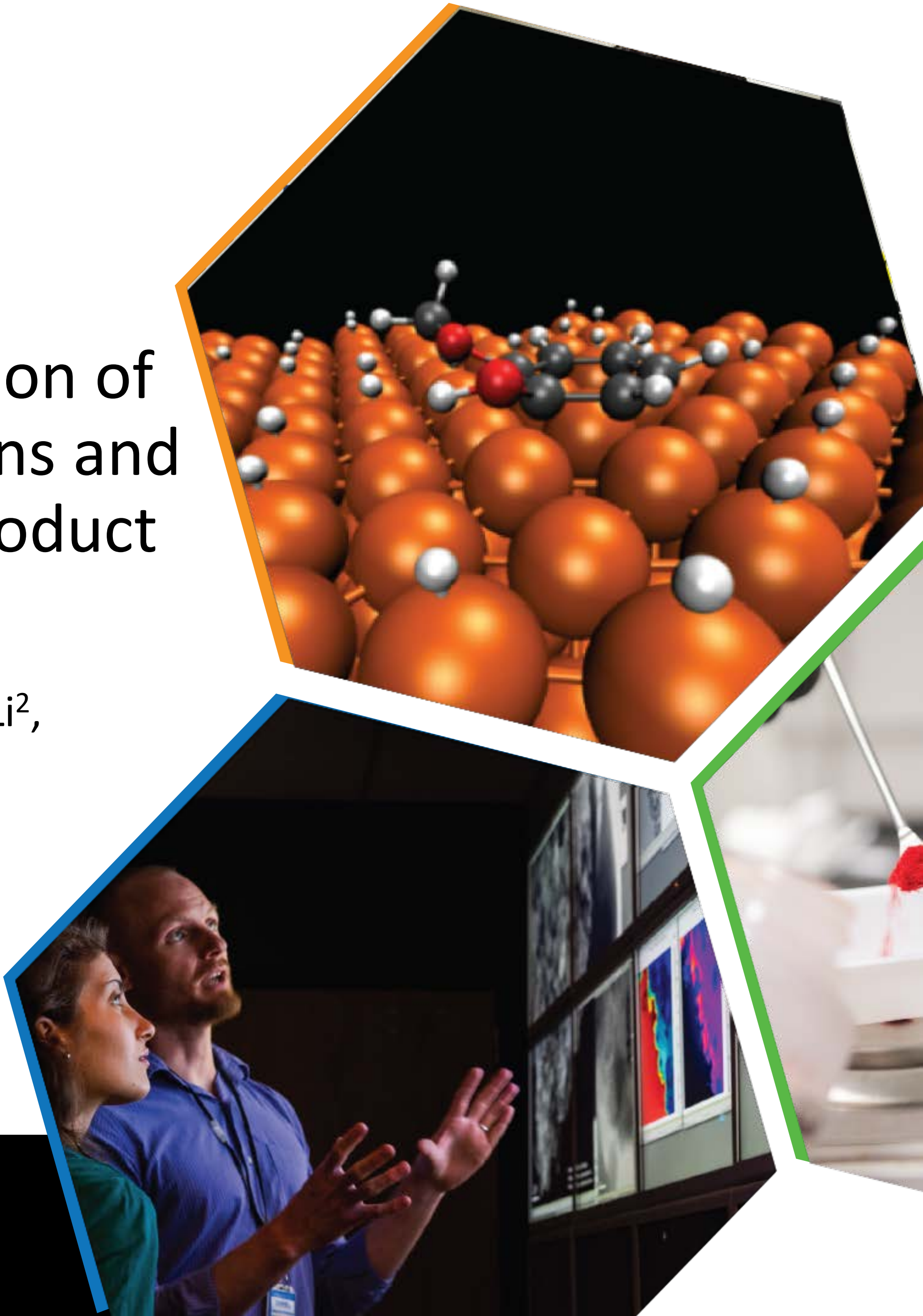
ChemCatBio
Chemical Catalysis for Bioenergy



Single-Step Catalytic Conversion of Ethanol to n-Butene-rich Olefins and 1,3-Butadiene Chemical Coproduct

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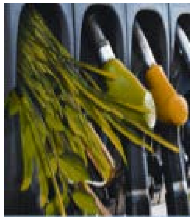
U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Three takeaways from this talk

- PNNL and ORNL have developed effective catalysts and processes for conversion of **ethanol** to **fuels** and **co-products.**
- We present a flexible catalytic process for the single-step conversion of ethanol to either **butadiene** or **n-butenes** using a mixed oxide catalyst (PNNL).
- We present the catalytic processing for producing either **C_{5+}/BTX hydrocarbons** or **C_{3+} olefins** using zeolite catalysts (ORNL).

Butadiene Uses

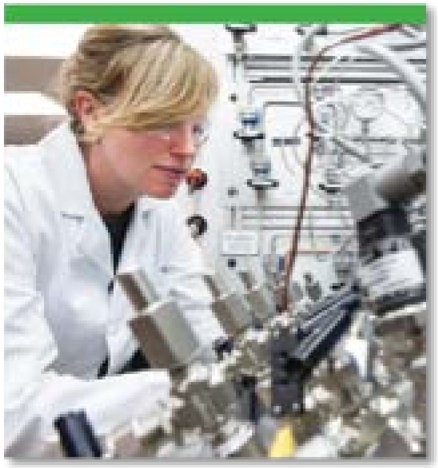
n-Butene Uses



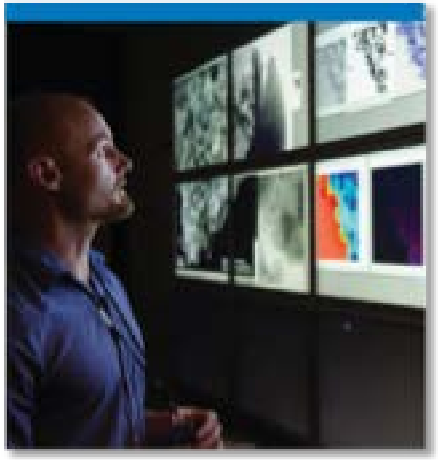
ChemCatBio (CCB) is a national-lab led R&D consortium dedicated to overcoming catalysis challenges for biomass conversion

- ChemCatBio is a node in DOE’s Energy Materials Network.
- It strives to accelerate the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals by leveraging unique capabilities of the US DOE national laboratories.
- The team comprises over 100 researchers from 8 national labs and has published more than 90 peer-reviewed manuscripts over its four years of operation.

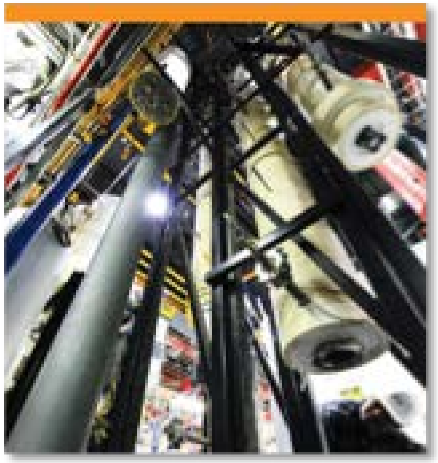
Advanced synthesis and Characterization



Analysis and Simulation



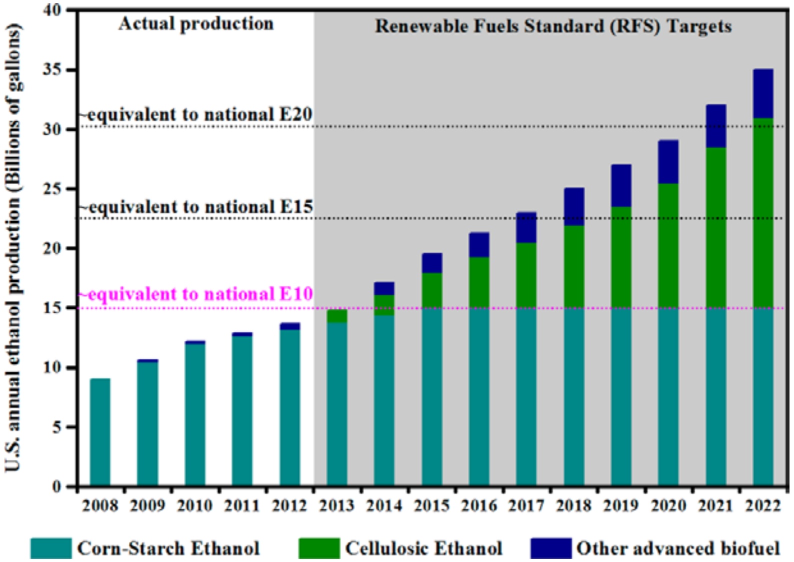
Evaluation across Scales



Ethanol - an attractive feedstock

- Ethanol is commercially produced from renewable biomass & waste sources.

- Current trend positive to future competitive ethanol production:
  - Ethanol "blendwall"
  - Advancement in production efficiency
  - Feedstock diversification

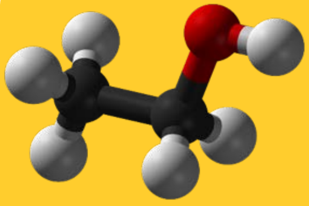


ACS Catal. 2014, 4, 1078-1090

PNNL & ORNL have found effective processes for converting ethanol to fuels and co-products

Biochemical or Thermochemical Conversion

PNNL



Ethanol

PNNL

ORNL

Being Commercialized

ethylene → butenes → Jet/Diesel Range Hydrocarbons

LanzaTech
capturing carbon. fueling growth.
&
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C5+ HCs → Gasoline/Jet BTX

Vertimass™
Transformative fungible biofuels.
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Prior Research (ChemCatBio)

ORNL → **C5+/BTX** — *Green Chemistry, 2017, 19, 4344*

C_{4+} Precursors

PNNL → **n-butanol + higher alcohols** — *Top Catal, 2016, 59, 46*
Catal Today, 2016, 269, 82

PNNL → **isobutene** — *Green Chemistry, 2016, 18, 1880*
Catal.Sci.Technol.2016, 6, 2325

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Current Research (ChemCatBio)

PNNL → **butadiene** — *Applied Catal B. 2018, 236, 1576*
Catalysis Today, 2019, DOI: 10.1016/j.cattod.2019.05.042

PNNL & ORNL → **n-butenes**

Oligomerization + Hydrogenation + Fractionation → Jet/Diesel Range Hydrocarbons

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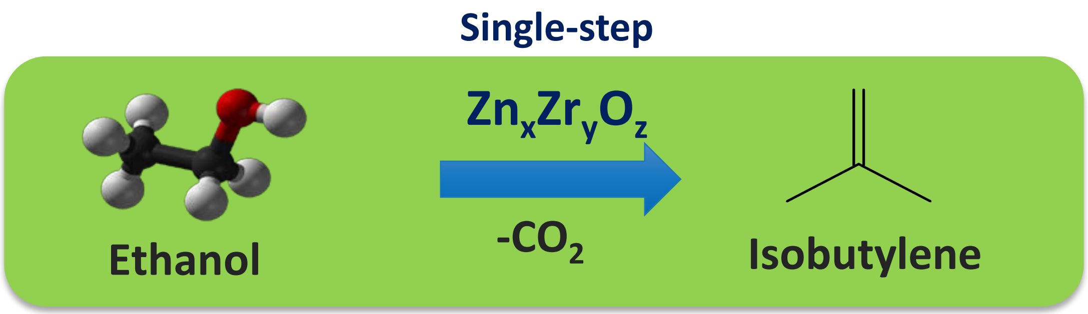
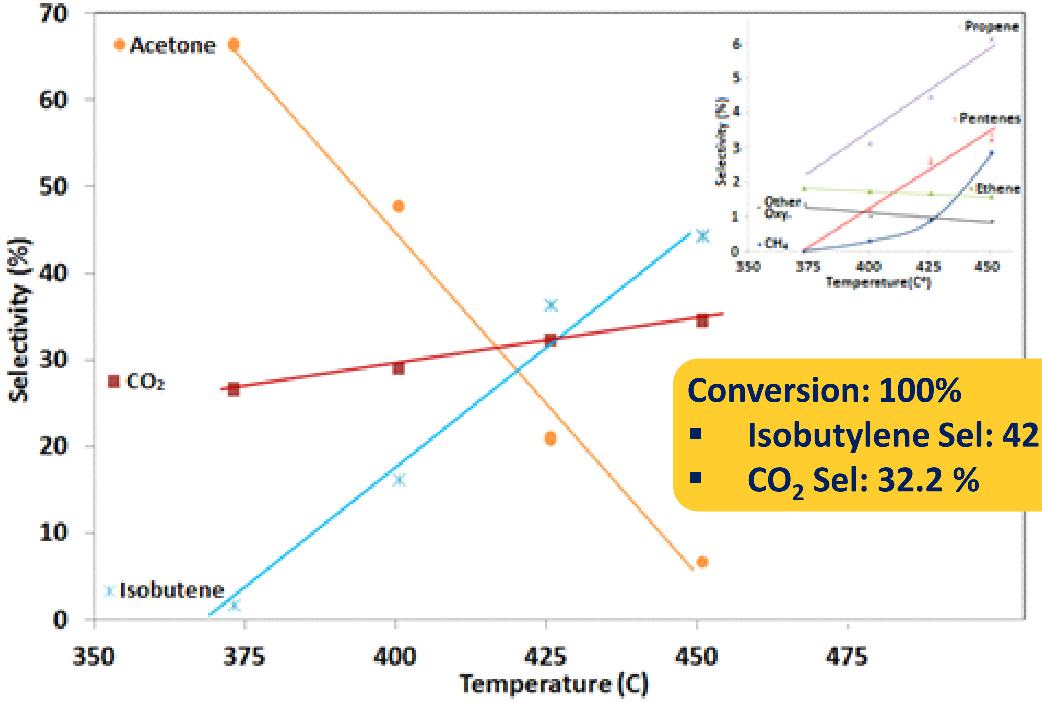
Single-step conversion of ethanol to isobutylene leads to the unavoidable formation of CO_2

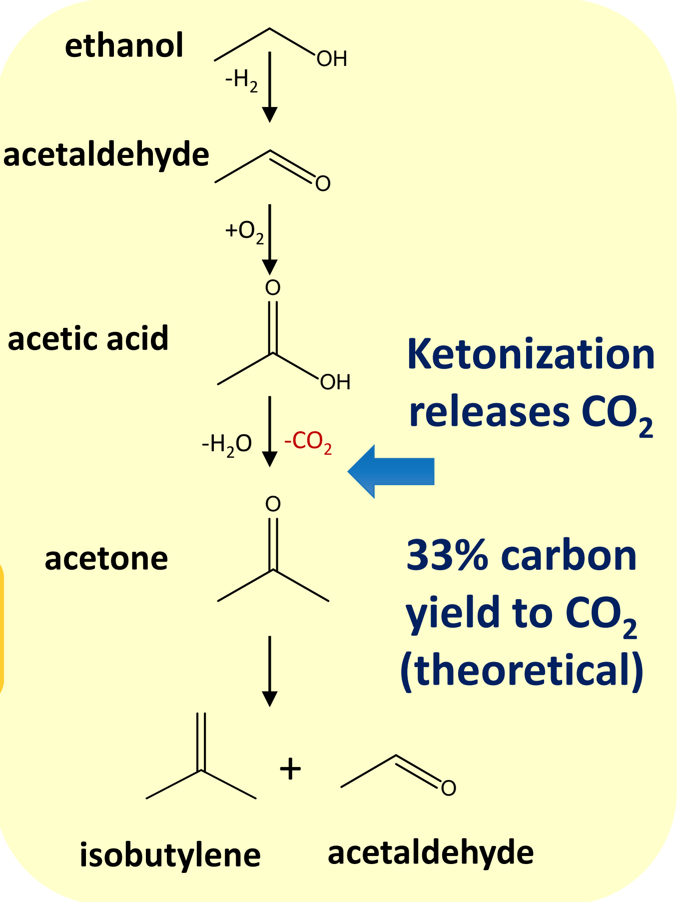
Catal.Sci.Technol.2016, 6, 2325
Green Chemistry, 2016, 18, 1880





Conversion: 100%
- **Isobutylene Sel: 42.4 %**
- **CO_2 Sel: 32.2 %**

Mechanism



Ketonization releases CO_2

33% carbon yield to CO_2 (theoretical)

Isobutylene production from ethanol is limited due to formation of CO_2

PNNL

Butadiene uses, production technologies, and market outlook

Butadiene Production: 11 MT/Year.

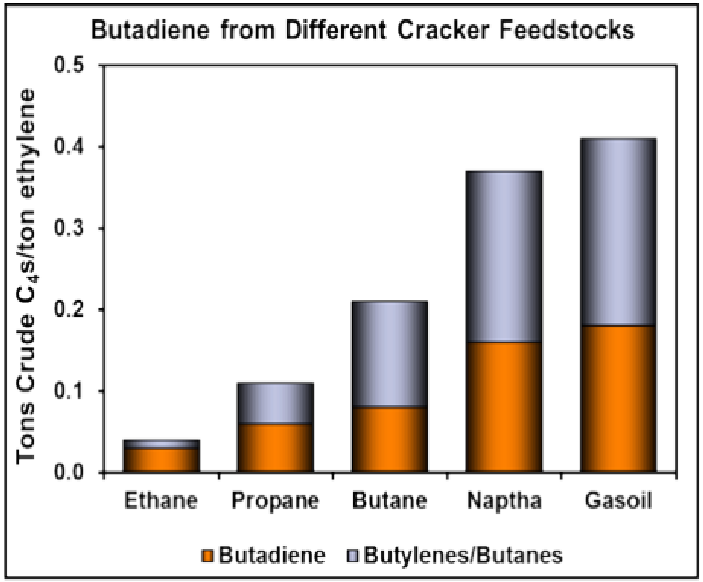
Butadiene Uses: synthetic rubbers, elastomers, polymer resins.

Production technologies

- Extraction from C4 hydrocarbons- ethylene steam cracker (SC)
  - BD is a by-product
  - 95% BD production
- Dehydrogenation of n-butane & n-butene
- Processing of renewable sources

Market outlook

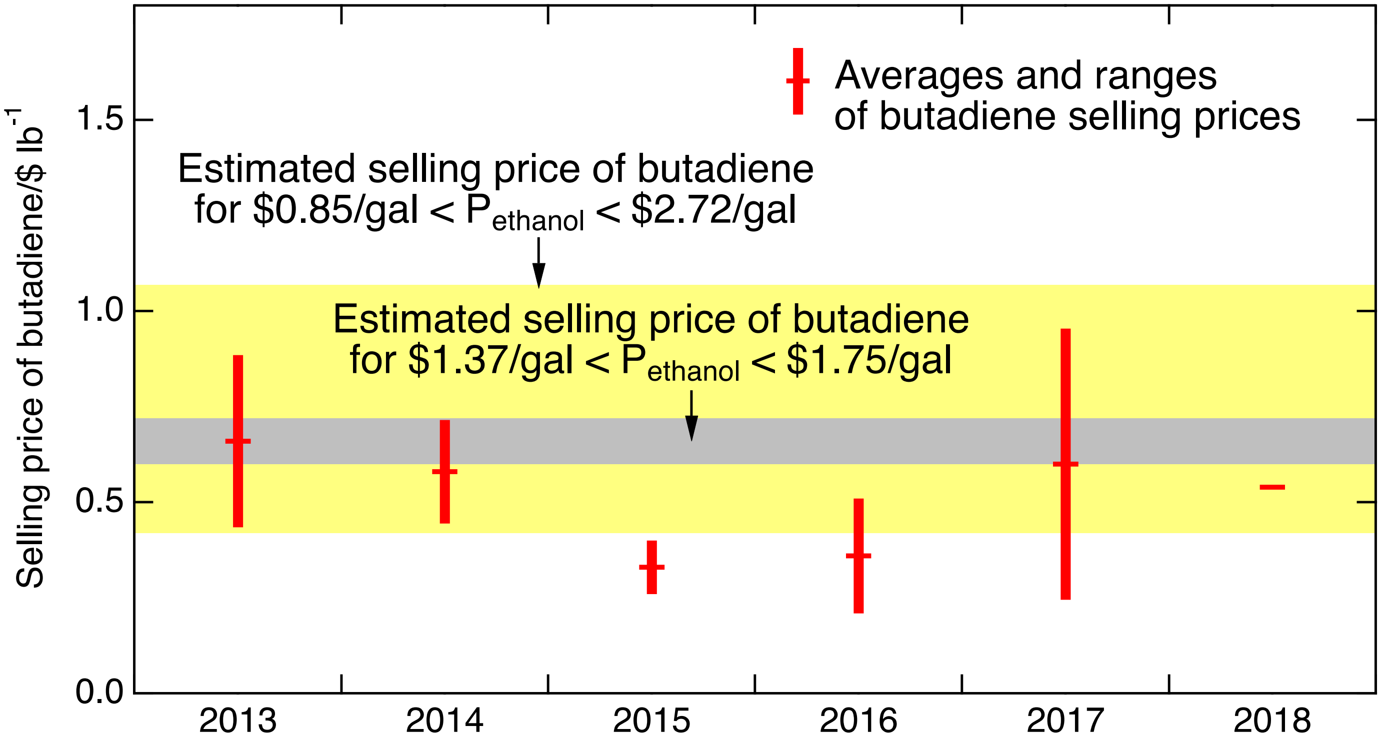
- The quantity of BD produced from SC depends of cracking feedstock.
- Low cost ethane obtained from shale gas is the preferred feedstock in USA .
  - Decline of BD co-production



Producing butadiene from ethanol can be cost competitive with current butadiene prices, with sufficiently low cost ethanol

US Delivered Prices for Butadiene

PPI adjusted to 2016



Ethanol Scale 50 M gal/year, 10% ROI

e.g. \$1.50/gal ethanol feedstock ➞ \$0.68/lb Butadiene selling price (~ current market price)

PNNL

PNNL Designed an Ethanol to Butadiene Catalyst with 1.5x Yield Over State of the Art on $Ag/ZrO_2/SiO_2$

- Historically, ethanol to butadiene catalyst yields low
- $Ag/ZrO_2/SiO_2$ multifunctional catalyst system developed that selectively enables **single-step** conversion of ethanol to butadiene
- Significantly more active than literature benchmark catalyst
- Produces butadiene with **89% ethanol conversion** and **74% selectivity**

Catalyst	Temperature ($^{\circ}C$)	WHSV (hr^{-1})	Conversion (%)	Butadiene selectivity (%)	Butadiene yield (%)
PNNL formulation[1]	325	0.47	89.2	73.6	61.5
Literature benchmark[2]	320	0.3	55.2	71.3	39.4

Feed: pure ethanol, 320-325°C, P = 1 atmosphere, 50% ethanol/N_2, WHSV = 0.3-0.5 hr^{-1}

[1] Dagle, V. L. et. al. *Applied Catalysis B* 2018, *236*, 576–587.
[2] Ivanova et. al., E. *J. Catal.* 2014, *316*, 121–129.

PNNL

We found SBA-16 to be the Best SiO_2 Support for Ethanol to Butadiene over $Ag/ZrO_2/SiO_2$

SiO_2 support	Conversion (%)	Butadiene selectivity (%)	Lewis acid sites (µmoles/g)
SG Davisil 636	82.7	65.2	32.2
SG Alfa Aesar	48.7	29.3	35.0
SG Davisil 646	76.1	75.3	22.8
SG Davisil 645 After ion-exchange	29.5 79.6	41.6 73.4	21.6 27.8
SG Davisil 923	84.8	56.8	31.0
SG KSKG-GOST-3956-76	84.7	78.3	26.1
SG KSMG-GOST-3956-76	100.0	0.0	NA
Fumed silica Cabosil EL90	37.1	39.2	NA
Fumed silica Aerosil 380	39.2	29.6	5.0
SBA-15	97.8	46.6	NA
SBA-16	**99.0**	**70.5**	**26.4**

$1Ag/4ZrO_2/SiO_2$ activity. WHSV: 0.23hr^{-1}, P_{EtOH}: 24.3% in N_2, P: 1 atm, T: 325°C.

- Screened catalysts using SiO_2 with different properties (e.g. surface area, porosity)
- Greatly influenced activity and selectivity to butadiene

The choice of SiO_2 support is key in effective catalyst design for butadiene production

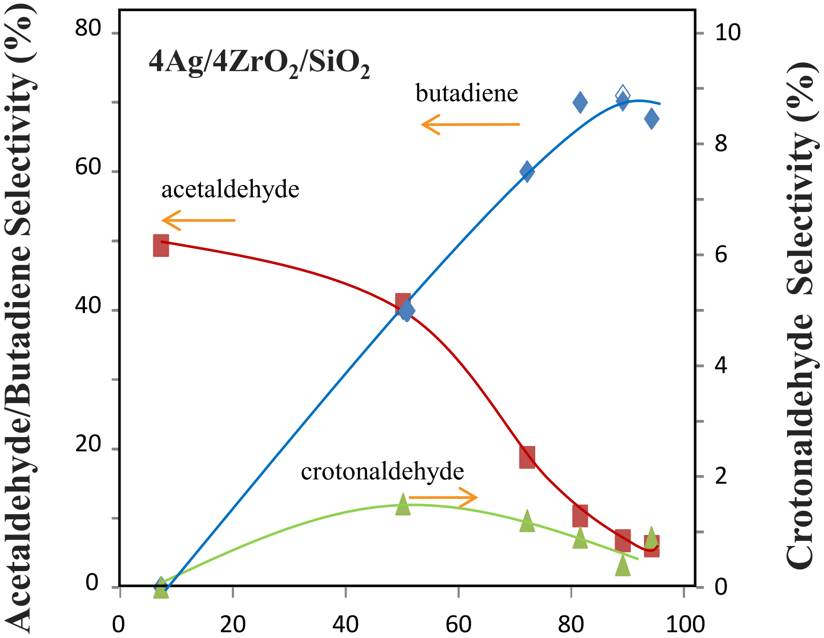
Dagle, V. L. et. Al. Applied Catalysis B 2018, *236*, 576–587

PNNL

Mechanism & Role of Catalyst Components were Confirmed over this Catalytic System

Intermediate Species

- Both acetaldehyde and crotonaldehyde are intermediates involved in BD formation
- Conversion and selectivity profiles supports the aldol condensation mechanism followed by MPV reaction.



T=325°C, P= 1 atmosphere, WHSV = 0.37-38.0 hr^{-1}, 50% Ethanol/N_2

Role of Ag, ZrO_2, and SiO_2

- ZrO_2 acid sites are responsible for undesired ethanol dehydration to ethylene and DEE
- Ag responsible for the dehydrogenation of ethanol to acetaldehyde
- Addition of ZrO_2 to Ag/SiO_2 does not have a significant impact on the conversion

Catalyst	EtOH Conv. (%)	Selectivities (%)			
		$C_2^=$	DEE	BD	AcH
SiO_2	7.2	26.4	2.2	0	69.6
$4ZrO_2/SiO_2$	14.8	47.9	46.9	0	2.6
$4Ag/SiO_2$	88.3	1.5	0.1	0.9	61.4
$4Ag/4ZrO_2/SiO_2$	89.2	5.5	3.0	73.6	6.7

T = 325°C, P = 1 atmosphere, WHSV = 0.47 hr^{-1}, 50% EtOH/N_2, SiO2: Davisil 646

Dagle, V. L. et. Al. Applied Catalysis B 2018, *236*, 576–587.

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SiO_2 Support Affects Surface Area, Ag Dispersion, and Subsequent Ethanol Conversion

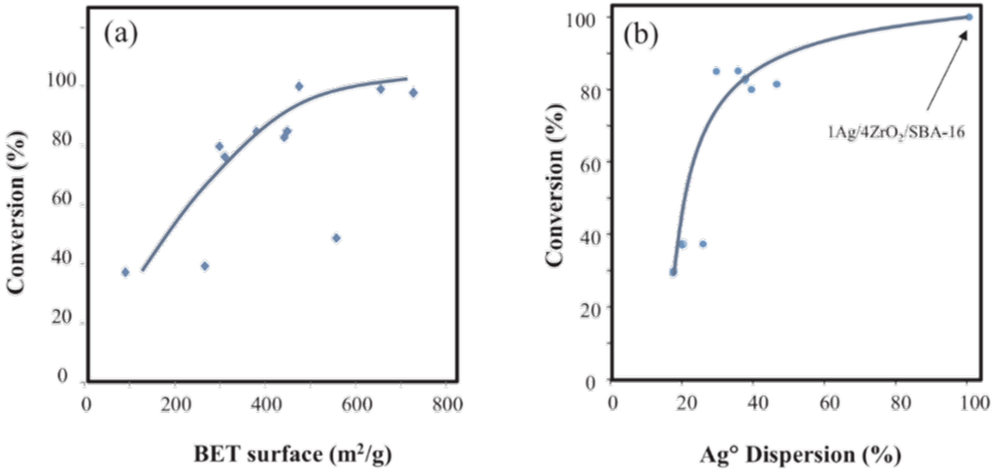
- Addition of ZrO_2 to Ag/SiO_2 does not have a significant impact on the conversion
- Conversion increases with catalyst surface area
  - Same Ag loading of 1% for all catalysts

Increase in conversion is due to increased Ag dispersion

Catalyst	Conversion (%)
SiO_2	7.0
$4ZrO_2/SiO_2$	14.8
$4Ag/SiO_2$	88.3
$4Ag/4ZrO_2/SiO_2$	89.2

T = 325°C, P = 1 atmosphere, WHSV = 0.47 hr^{-1}, 50% $EtOH/N_2$, SiO2: Davisil 646

$1\%Ag/4\%ZrO_2$ – varied SiO_2 supports



Dagle, V. L. et. Al. Applied Catalysis B 2018, *236*, 576–587

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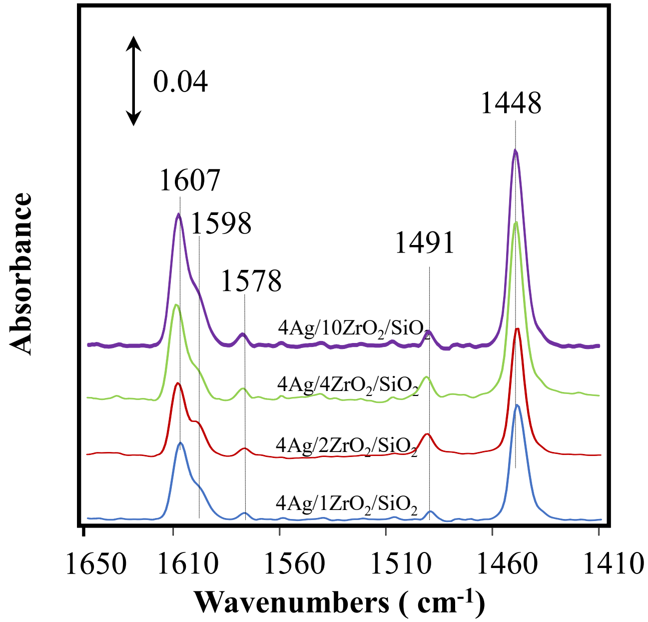
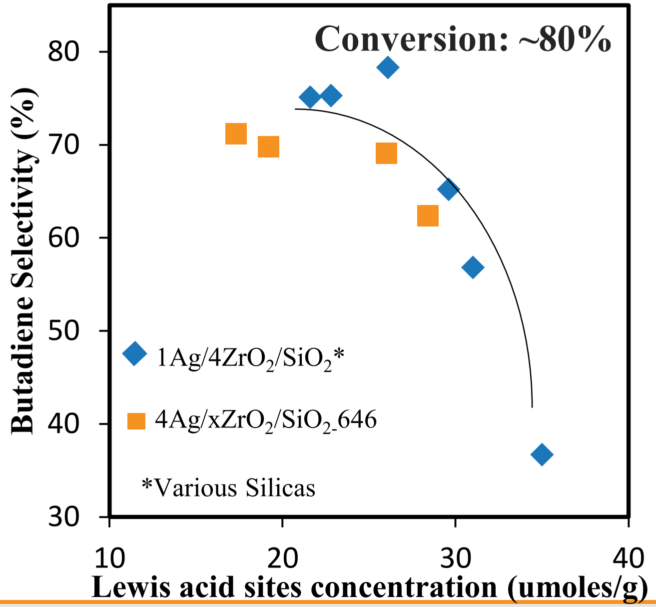
SiO_2 Support Interaction with ZrO_2 Affects Catalyst Acidity and Subsequent Butadiene Selectivity

- Presence of Lewis acid sites
- Butadiene selectivity decreases as Lewis acid site concentration increases
- Evidence of a relationship between butadiene selectivity and acid sites concentration.

The interaction between ZrO_2 and SiO_2 varies greatly depending on the SiO_2 support which affects the quantity of the acid sites and the butadiene selectivity





Dagle, V. L. et. Al. Applied Catalysis B 2018, *236*, 576–587

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Ag Particle Size Affects Selectivity in Ethanol to Butadiene Reaction

Two DFT models considered:

- Dispersed Ag representative of small Ag particles
- Ag nanoparticle (NP) surface representative of larger Ag particles

DFT calculations suggested:

- **Larger Ag particles** ➔favor **ethylene** formation through ethanol dehydration
- **Smaller Ag particles** ➔favor formation of acetaldehyde for **butadiene**

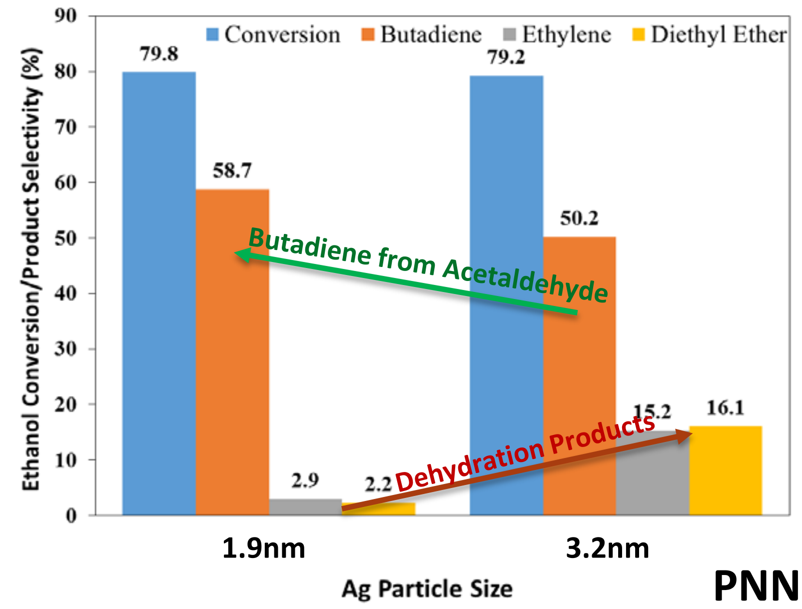
- **Experimental Results Validate Calculated DFT Trends**

Greater Ag dispersion inhibits the formation of dehydration side products

DFT Calculation Results

Catalyst	ΔG ethylene	ΔG acetaldehyde
Dispersed $Ag/ZrO_2/SiO_2$	1.93	-2.69
NP $Ag/ZrO_2/SiO_2$	-0.74	-0.63
ZrO_2/SiO_2	-1.36	-

Experimental Results



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CCPC: Consortium for Computational Physics and Chemistry

Single step formation of butenes from ethanol over $Ag/ZrO_2/SiO_2$ is observed under reducing conditions

A Flexible Process for Production of Butadiene or Olefins fuels Precursors

Feed	Conv (%)	Selectivity (C mol %)							
		$C_2^=$	$C_3^=$	$C_4^=$	Butadiene	DEE	C_2-C_5 alkanes	Oxy	Total Olefins + DEE
EtOH in inert	99.0	5.8	2.8	11.2	70.5	2.6	3.4	3.7	92.9
EtOH in reducing environment	93.9	25.7	2.0	57.7	0.0	6.0	6.1	2.5	91.4

- Butadiene formed in inert environment
- Butene-rich olefins formed in reducing environment
- Olefin double bonds remain even under reducing environment, provided suitable catalyst and processing conditions.

Impact: Producing butene-rich olefins directly from ethanol reduces a unit operation thereby representing a major improvement to the state of the art.

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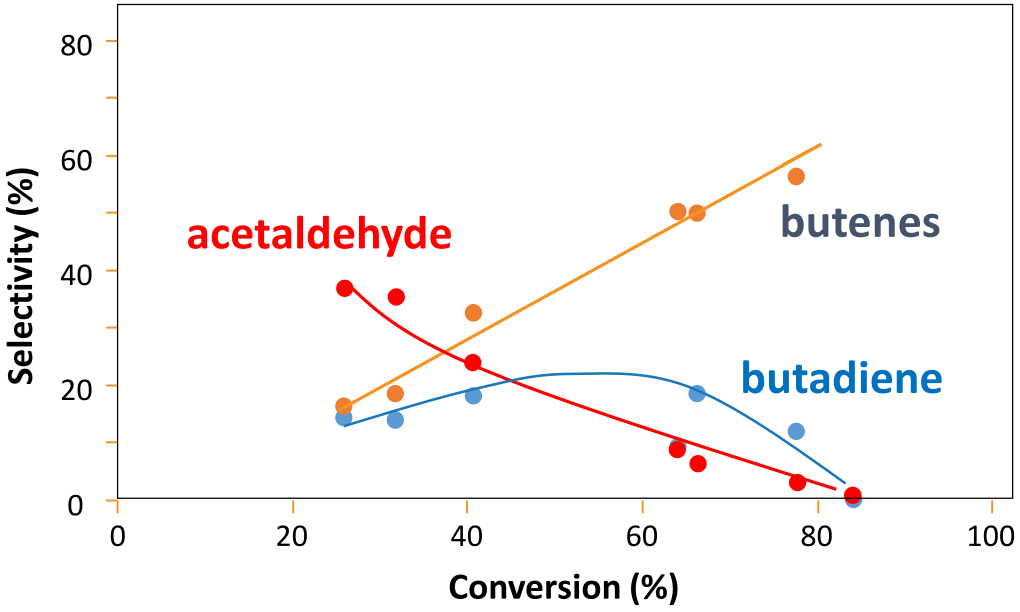
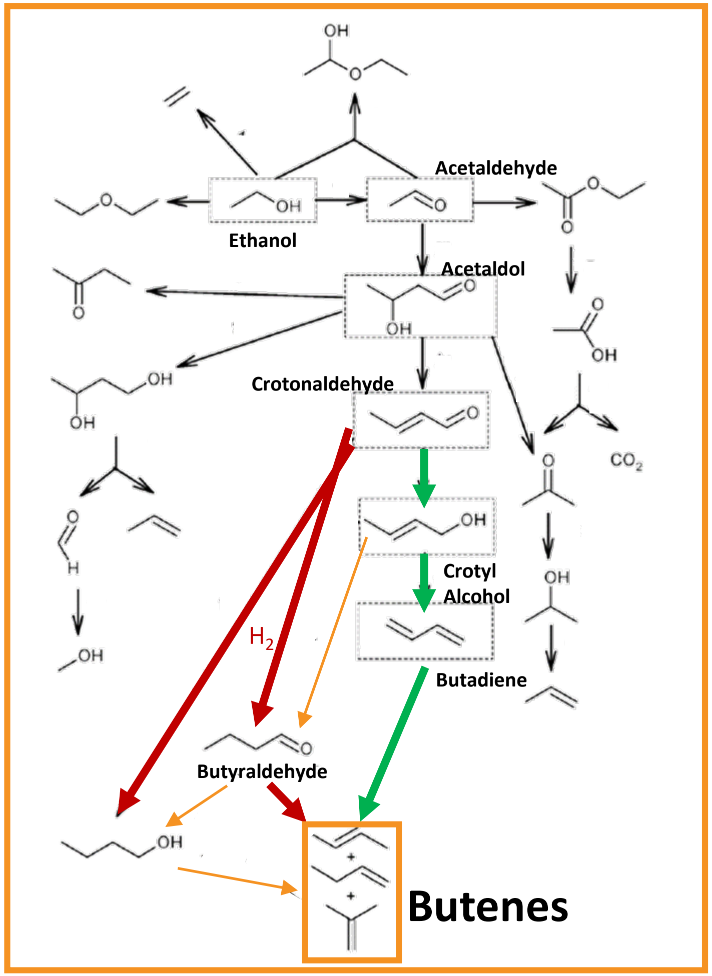
Butenes mostly produced from butadiene intermediate

Space Velocity Profile



Possible Pathways



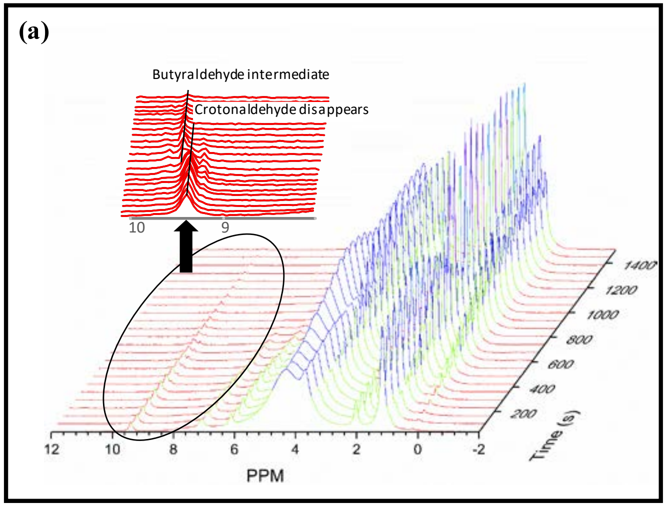
Makshina, E. V. et Al. *Chem. Soc. Rev.* 2014, *43* (22), 7917–7953.

Preliminary operando NMR & catalytic performance:

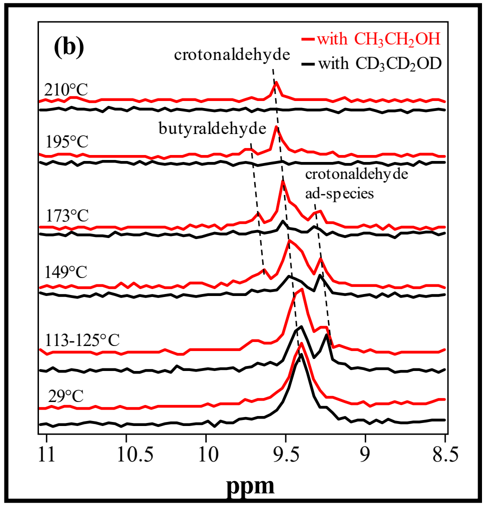
- n-Butenes are formed through butadiene intermediate at high conversion
- Also through butyraldehyde at low conversion

Operando NMR confirmed n-butenes also produced from butyraldehyde

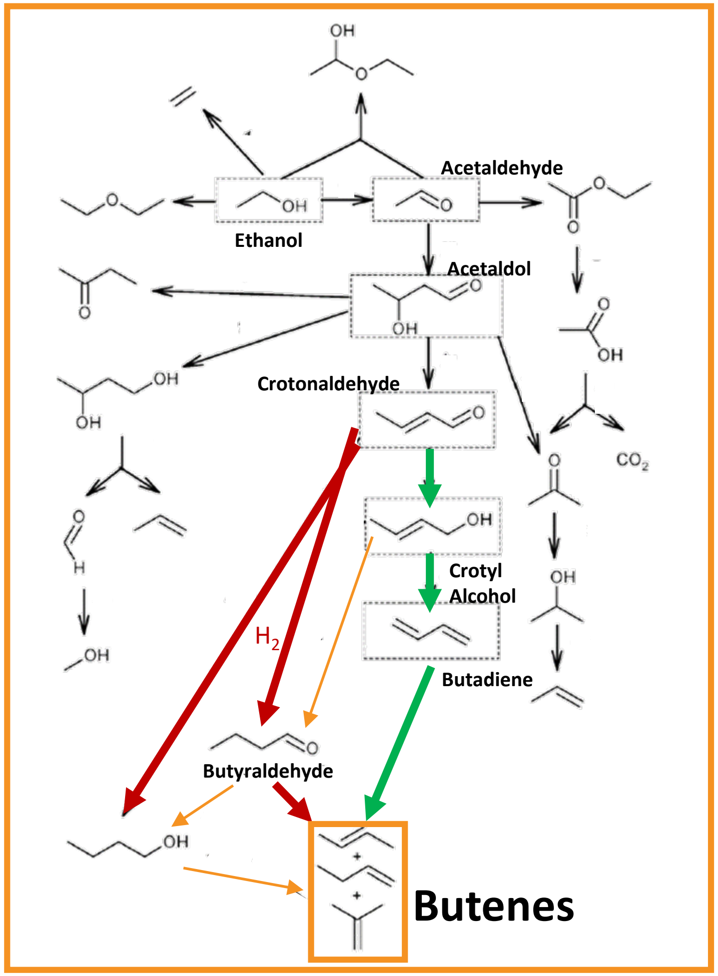
NMR operando



NMR operando



Possible Pathways



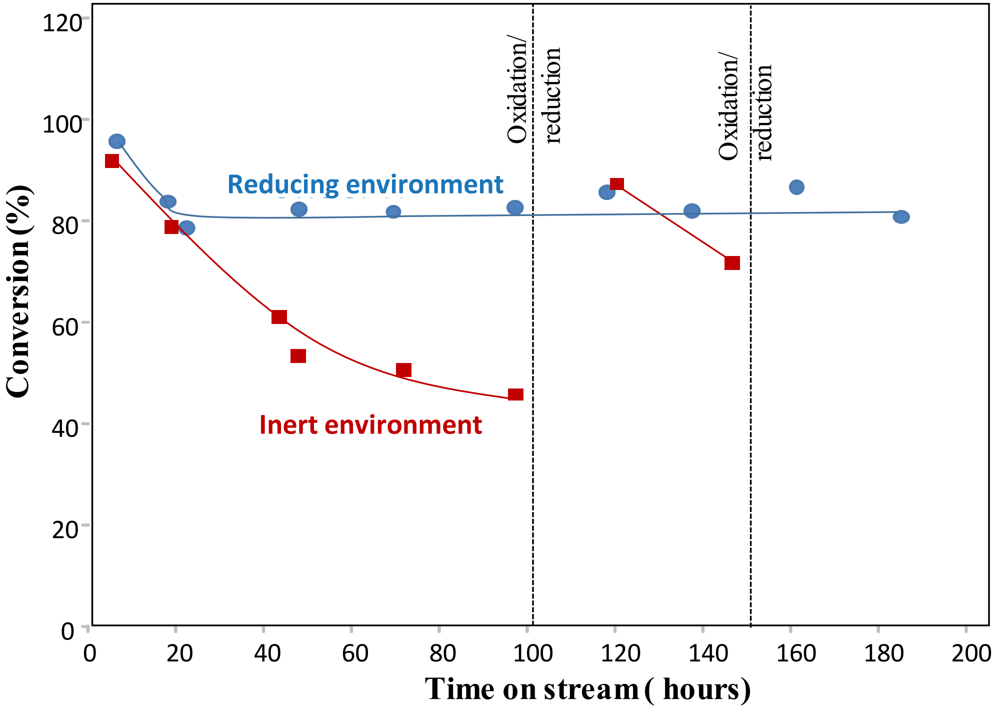
Makshina, E. V. et Al. *Chem. Soc. Rev.* 2014, *43* (22), 7917–7953.

- **Butyraldehyde identified as an intermediate**
  - Product evolution confirms butyraldehyde pathway
- Peaks characteristic of butadiene seen in **high conversion** experiments

PNNL

Lifetime study shows $Ag/ZrO_2/SiO_2$ exhibits higher degree of stability under reducing environment

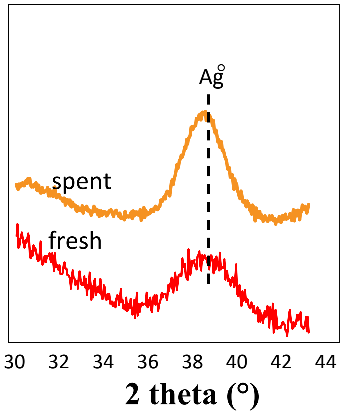
Lifetime study: inert vs. reducing



Catalyst treatment	Total carbon weight (%)	Ag° particle size (nm)
Reduced	0.02	2.9
Spent-reducing atmosphere	2.38	3.9
Spent – inert atmosphere	5.47	4.3

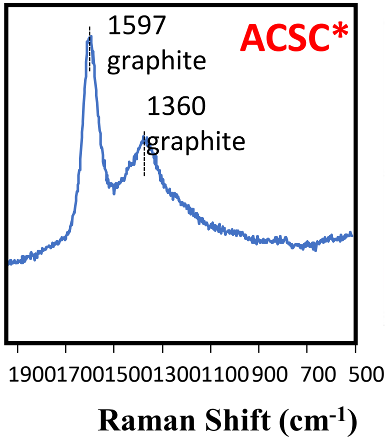
Total carbon weight and Ag° particle size after lifetime studies vs. reduced catalyst. Particle size derived from TEM images and XRD.

XRD



XRD patterns before (reduced) and after reaction.

Raman



- Coking problematic under inert environment (butadiene) but catalyst regenerable
- Conversion stable for up to 180 hours under reducing environment (butenes)

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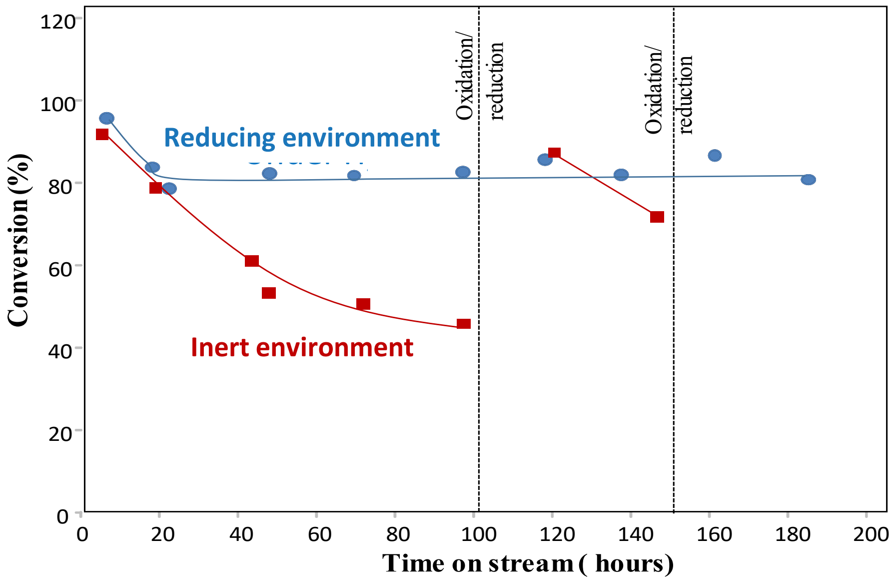
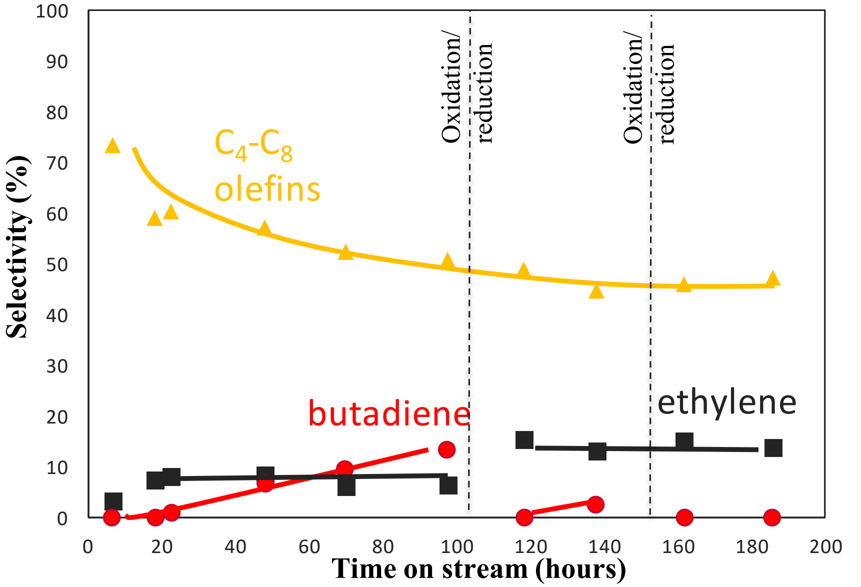
*ACSC: Advanced Catalyst Synthesis and Characterization

Product selectivity under reducing environment during lifetime study

Lifetime study: inert vs. reducing



Products Selectivity: reducing environment



- Under reducing environment butadiene product selectivity gradually increases with time
- Regeneration mitigates butadiene yield in product slate

PNNL

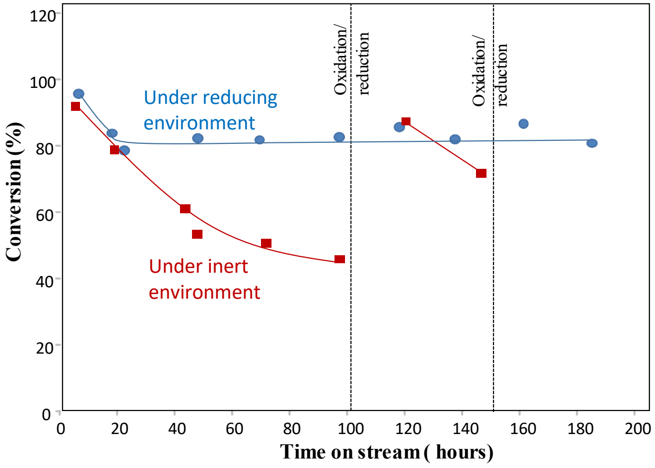
A Flexible process for single step conversion of ethanol to butadiene and olefins fuels precursors

Key points:

- **A flexible process for production of butadiene or butene-rich olefins from Ethanol**
  - Single step process
  - Under inert: butadiene product
  - Under reducing environment: butene-rich olefins product
- **Best catalyst:**
  - 70% selectivity to butadiene at 99% conversion
  - 85% selectivity to olefins at 94% conversion
- **Catalyst lifetime study shows reversible deactivation**

Feed	**Conv (%)**	**Selectivity (C mol %)**		
		$C_2^=$	**$C_4^=$**	**Butadiene**
EtOH in inert	99.0	5.8	11.2	**70.5**
EtOH in reducing environment	93.9	25.7	**57.7**	0.0

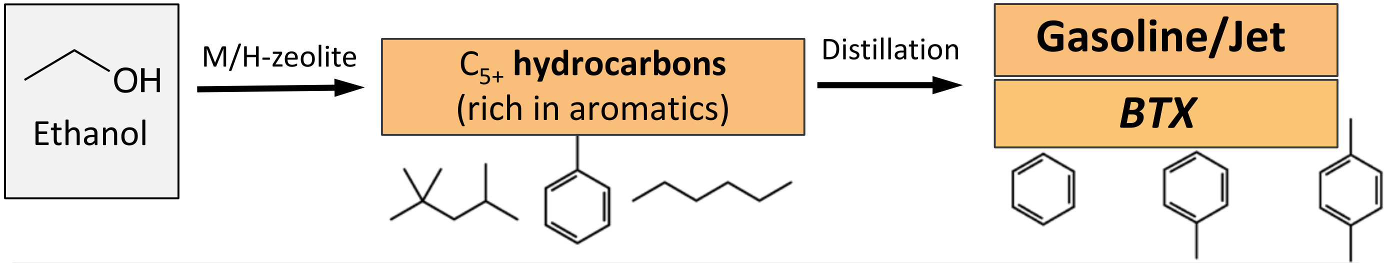
Lifetime study



contact: robert.dagle@pnnl.gov vanessa.dagle@pnnl.gov

Zeolite catalysis for selective ethanol conversion to C_{5+} HC_s and C_{3+} olefins

Ethanol to hydrocarbons (C5+, BTX) over M/H-zeolite



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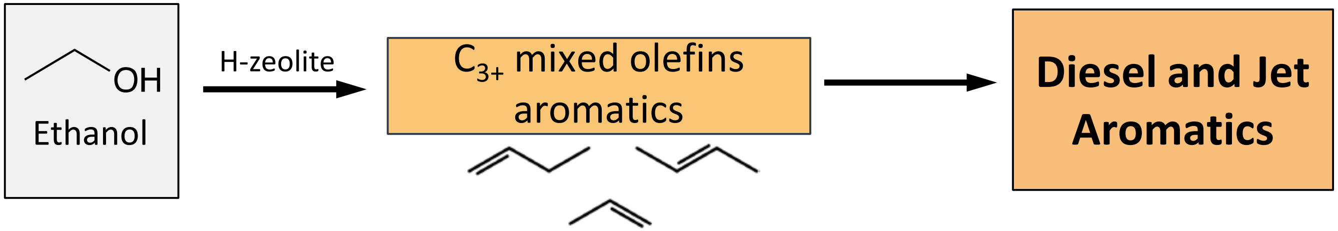
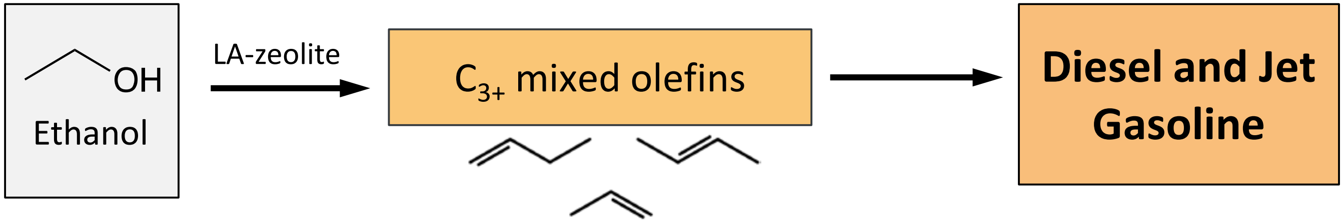
US 9278892 B2

- Vertimass is commercializing this technology with DOE-BETO support
- ChemCatBio offers advanced characterizations to accelerate commercial catalyst development (through Directed Funding Assistance)

Ethanol to C_{3+} olefins over 2D pillared H-zeolite



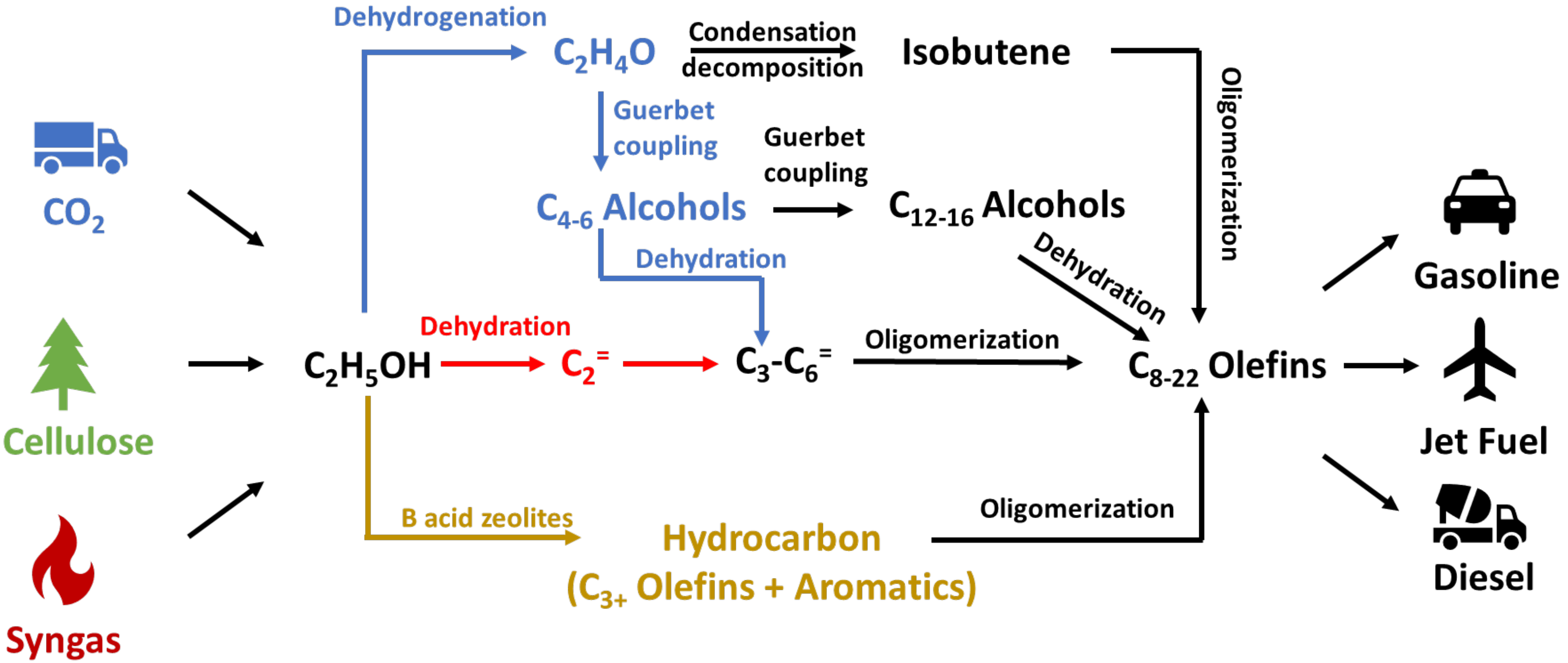
Ethanol to C_{3+} olefins over Lewis acid zeolite



ORNL

contact: liz3@ornl.gov Zhenglong Li

Ethanol to jet: C_{3+} olefins are important intermediates



CO_2

Cellulose

Syngas

Dehydrogenation

C_2H_4O

Condensation decomposition

Isobutene

Guerbet coupling

C_{4-6} Alcohols

Guerbet coupling

C_{12-16} Alcohols

Dehydration

Dehydration

Oligomerization

C_2H_5OH

Dehydration

$C_2^=$

C_3-$C_6^=$

Oligomerization

C_{8-22} Olefins

B acid zeolites

Hydrocarbon (C_{3+} Olefins + Aromatics)

Oligomerization

Gasoline

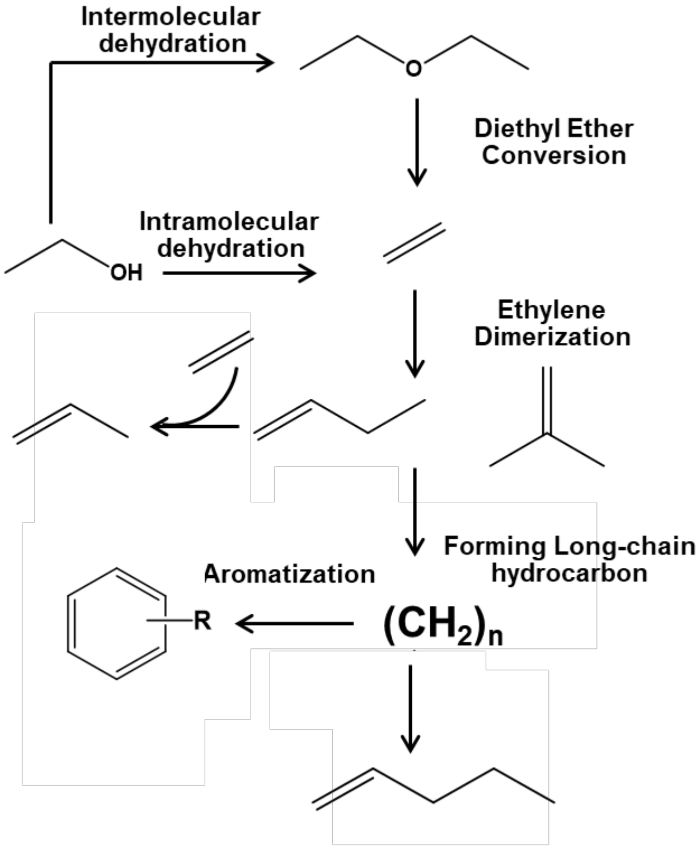
Jet Fuel

Diesel

- Develop new catalyst and pathway for **one-step** ethanol to C_3-C_6 olefins production
  - **Bypass ethylene step** (endothermic), reduce one unit operation
  - **Reduce** ethylene and **CO_2** formation, increase carbon efficiency

ORNL

Ethanol one-step to C_{3+} olefins via ethylene over H-Zeolite



Intermolecular dehydration

Diethyl Ether Conversion

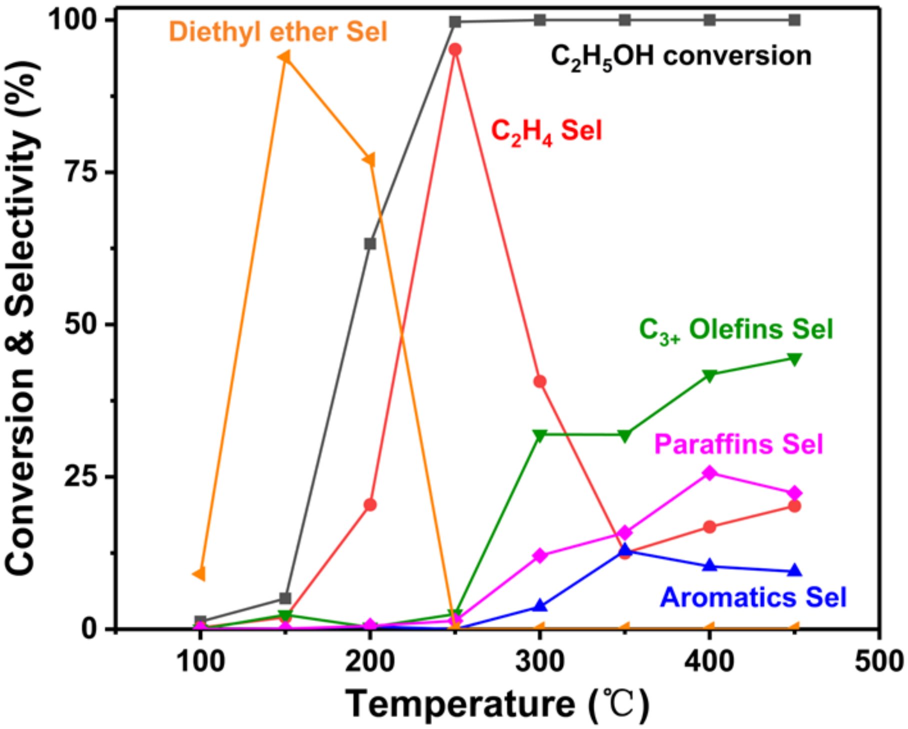
Intramolecular dehydration

Ethylene Dimerization

Forming Long-chain hydrocarbon

Aromatization

$(CH_2)_n$



- Over H-zeolite, ethylene is an important intermediate
- Paraffins and aromatics are major co-products

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Ethanol one-step to C_{3+} olefins: MFI is a good candidate

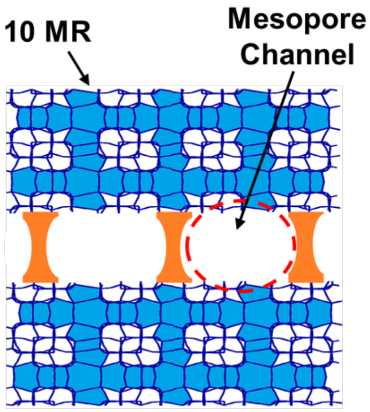
MFI for ethanol to C3+ olefins

- Both H-ZSM-5 and H-SSZ-13 favor C_{3+} olefins formation
- Pore confinement effect
- Coke formation is a major challenge, especially for small-pore SSZ-13

Catalyst	Pore ring	SAR	Ethylene Con (%)	Propene Sel (%)	Butenes Sel (%)	C_1-C_3 Alkanes Sel (%)
H-MOR	12	11.2	2.4	38.5	21.2	25.8
H-BEA		11.4	9.1	43.4	20.8	25.7
H-EU-1	10	10.3	30.3	32.3	22.3	26.3
H-ZSM-5		11.2	57.2	40.1	21.5	18.3
H-SSZ-13	8	8.4	82.9	59.5	9.8	27.9

Dai, Weili et. al Journal of catalysis. 314 (2014): 10-20.

2D Pillared-MFI: address coke formation and improve C3+ olefins selectivity



Hierarchical structure and reduced diffusion length to reduce coke formation

	External Surface Acid Site	Pore Mouth Acid Site	Internal Micropore Acid Site
Conventional MFI	3.2 %	N/A	96.8 %
Pillared MFI	32 %	5 %	63 %

Microporous and Mesoporous Materials, 2017, 241, 43-51.

Acid site distribution impact on product distributions?

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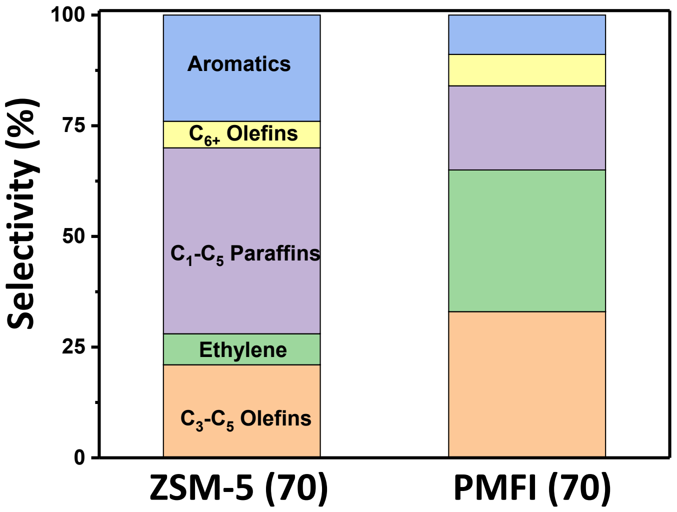
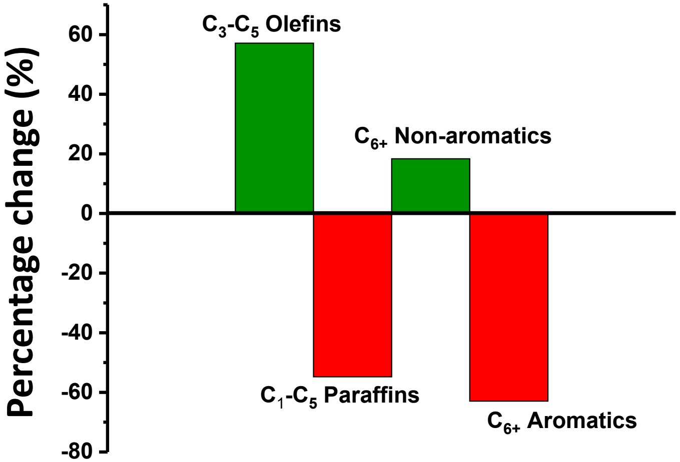
Pillared MFI to improve C_{3+} olefin selectivity

- **Product distributions (100% ethanol conv)**
  - 400 °C, WHSV = 1.6 h^{-1}, ambient pressure





- **Product distributions (60-62% ethylene conv)**

Catalyst	ZSM-5 (70) %	PMFI (70) %
Ethylene	60	62
C_3-C_4 olefins	**15**	**32.7**
Aromatics	3.7	4.8
Ethane	0.5	0.4
Propane	1.9	2.0
Butane	9.6	5.7

- Conventional ZSM-5 produces 30% more coke than PMFI
- Pillared MFI is an interesting catalyst for ethanol to C3+ olefins
- Mechanism to be studied more, especially the role of water
- Reduce ethylene and paraffins

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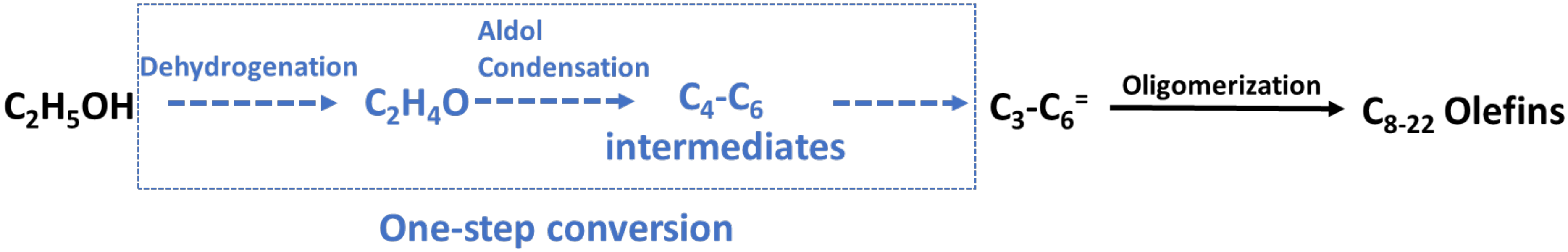
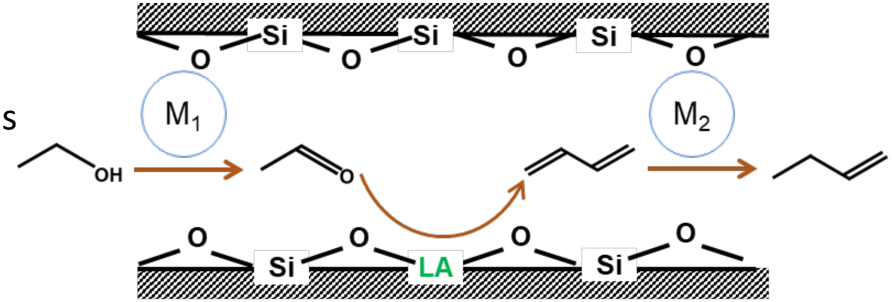
Multifunctional Lewis acid zeolite for ethanol to C_{3+} olefins



C_2H_5OH --Dehydrogenation--> C_2H_4O --Aldol Condensation--> C_4-C_6 intermediates --> C_3-$C_6^=$ --Oligomerization--> C_{8-22} Olefins

One-step conversion

- ***Develop multifunctional zeolite catalysts for cascade ethanol conversion to olefins***
    1. Dehydrogenation: Cu, Zn, Ag
    2. Aldol condensation: Lewis acid sites or basic sites
    3. Dehydration: Brønsted acid or Lewis acid sites
    4. Transfer hydrogenation: Lewis acid sites



- ***Choice & balance of the sites are critical***

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EtOH – direct C_{3+} olefins over Cu-Zn/Hf-BEA (one example)

Focus: maximize C_{3+} olefins yield from ethanol

- Critical for distillate yield and minimum fuel selling price (MFSP)
- Different Lewis acid zeolites: metal centers, zeolite topology
- Different metal combinations

Cu-Zn/Hf-BEA to achieve high C_{3+} olefins

WHSV (h^{-1})	Ethanol vapor pressure (kPa)	Conversion (%)	Ethylene	Butenes	C5+ Olefins	C3+ Olefins (%)	Total Olefins (%)	BD
0.32	1.6	100	34	55	3	65	99	0
0.32	8	100	30	49	8	65	95	1.0
0.32	16	100	28	45	11	67	95	2.0

400 °C, 1 atm, under H_2, numbers shown for all the products are selectivity

- Complete ethanol conversion, max C_{3+} olefins of 67%, 99% total olefins
- Ethanol vapor pressure affects olefin distribution
- On Cu-Zn/Hf-BEA, need to study approach to minimize ethylene formation

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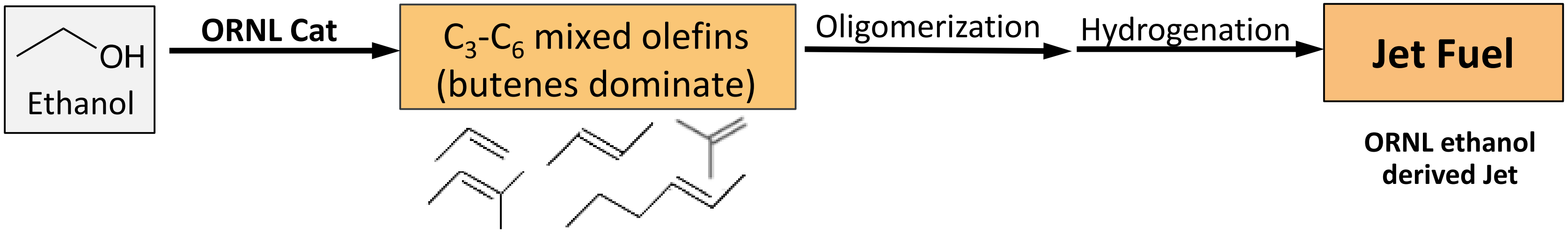
Ethanol to jet fuel and co-product via C_{3+} olefins



ORNL ethanol derived Jet

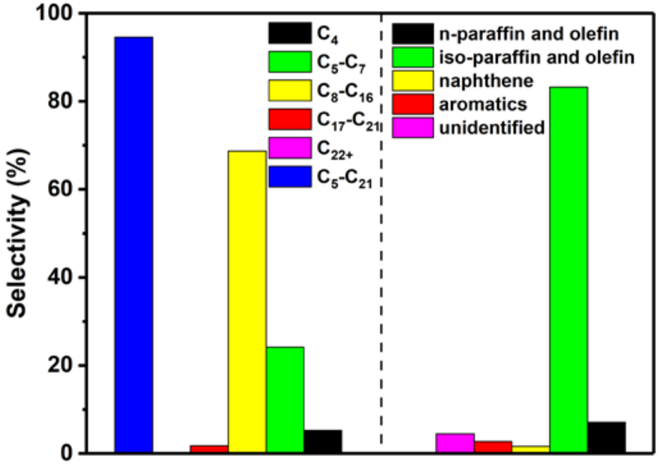
Compared with ethanol to jet via two-step ethanol-ethylene-C_{3+} olefins:

- Significantly increase C_{3+} olefins in one step (one pass)
- Bypass the ethylene production step: first step is slightly exothermic (-0.14 MJ/Kg)
- Avoid ethylene separation step
- Opportunity to reduce Capex and Opex

Mixed C_3-C_6 olefins oligomerization

- 68% Jet, 24% gasoline
- 95% liquid HCs
- Isoparaffinic

ORNL ethanol derived Jet-range HCs



High overall carbon efficiency: **~84% of theoretical yield** in final fuels

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Summary

- PNNL and ORNL have developed catalysts and processes for conversion of ethanol to fuels and co-products.
- A flexible catalytic process has been demonstrated for the single-step conversion of ethanol to either butadiene or n-butenes, in a cascading sequence of catalytic reactions.
- High activity and **butadiene** selectivity under **inert** atmosphere
- High activity and **butene** selectivity when under **reducing** atmosphere
- Bifunctional metal-assisted, Lewis acid-catalyzed systems present all the required active sites necessary.
  - Ag-ZrO_2/SiO_2 (PNNL)
  - Cu-Zn/Hf-BEA (ORNL)

What's next?:

- Improve C_{3+} olefin selectivity
- Enhance stability
- Evaluate with real fermentation broth
- Demonstrate conversion to distillate-range

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