibo Haiyi Fine Chemical Co. (a subsidiary of Wonfull) constructs a unit (2700 BBL/day) and starts up
  - RON: 96-98

T. F. Degnan, Focus on Catalysts, April 2016

Acknowledgements



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- John Di Iorio (former)
- Sopuru Ezenwa
- **Jamie Harris (former)**
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- Claire Nimlos

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- **Juan Carlos Vega-Vila (current)**
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- **YoonRae Cho (current UG)**

- Yury Zvinevich

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P2SAC

Purdue Process Safety & Assurance Center