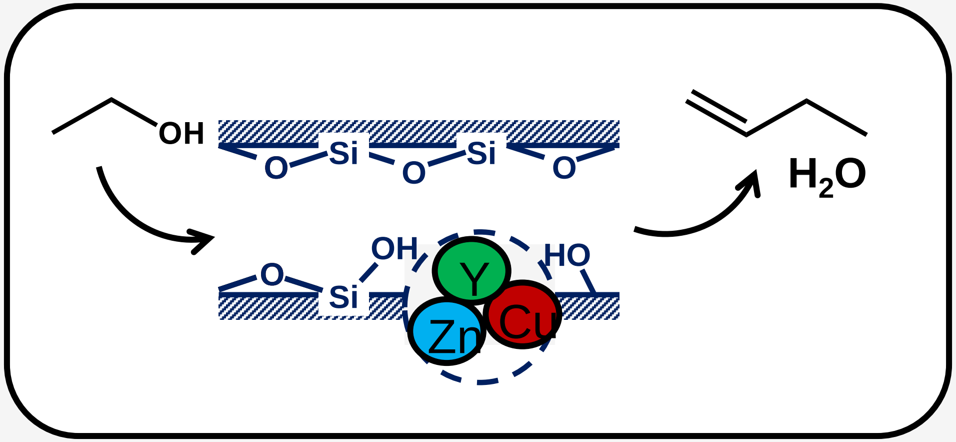
Quantification of Active Sites for Ethanol Upgrading over Yttrium-Containing Beta Zeotypes



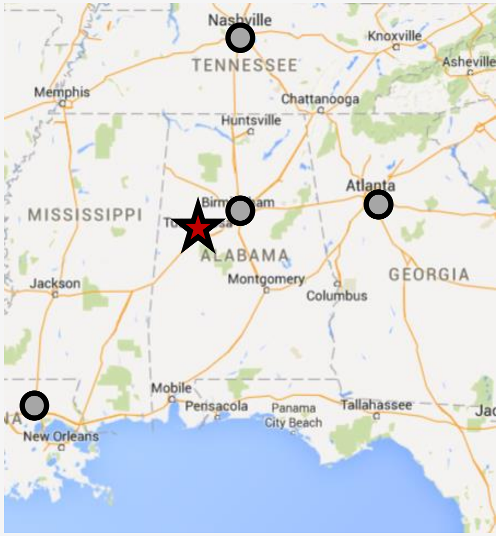
James W. Harris

Department of Chemical and Biological Engineering
The University of Alabama

Halder Topsoe Catalysis Forum
Gilleleje, Denmark
September 13th, 2023

The University of Alabama

Tuscaloosa, AL



Capstone state public university of Alabama (est. 1831)

1000 acre residential campus

37,842 students (2020)

Tuscaloosa, AL (pop. 101,129)

The University of Alabama

Tuscaloosa, AL

- 3rd oldest engineering program in the US (1837)
- Chemical engineering program over 100 years old (1910)
  - >600 UG students; 6th largest in US & Canada
  - ~55 PhD Students, 19 Faculty

Ranked #1 for **Goldwater Scholars** since 2007

Often ranked in the top 5 in the nation for **National Merit Finalists**

The University of Alabama

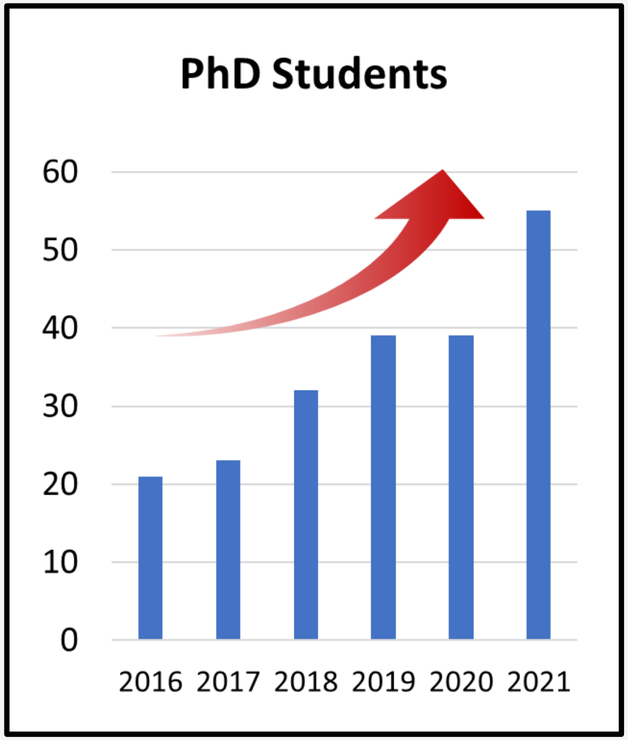
Tuscaloosa, AL

Rapid Expansion of Faculty Expertise

- **8 assistant professors**
- **~30% of the faculty have received NSF-CAREER Awards**

A Period of Unprecedented Growth

- **Number of PhD students up 260% in over five years**
- **External research funding growing at an average pace of 36% per year over the last five years**



Harris Laboratory Personnel

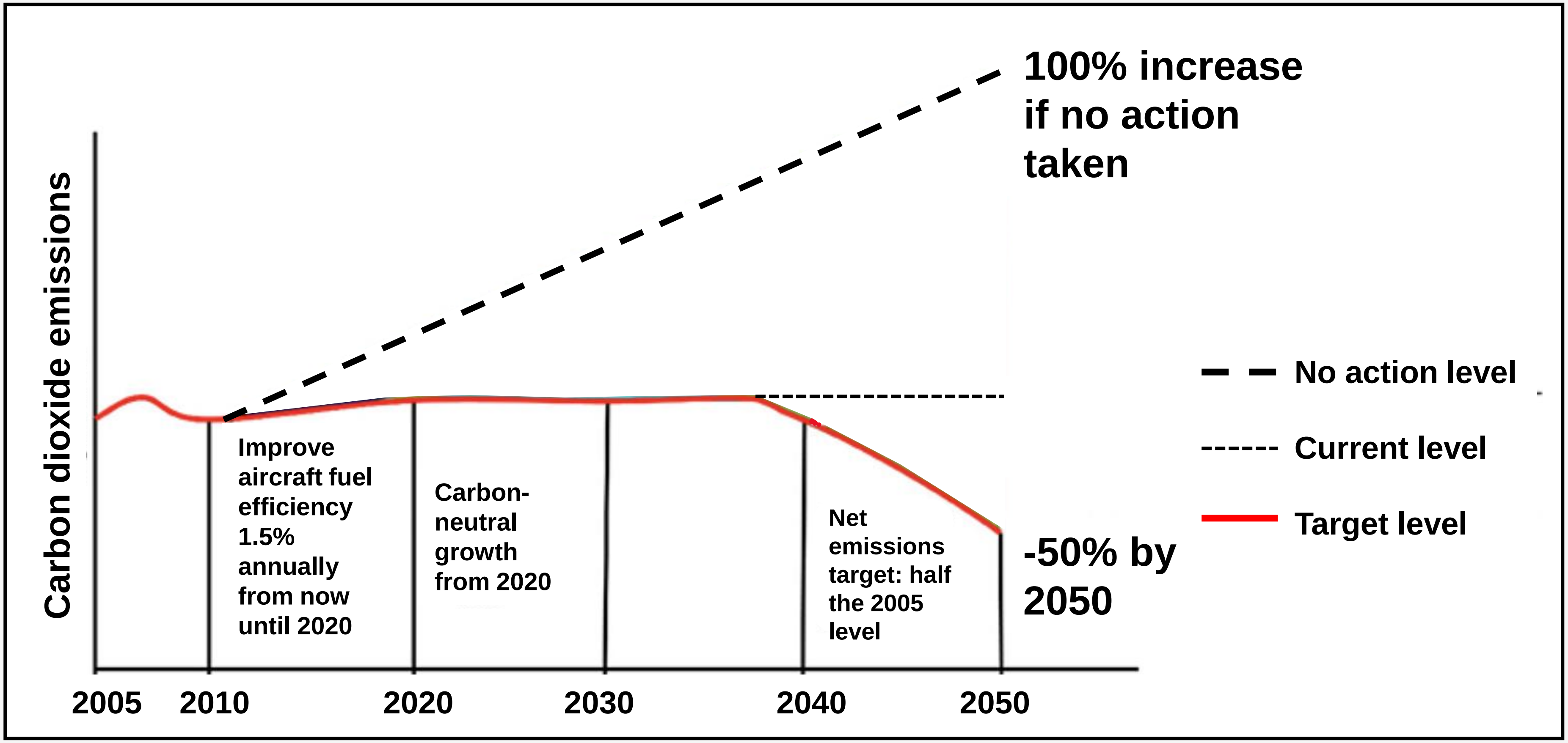
Research Group

1 Postdoc:
Dr. Adam Twombly

6 PhD Students:
Alex Minne
Syd Foster
Ethan Iaia
Shivangi Borate
Elyse Kimpiab
Britney Mack

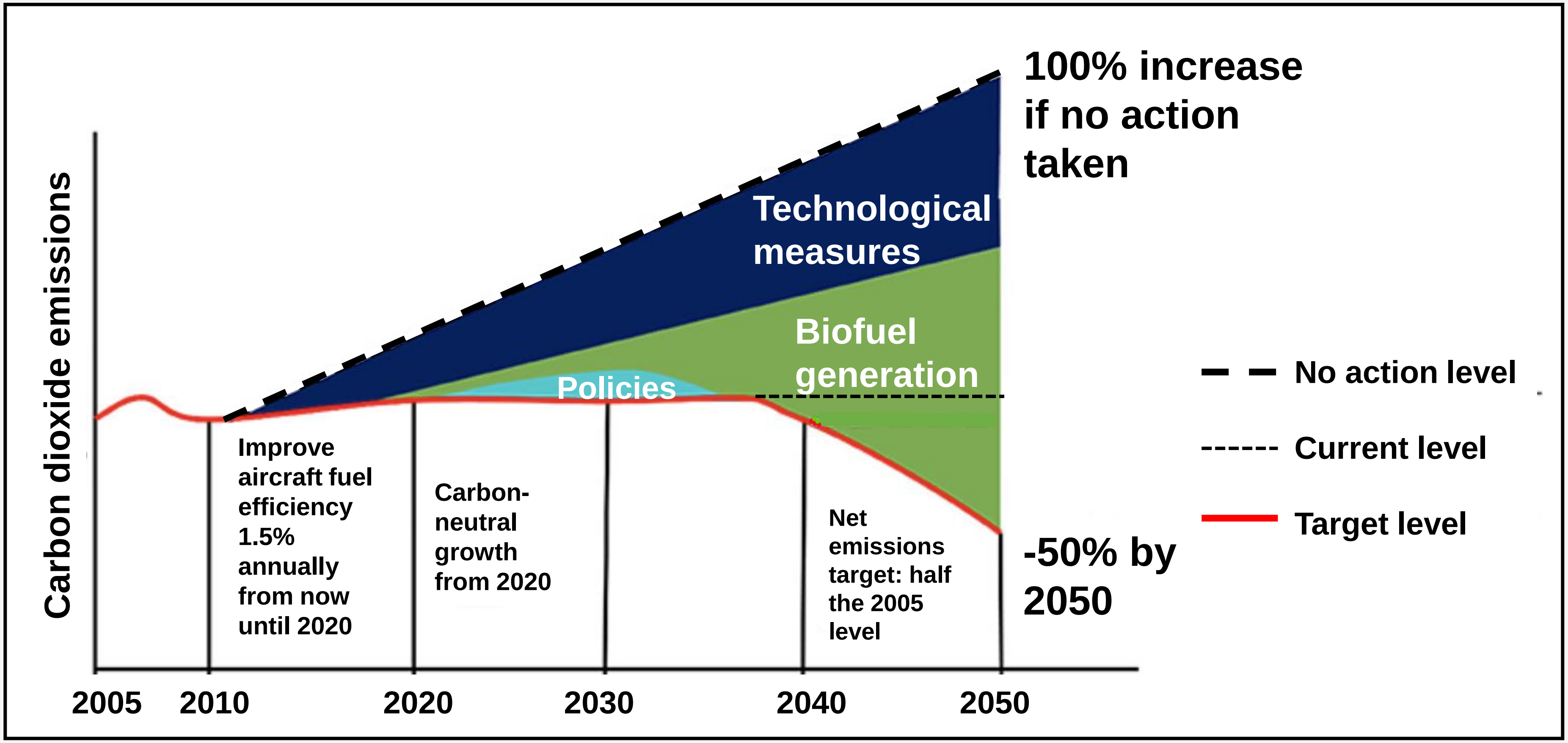
5 B.S. ChBE students
Treycen Garton
Adam Honson
Mary Elizabeth Martin
Gabe Miller
Katherine Perkinson

IATA's target net carbon emission



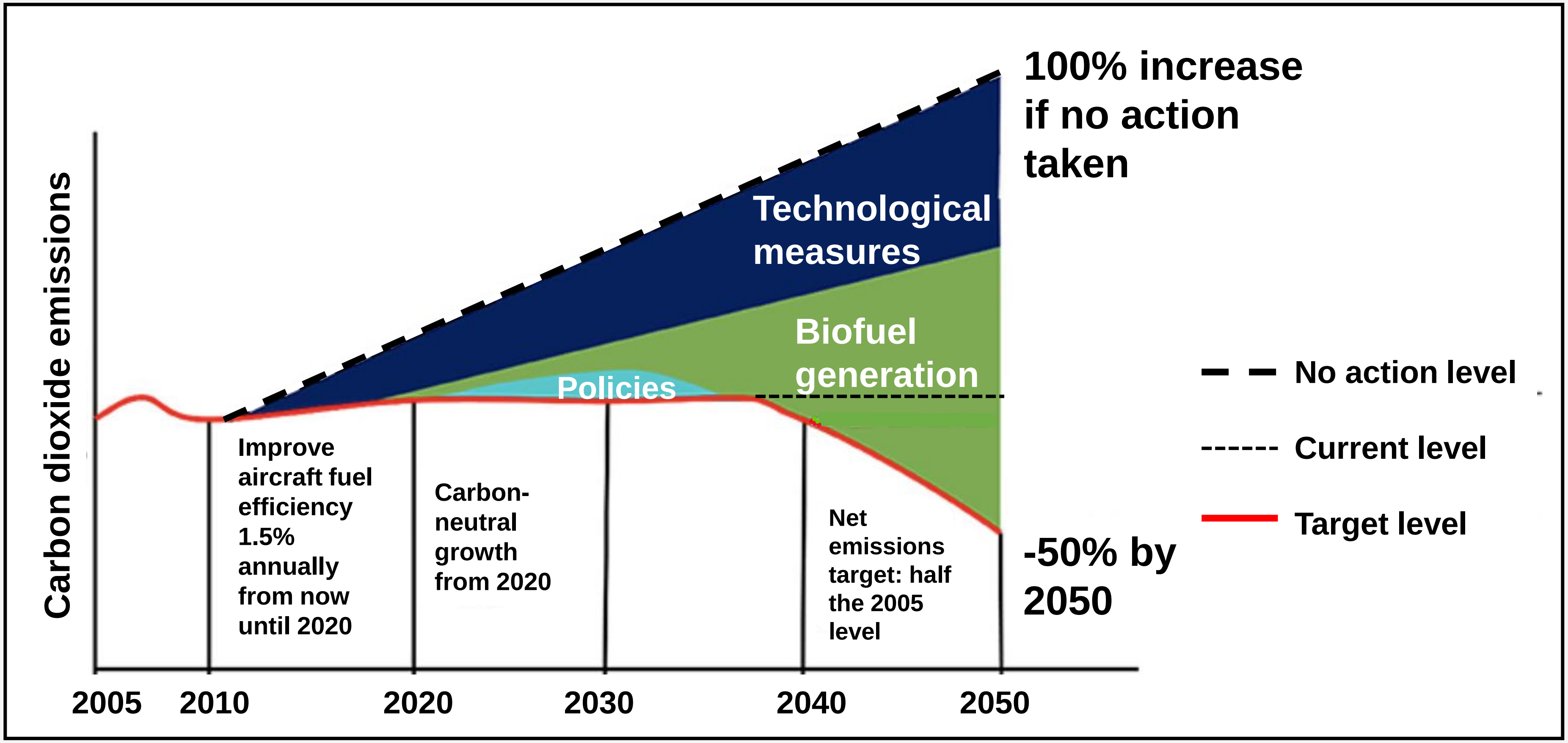
Doliente et al., *Front. Energy Res.*, 19 (2020) 110

IATA's target net carbon emission



Doliente et al., *Front. Energy Res.*, 19 (2020) 110

IATA's target net carbon emission



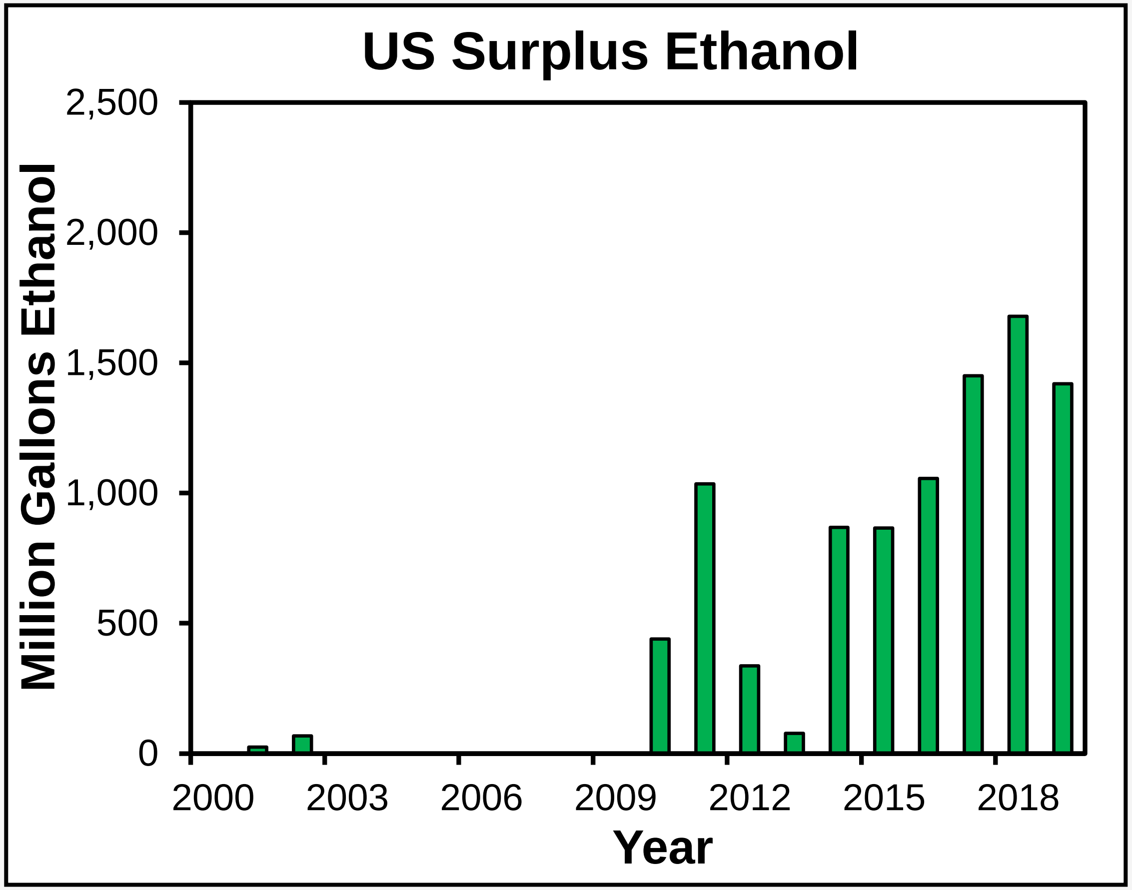
Highest mitigation contribution from sustainable jet fuel (SAF) generation

Doliente et al., *Front. Energy Res.*, 19 (2020) 110

Increasingly Large Ethanol Surplus

Biomass (Corn)

Ethanol



Monthly Energy Review (2018) US Energy Information Administration, DOE

Upgrading Ethanol to Jet Fuel

Biomass (Corn)

Ethanol

Jet Fuel ($C_{>9}$)

Alkanes, Olefins, BTX

Upgrading Ethanol to Jet Fuel

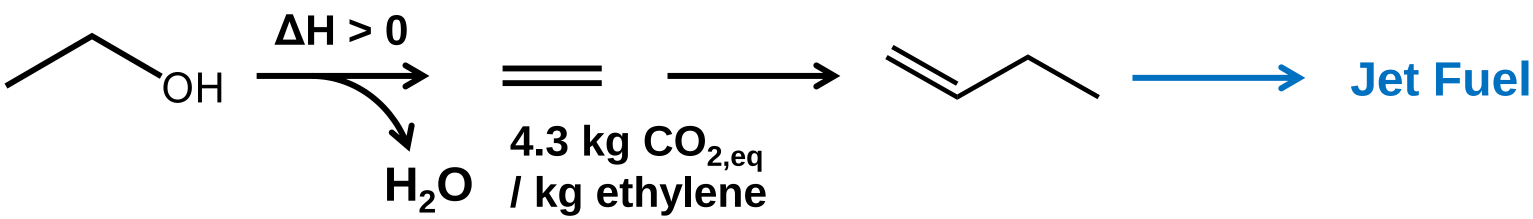
Biomass (Corn)

Ethanol

Jet Fuel ($C_{>9}$)

Alkanes, Olefins, BTX

Current Route:



Upgrading Ethanol to Jet Fuel

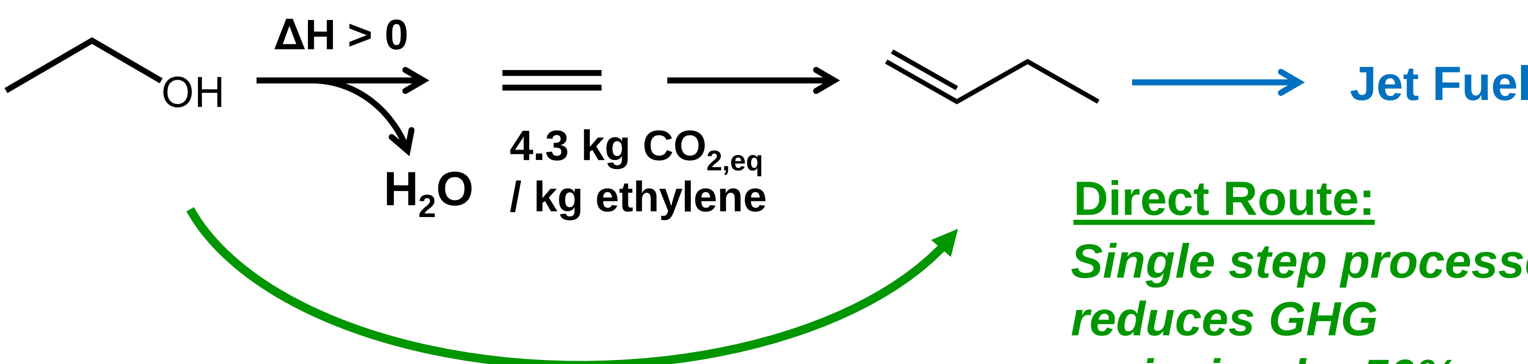
Biomass (Corn)

Ethanol

Jet Fuel ($C_{>9}$)

Alkanes, Olefins, BTX

Current Route:



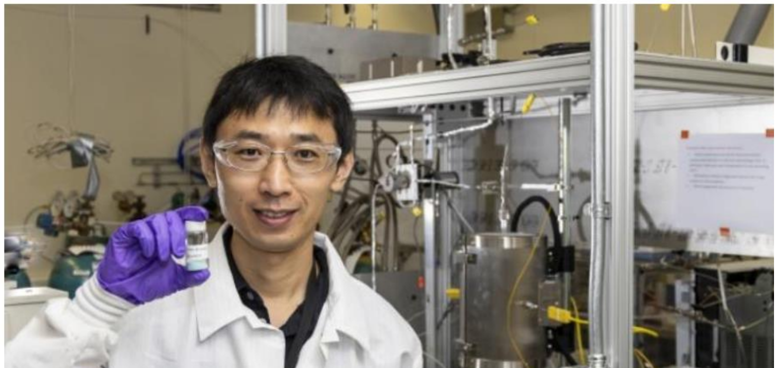
Direct Route:

Single step processes reduces GHG emission by 50%

Tao et al., *Green Chemistry,* 19 (2017) 1082-1101

Upgrading Ethanol to Jet Fuel

Prometheus Fuels licenses energy-saving ORNL ethanol-to-jet-fuel process



Vertimass licenses ORNL biofuel-to-hydrocarbon conversion technology

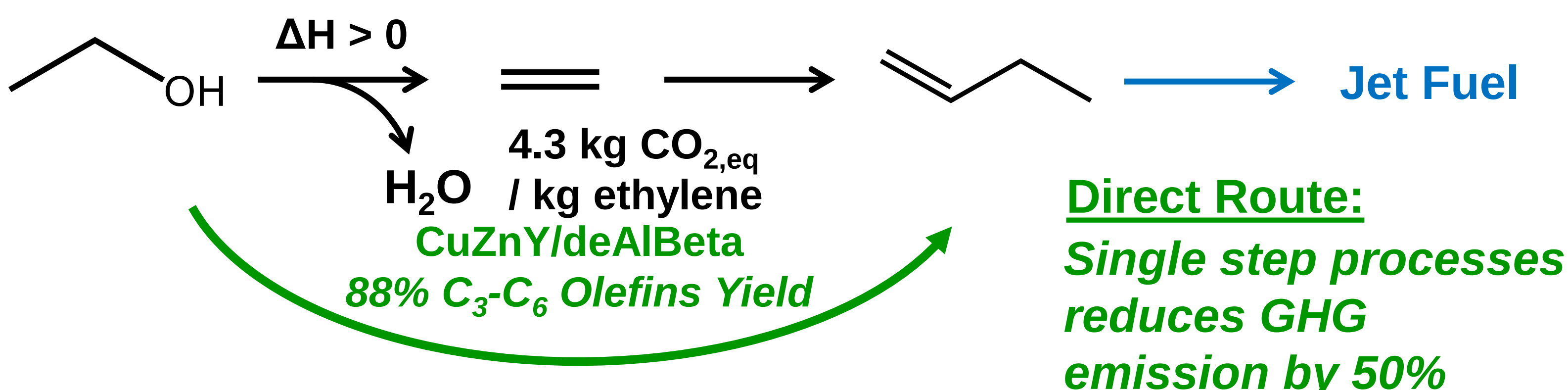
Topics: Materials • Clean Energy • Functional Materials for Energy • Biological Systems

March 6, 2014

OAK RIDGE, Tenn., March 6, 2014 — Vertimass LLC, a California-based start-up company, has licensed an Oak Ridge National Laboratory technology that directly converts ethanol into a hydrocarbon blend-stock for use in transportation fuels.

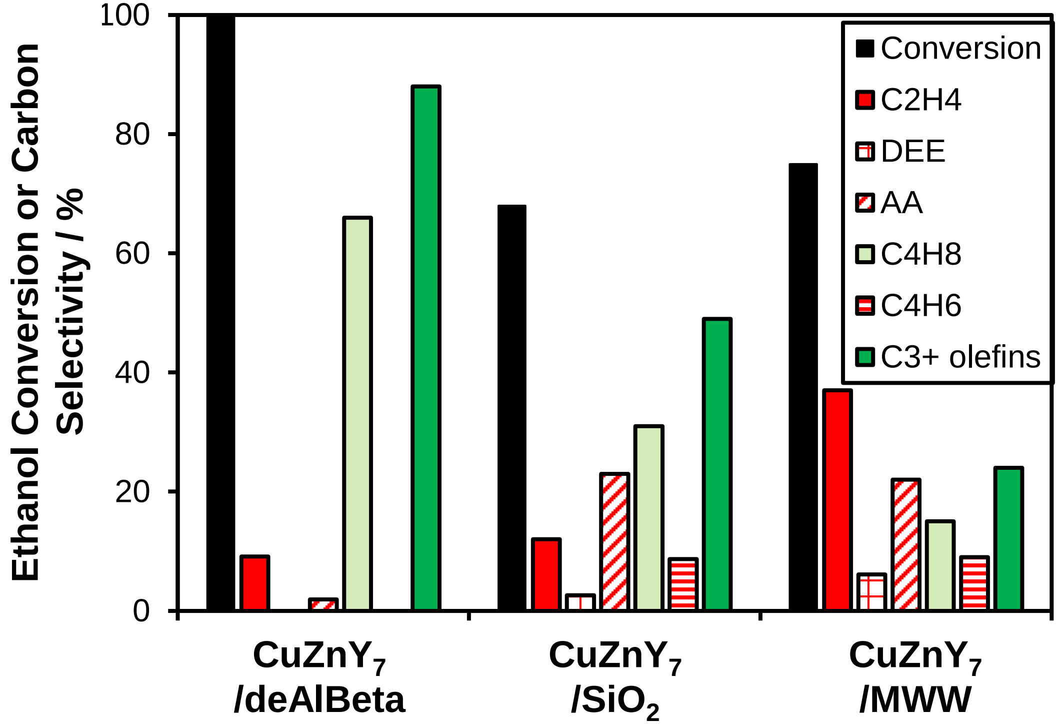
The ORNL technology offers a new pathway to

Current Route:



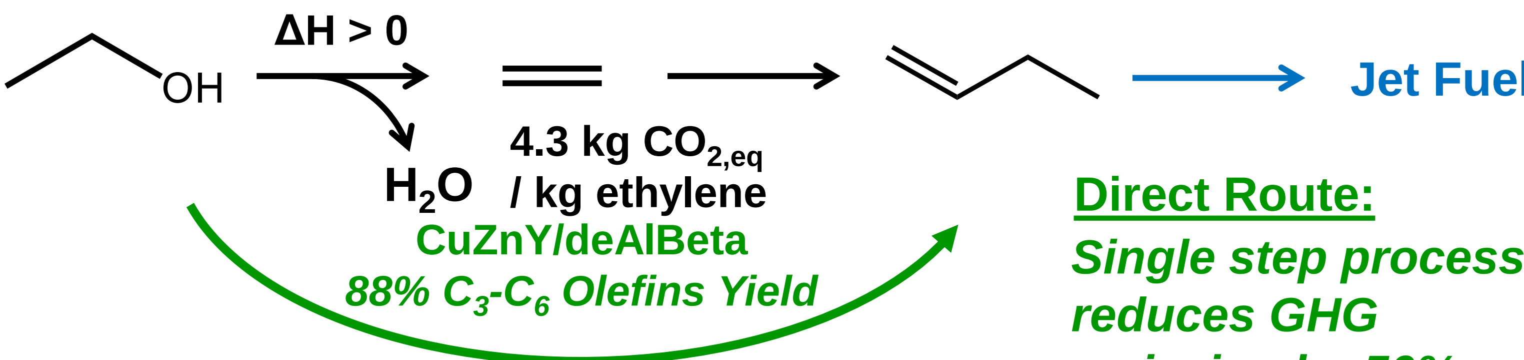
A cheaper and more sustainable route for converting ethanol to jet fuel

Upgrading Ethanol to Jet Fuel over CuZnY/deAlBeta



Reaction Conds.:
623 K, 7.1 kPa
C_2H_5OH, 94.3 kPa
H_2, WHSV 0.51 h^{-1}

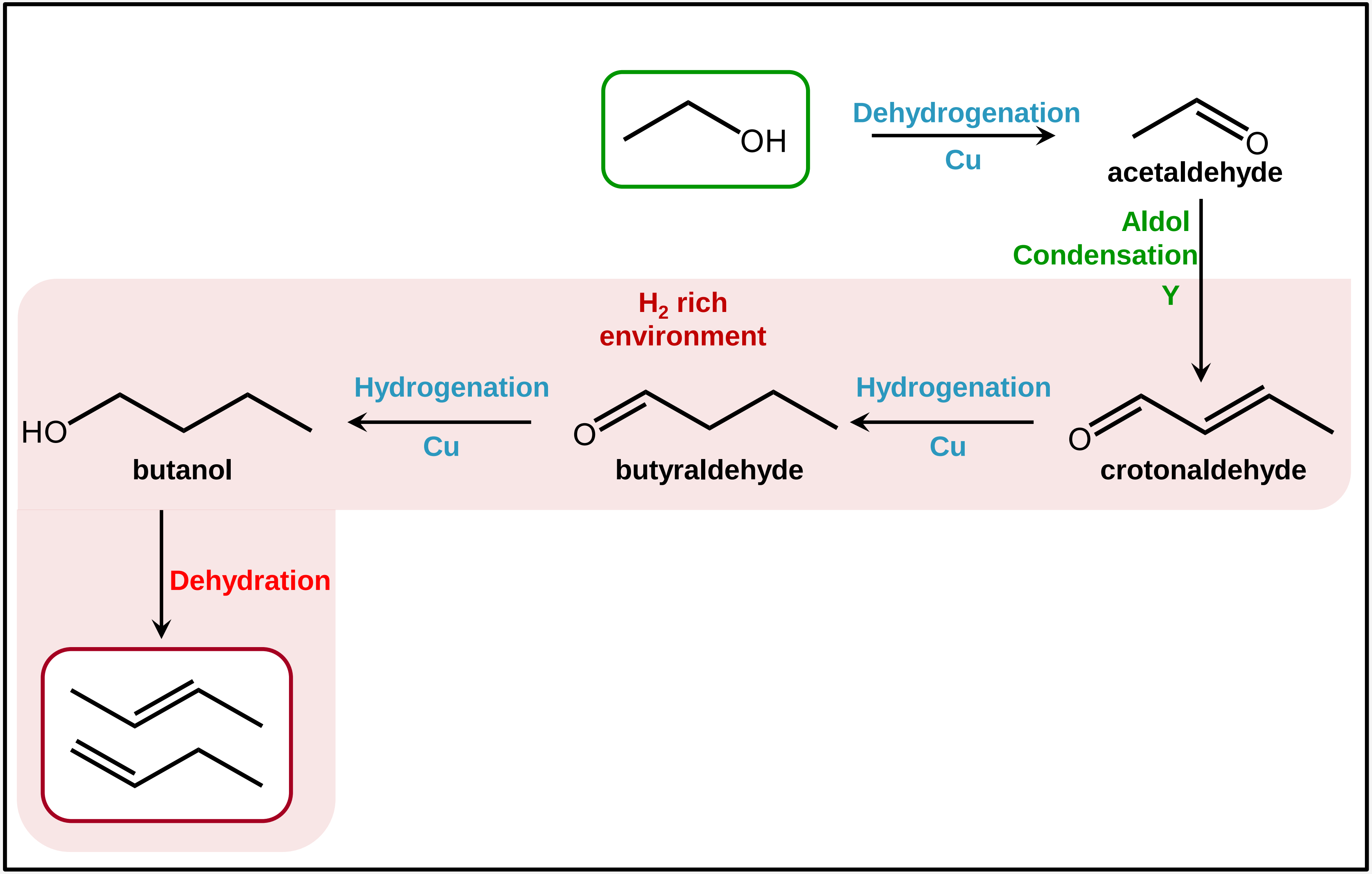
Zhang et al., *ACS Catal.*, 11 (2021) 9885-9897



Direct Route:
Single step processes reduces GHG emission by 50%

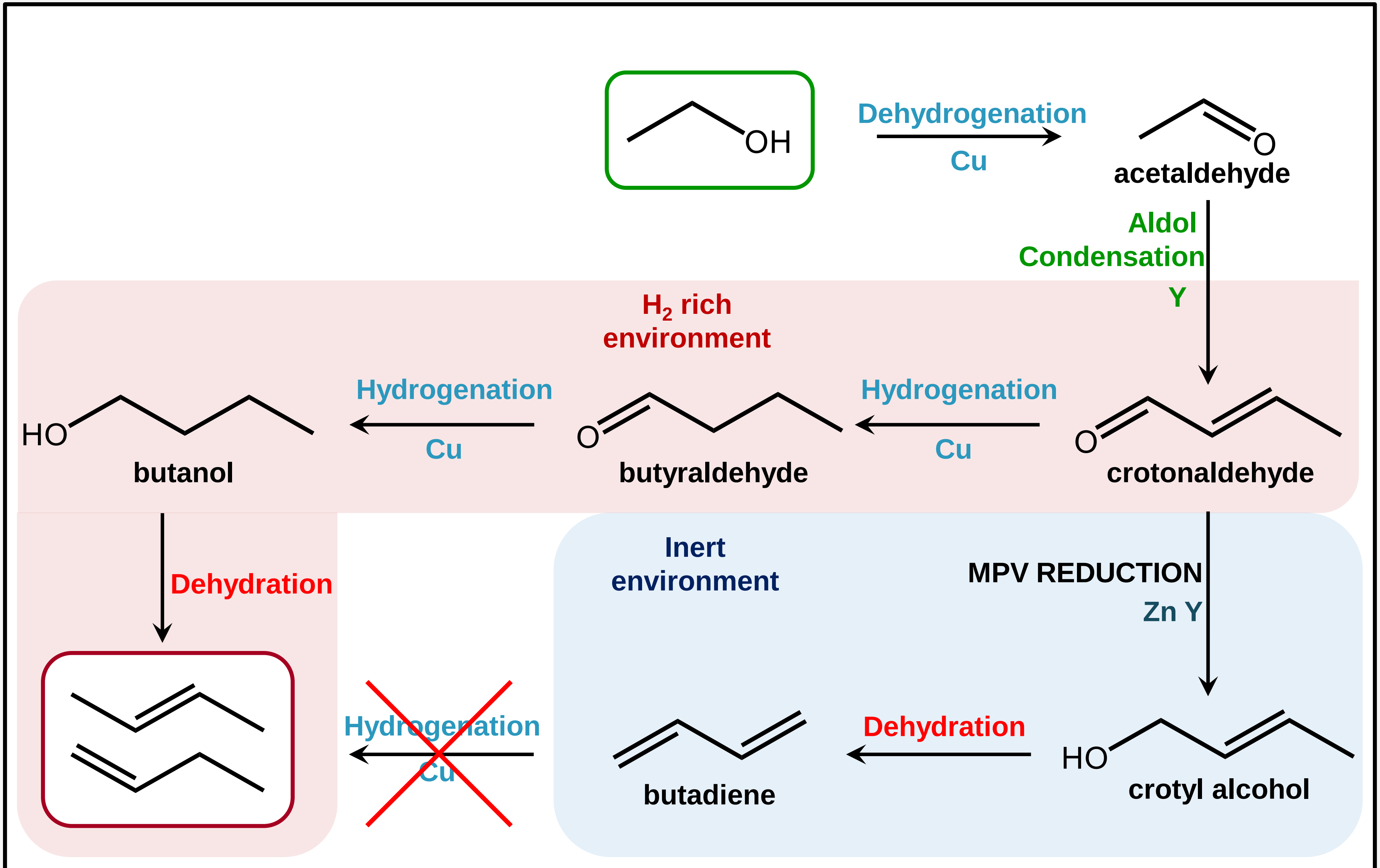
High selectivity to C_{3+} olefins without significant C_2H_4 ,DEE, or C_4H_6 formation

Proposed Ethanol to Butene Reaction Pathway



Zhang, Wegener, Samad et al., *ACS Catal.*, 11 (2021) 9885-9897

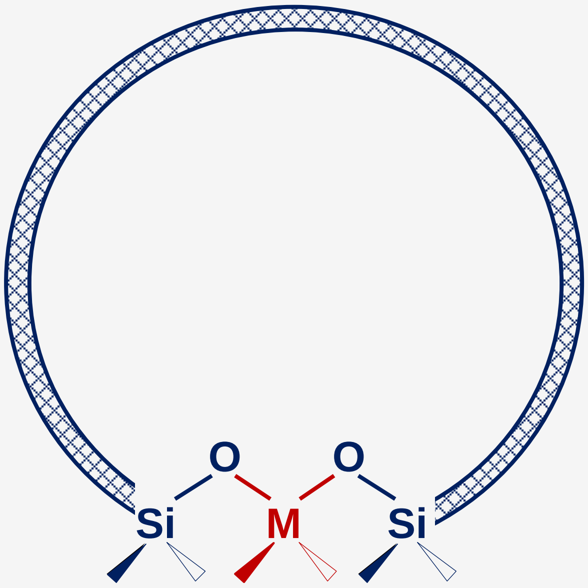
Proposed Ethanol to Butene Reaction Pathway



Zhang, Wegener, Samad et al., *ACS Catal.*, 11 (2021) 9885-9897

Metal-containing porous catalysts have broad site distributions

Secondary Confining Pore



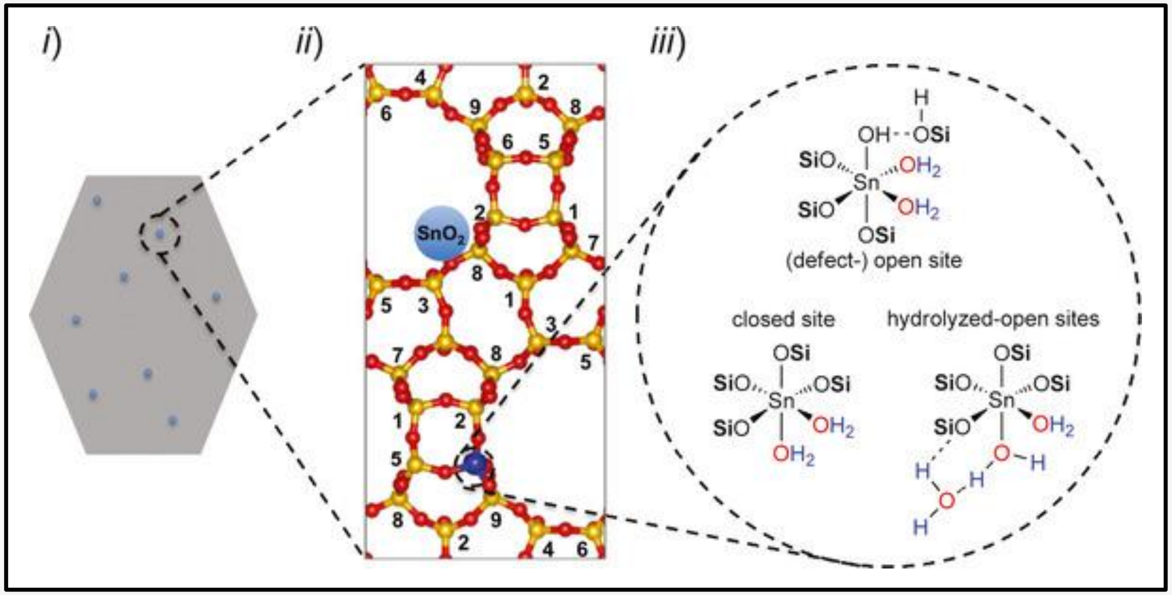
Primary Binding Site

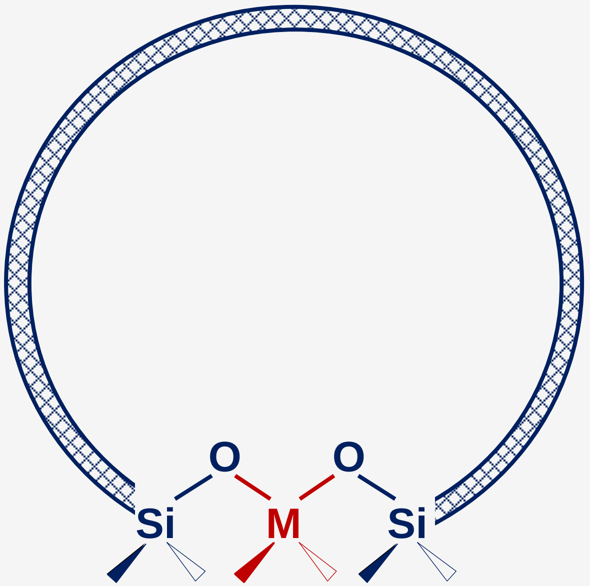
- Different oxidation number
- Different T-sites / pore geometry
- Spatial distributions
- Different local coordination

Harris et al., *ACS Catal*., 10 (2020) 9476-9495

Metal-containing porous catalysts have broad site distributions

Zeolites With Framework Metal Atoms

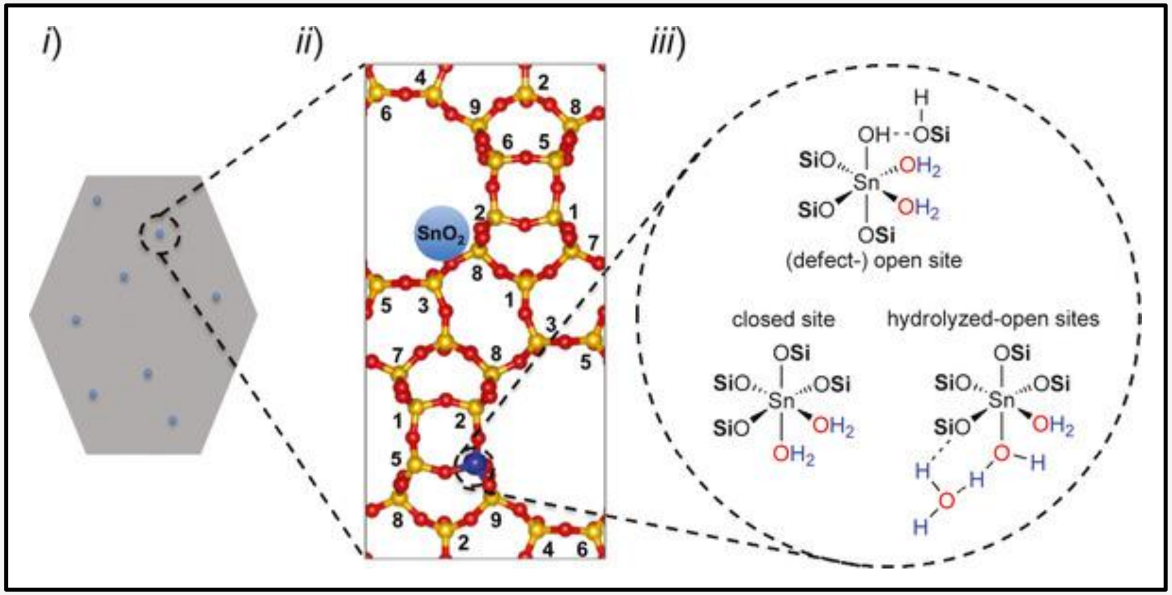




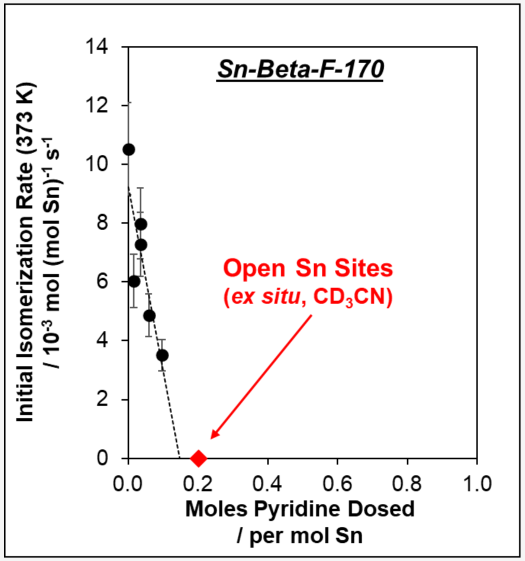
Wolf et al., *Helv. Chim. Acta*, 99 (2016) 916-927

Metal-containing porous catalysts have broad site distributions

Zeolites With Framework Metal Atoms



~20% of Sn in Sn-Beta catalyzes glucose isomerization



Harris et al., *J. Catal*., 335 (2016) 141-154

Wolf et al., *Helv. Chim. Acta*, 99 (2016) 916-927

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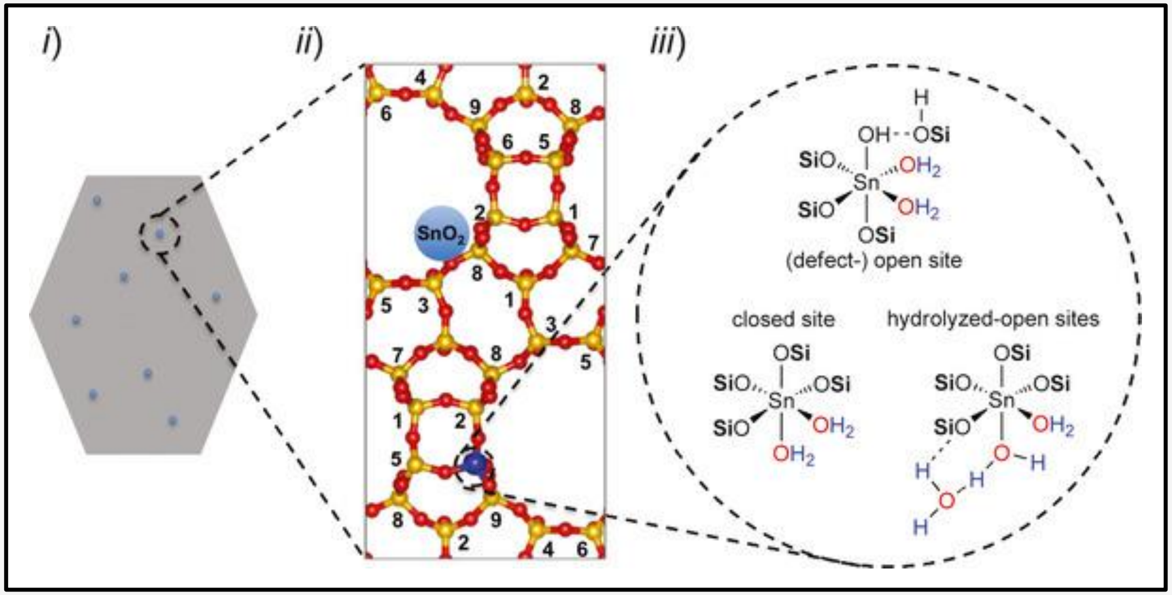
Zeolites With Framework Metal Atoms



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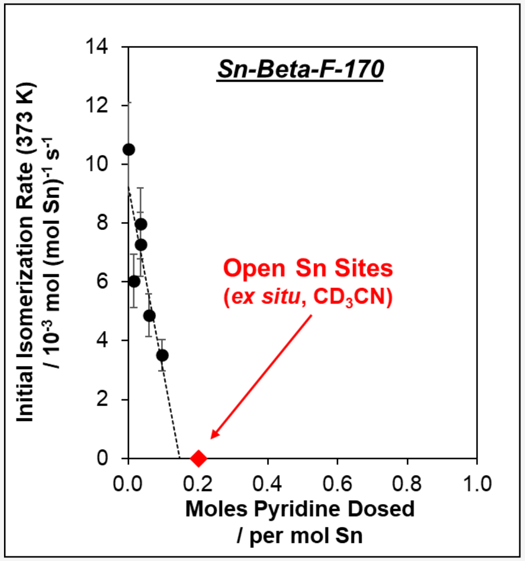
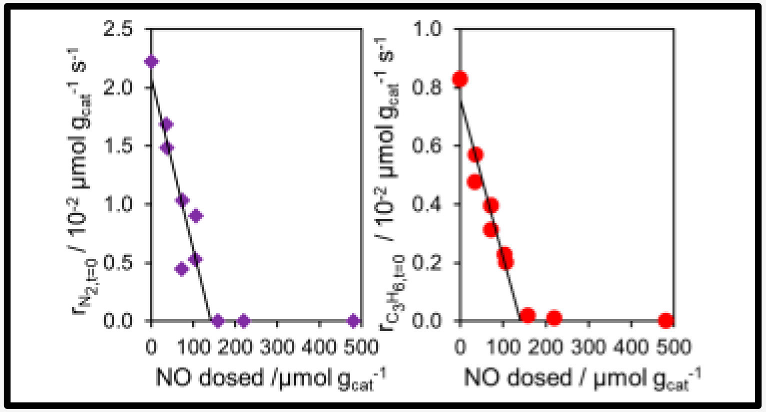


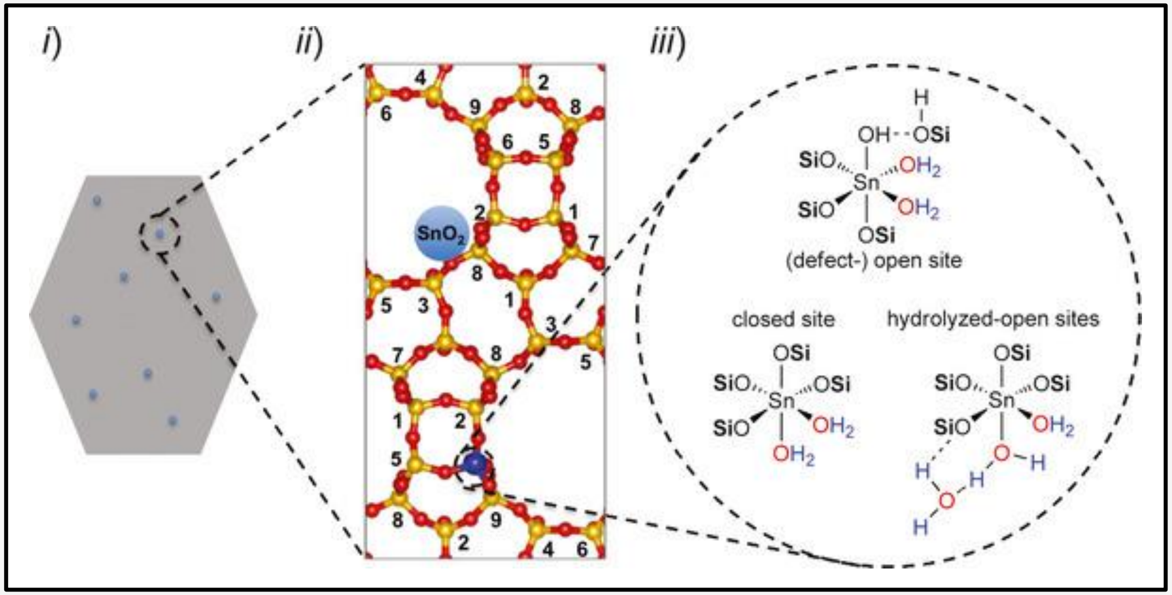
~6% of Fe in MIL-100(Fe) catalyzes C-H bond activation



Simons et al., *JACS*, 141 (2019) 18142-18151
Harris et al., *J. Catal.*, 335 (2016) 141-154
Wolf et al., *Helv. Chim. Acta*, 99 (2016) 916-927

Metal-containing porous catalysts have broad site distributions

Zeolites With Framework Metal Atoms



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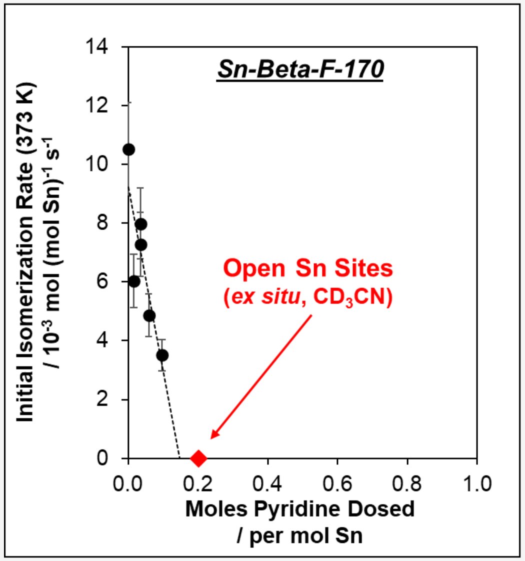

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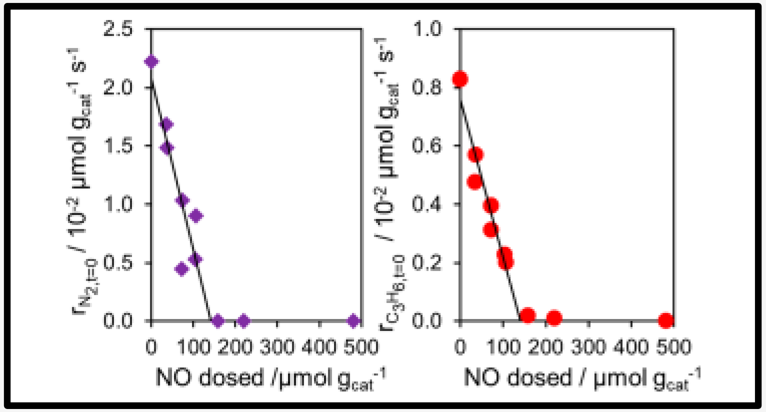
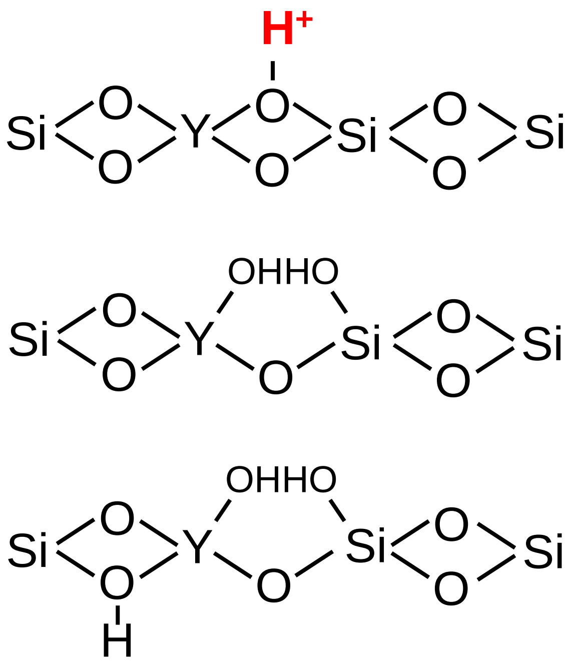


Need to quantify the subset of sites that perform the catalysis!

Simons et al., *JACS*, 141 (2019) 18142-18151
Harris et al., *J. Catal.*, 335 (2016) 141-154
Wolf et al., *Helv. Chim. Acta*, 99 (2016) 916-927

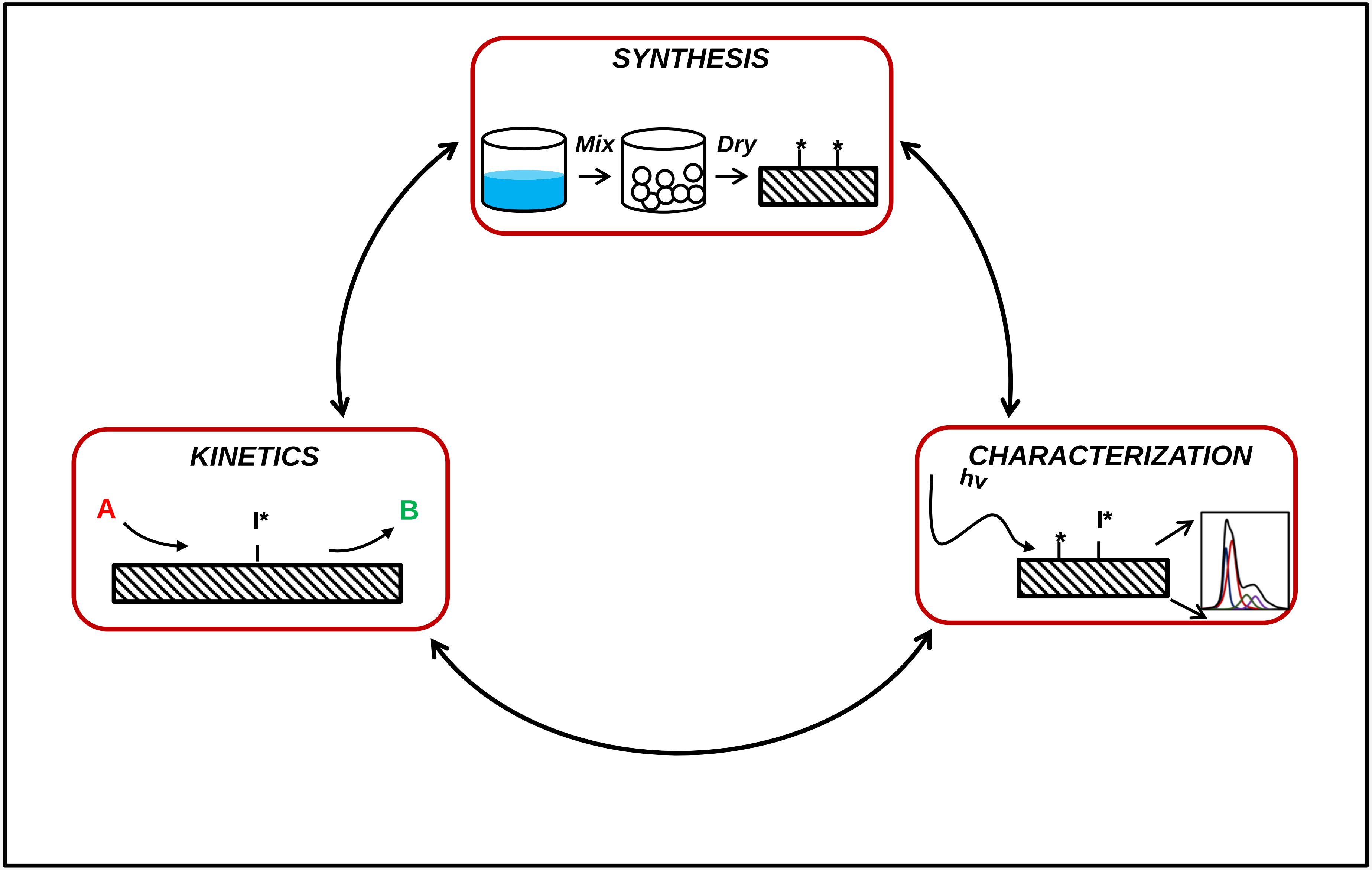
What sites are relevant in (Cu, Zn)Y/deAlBeta catalysts?

What are the active sites and how many are there?

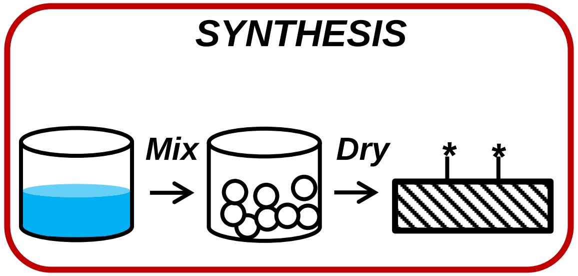


???

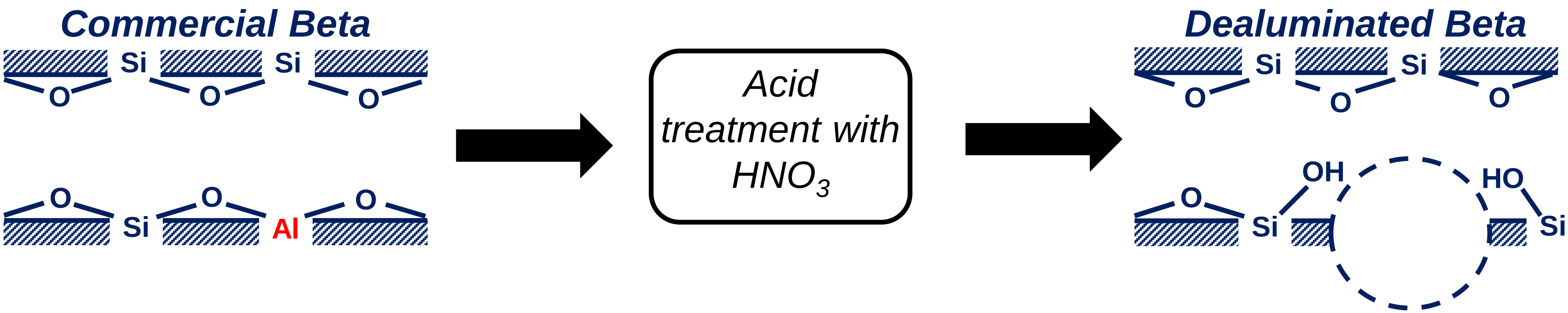
Research Strategy



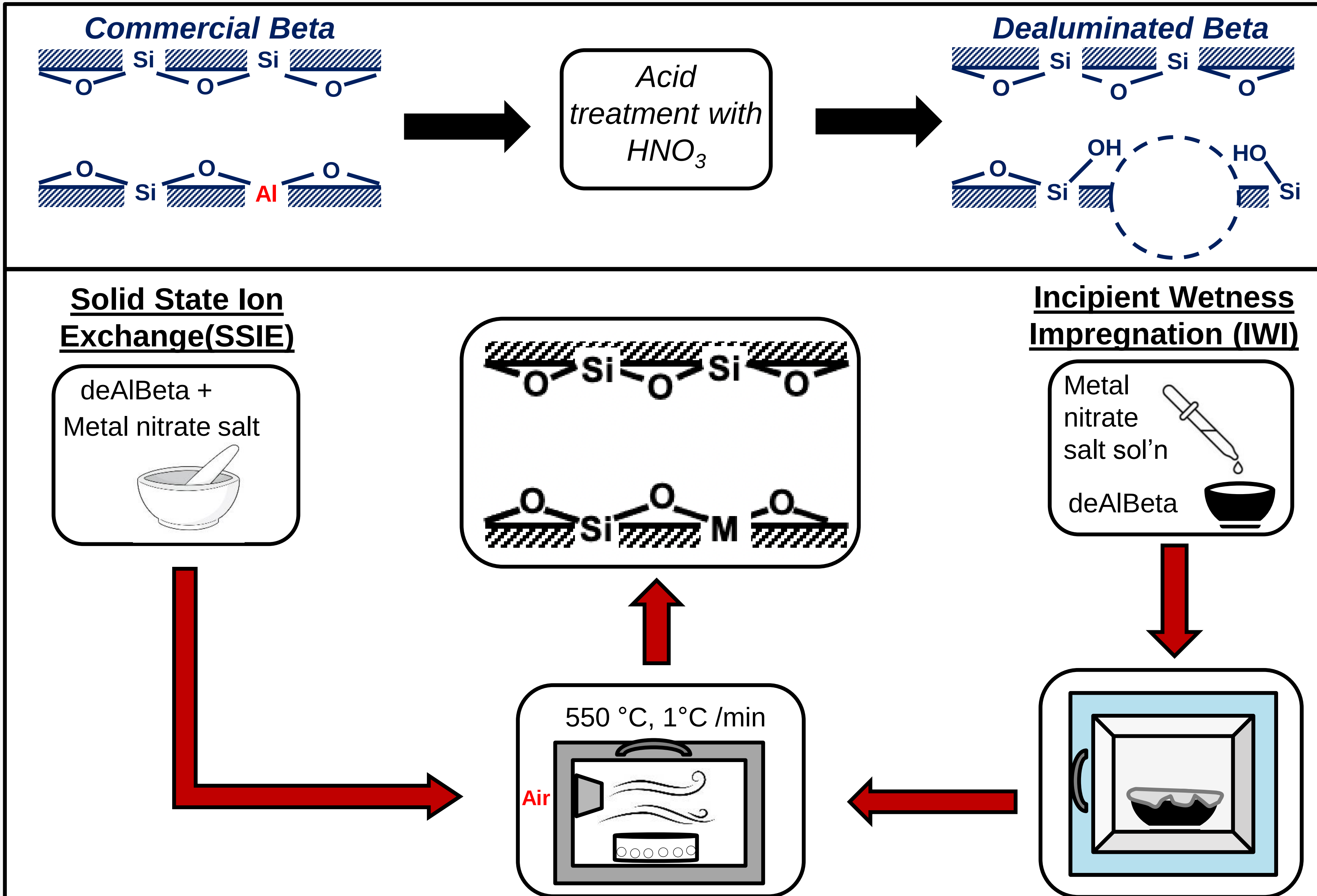
Synthesizing Beta zeolite



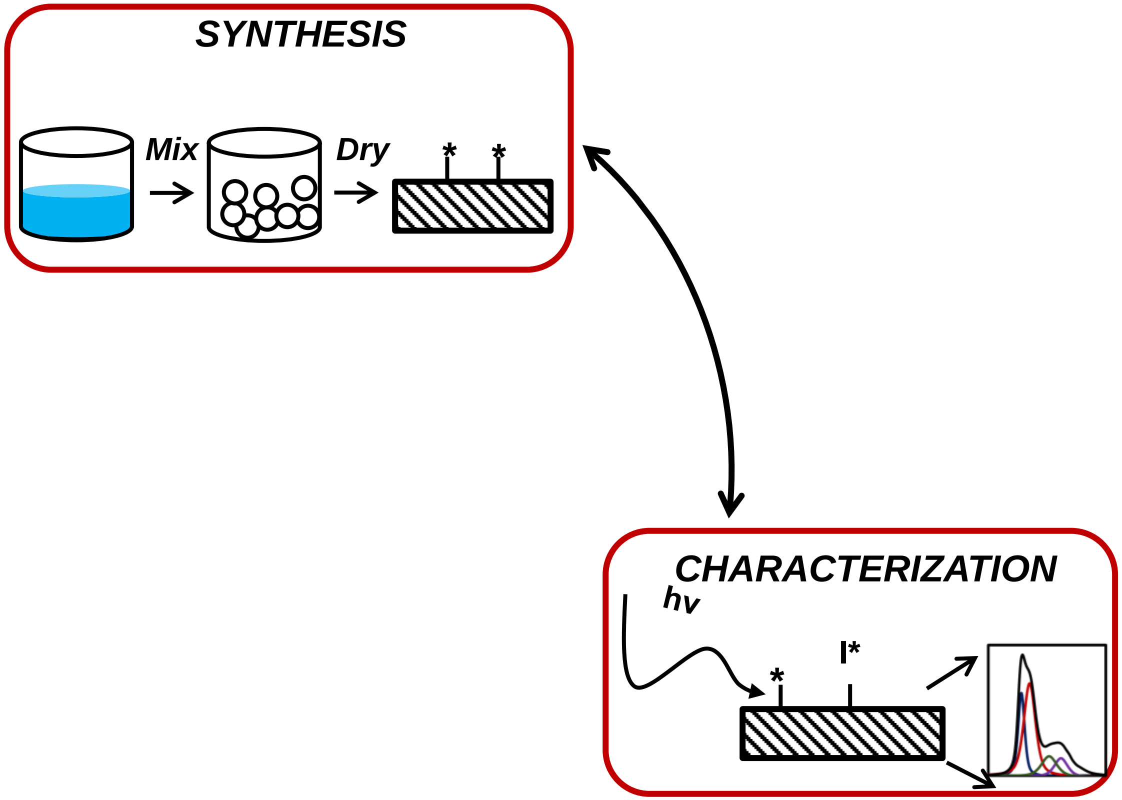
Dealuminating Beta zeolite



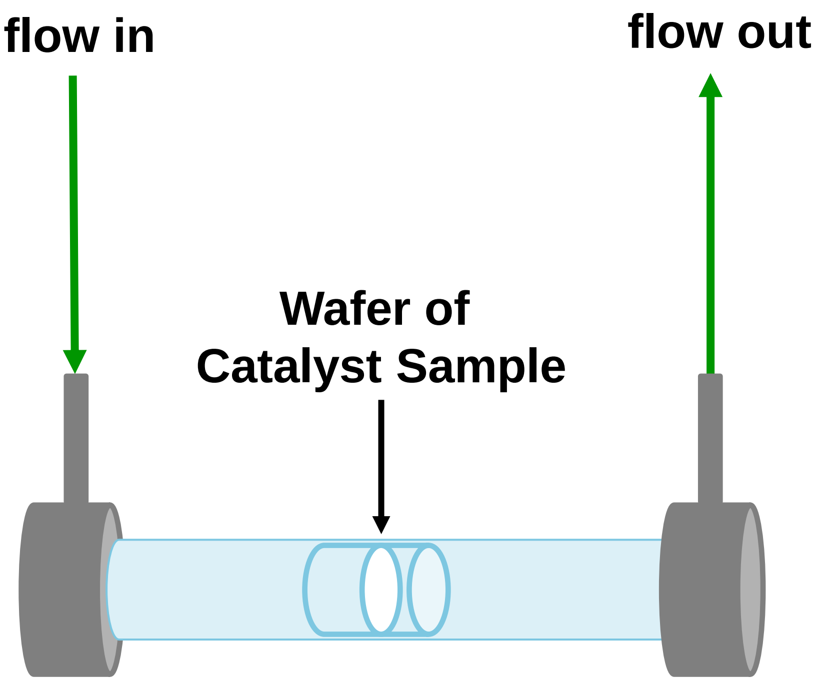
Metal incorporation into dealuminated Beta (deAlBeta)



Characterizing the catalysts

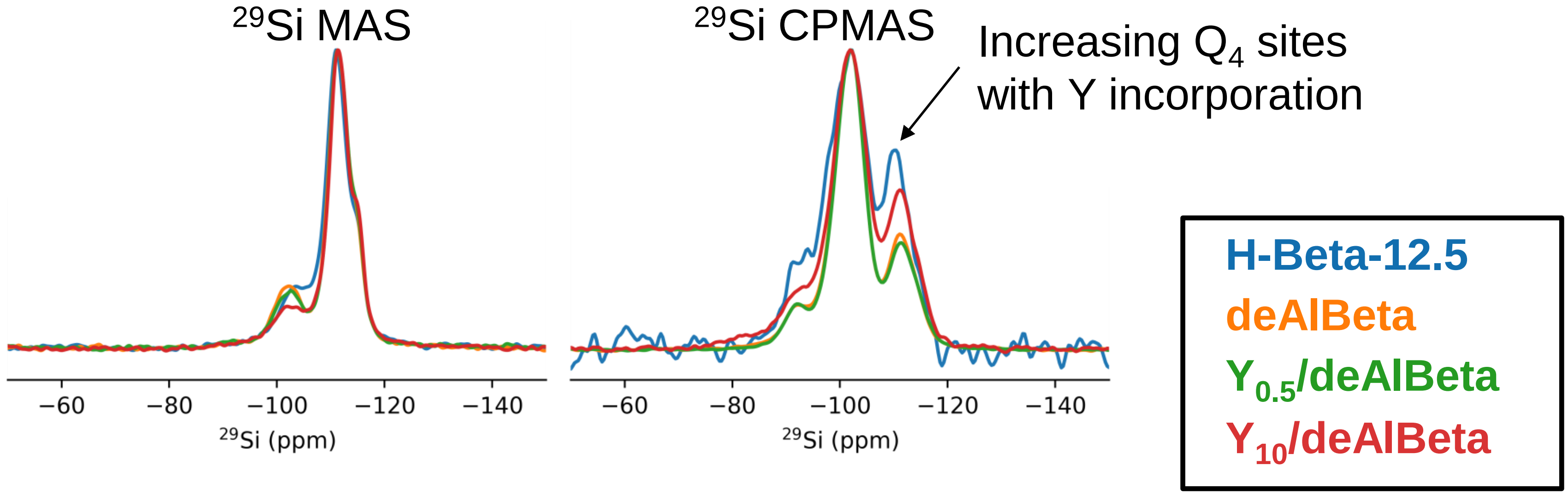


Fourier Transformed Infrared Spectroscopy



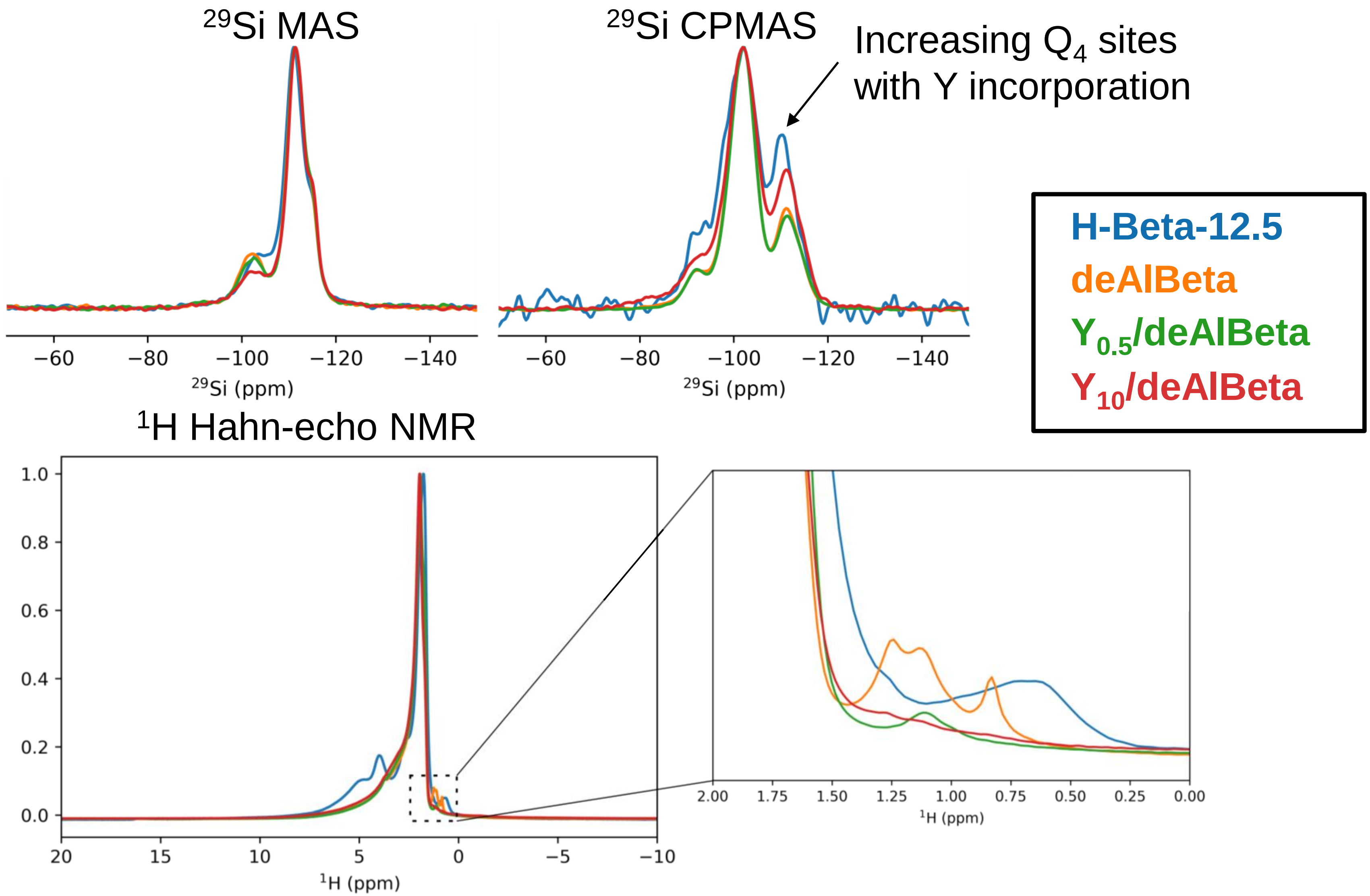
Cybulskis, Harris et al., *Rev. Sci. Inst.*, 87 (2016) 103101

SSNMR of Y/deAlBeta Samples



Data collected by Carlos Bornes (Mafra group), U. Aveiro, Portugal

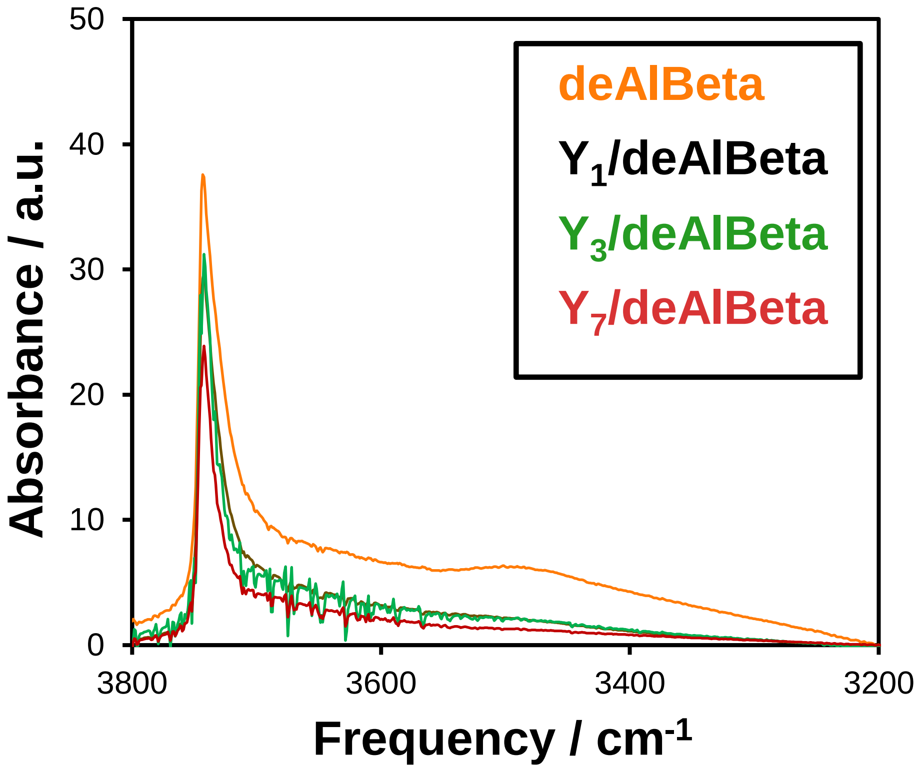
SSNMR of Y/deAlBeta Samples

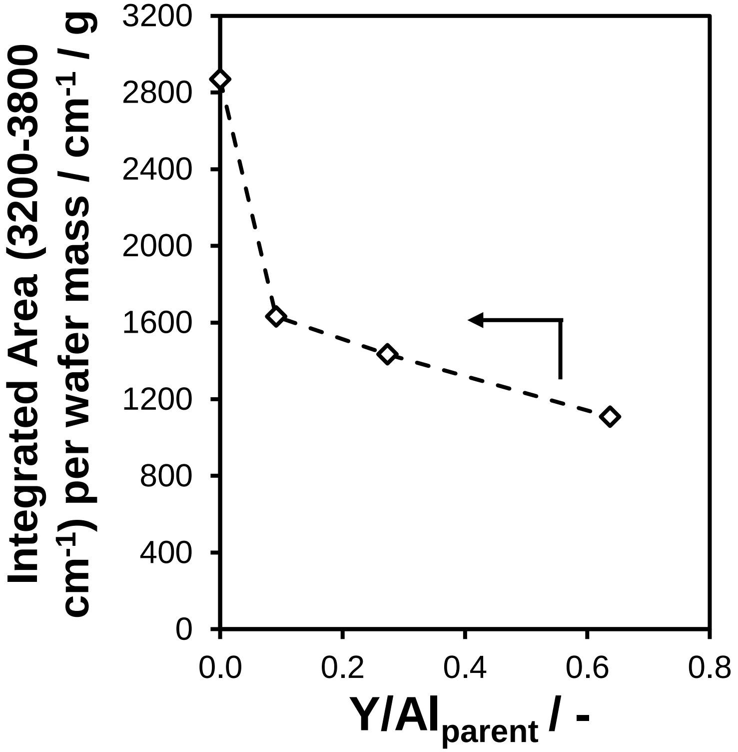


Hydroxyls generated by dealumination are largely eliminated by 0.5 wt% Y ($0.05\ Y/Al_{parent}$), and completely by 10 wt% Y ($0.9\ Y/Al_{parent}$)

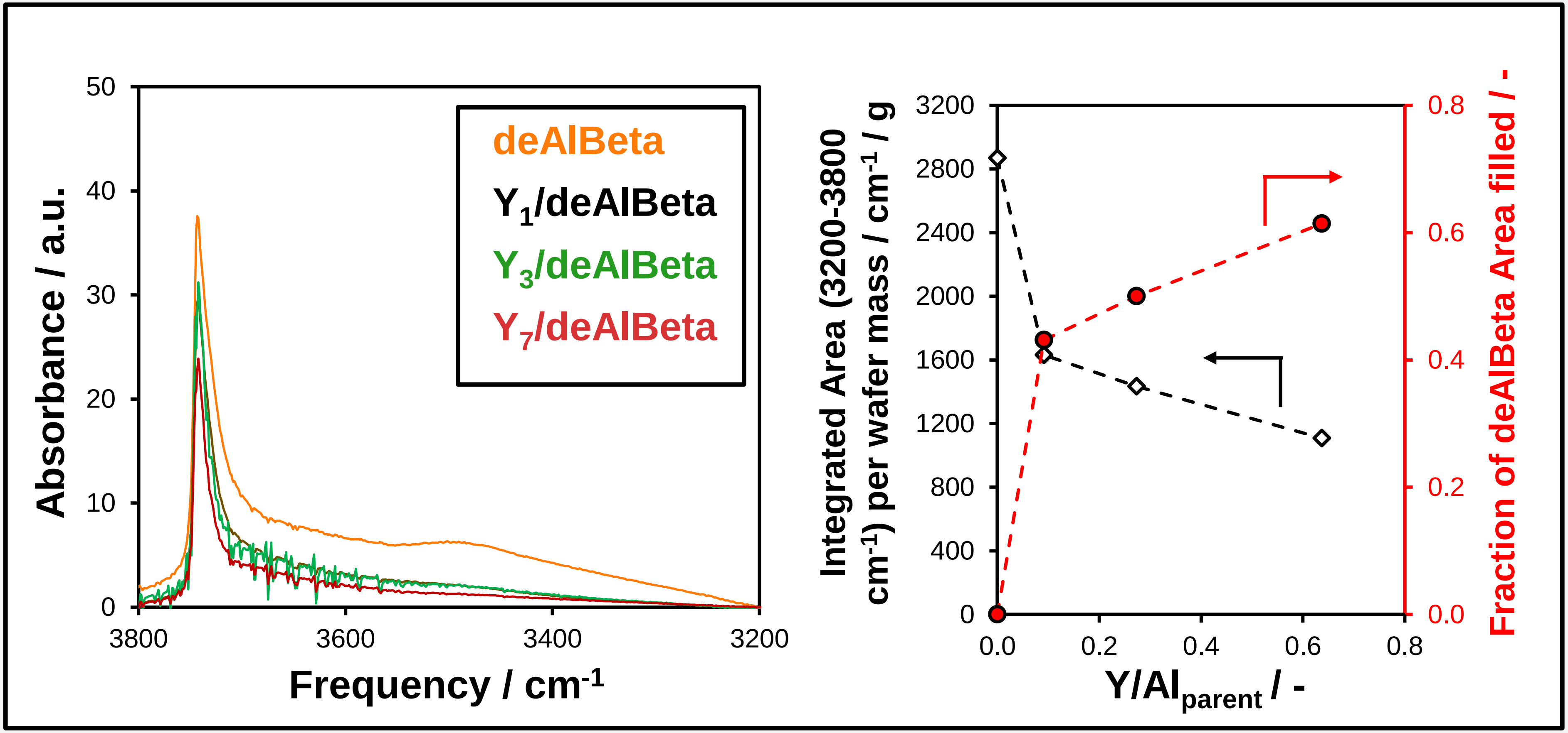
Data collected by Carlos Bornes (Mafra group), U. Aveiro, Portugal

IR of Y/deAlBeta Samples – O-H region



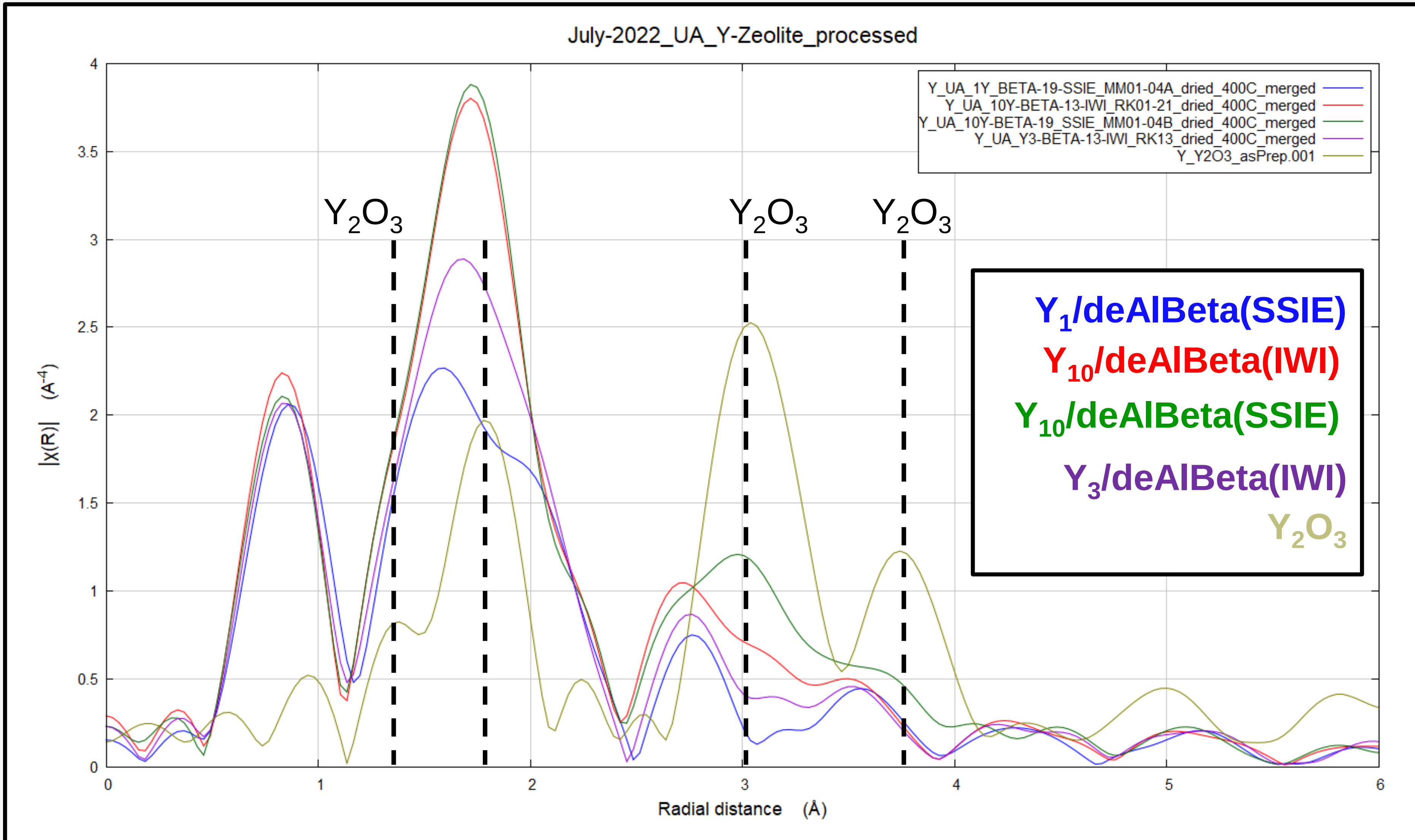


IR of Y/deAlBeta Samples – O-H region



Y incorporation by SSIE results in decreased v(O-H) region area, suggesting incorporation of Y at vacancies formed from dealumination

Y k-edge EXAFS of Y/deAlBeta samples



Above 1 wt%, all samples have some oxide-like peaks

Y k-edge EXAFS of Y/deAlBeta samples

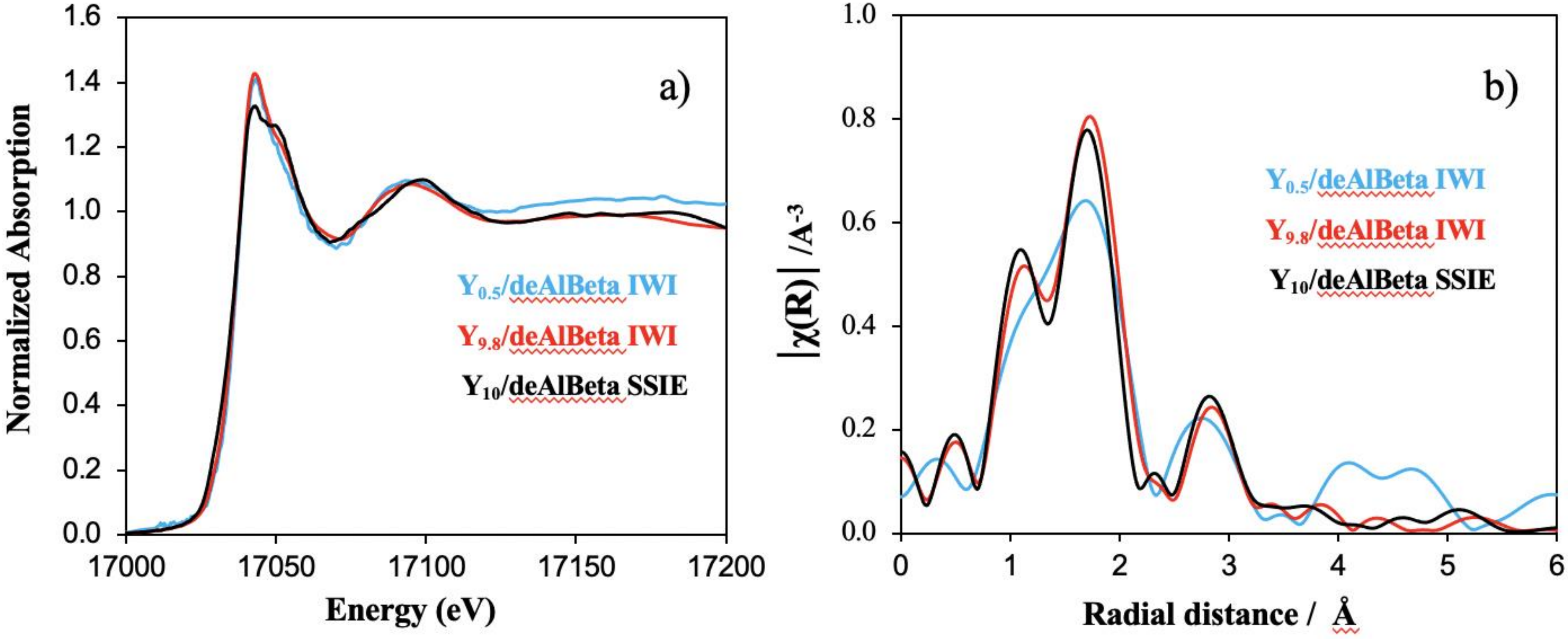
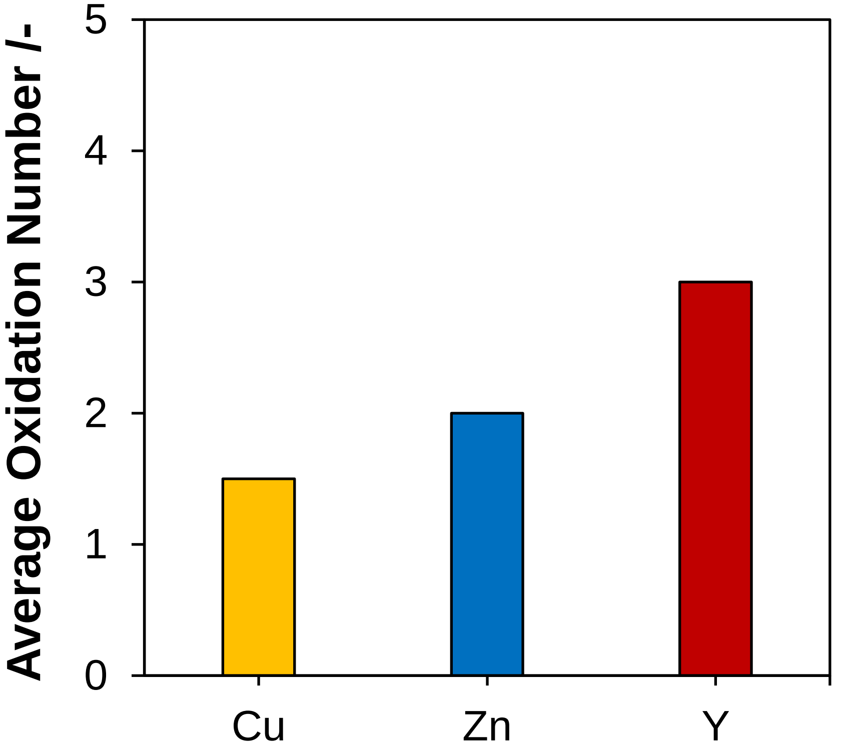


Figure 3 Y K edge XAS spectra of Y/deAlBeta of varied loading and synthesis techniques (a) XANES spectra, (b) k^2-Weighted FT EXAFS

Above 1 wt%, all samples have some oxide-like peaks

In-Situ Transmission X-ray Absorption Spectroscopy

XANES

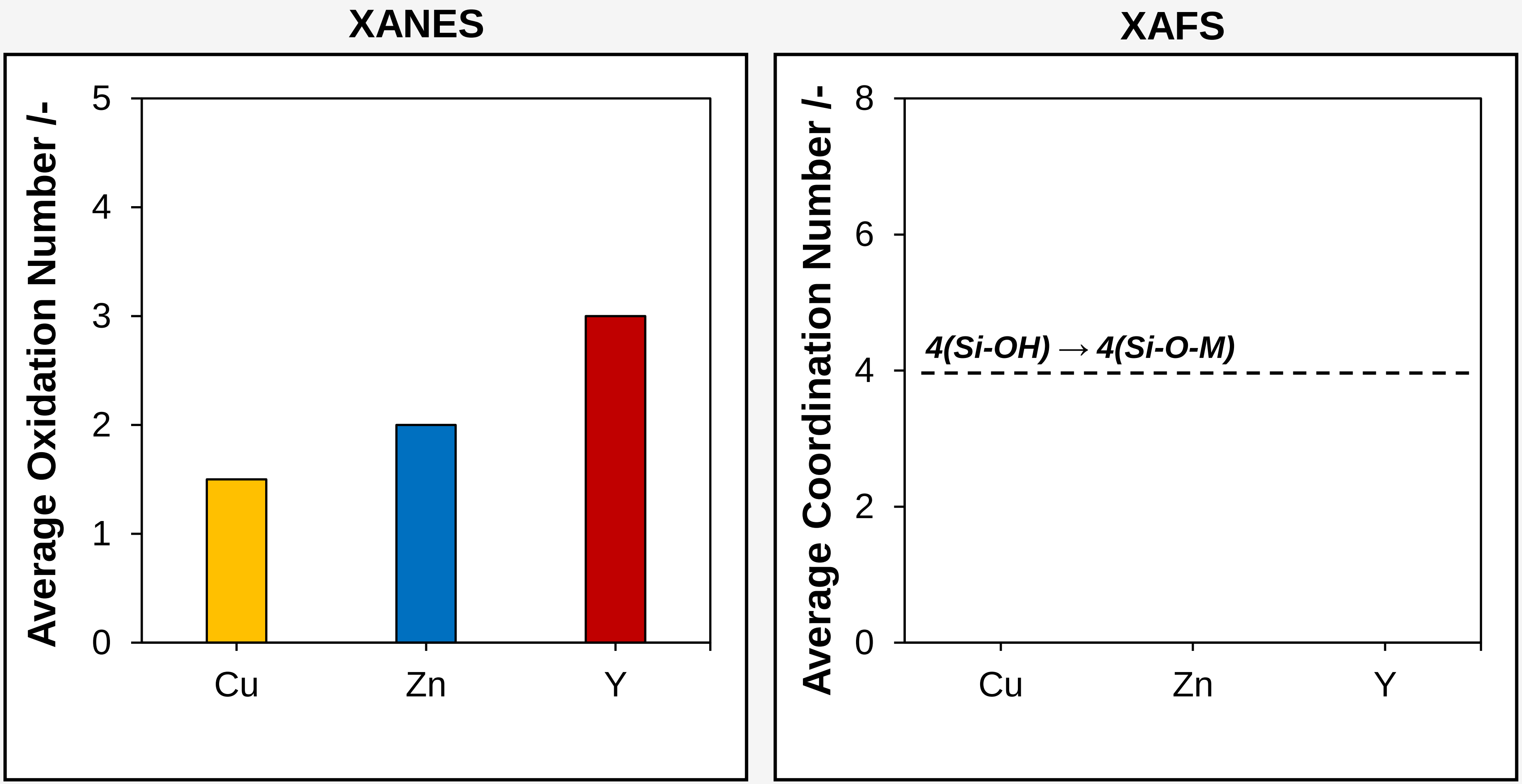


Argonne National Laboratory
Advanced Photon Source (APS)

After treatment in flowing 3.5 kPa $H_{2,}$ 98 kPa He, for 2 h at 673 K

Zhang, Wegener, Samad et al., *ACS Catal.,* 11 (2021) 9885-9897

In-Situ Transmission X-ray Absorption Spectroscopy

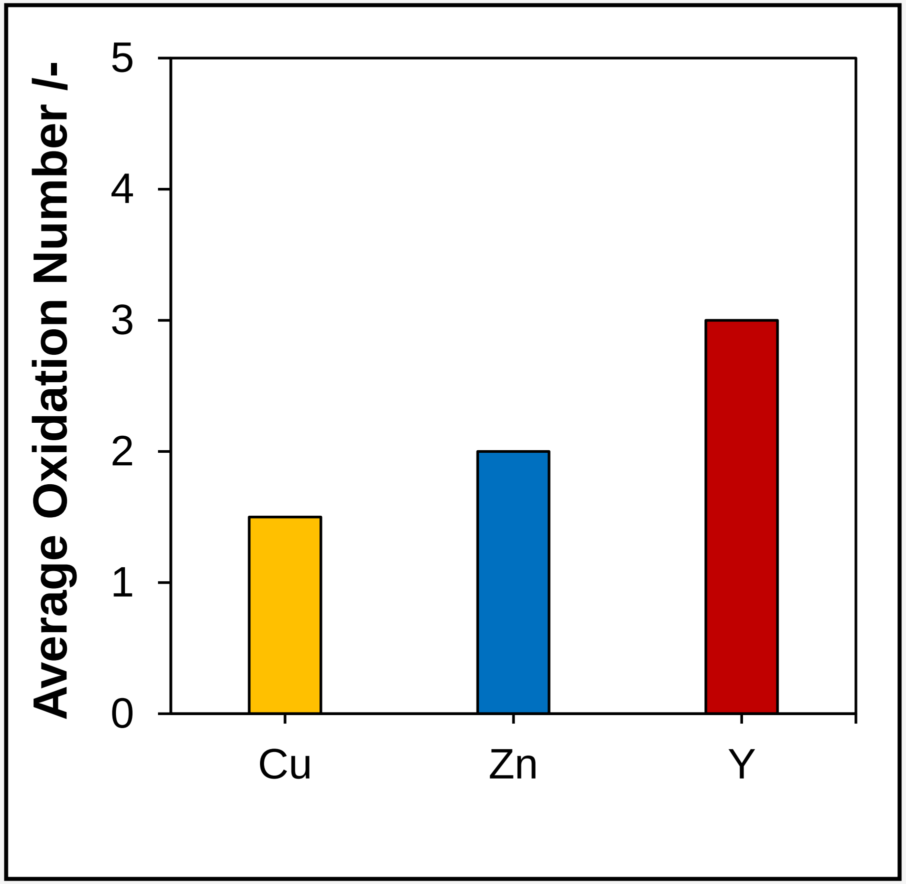


After treatment in flowing 3.5 kPa H_2, 98 kPa He, for 2 h at 673 K

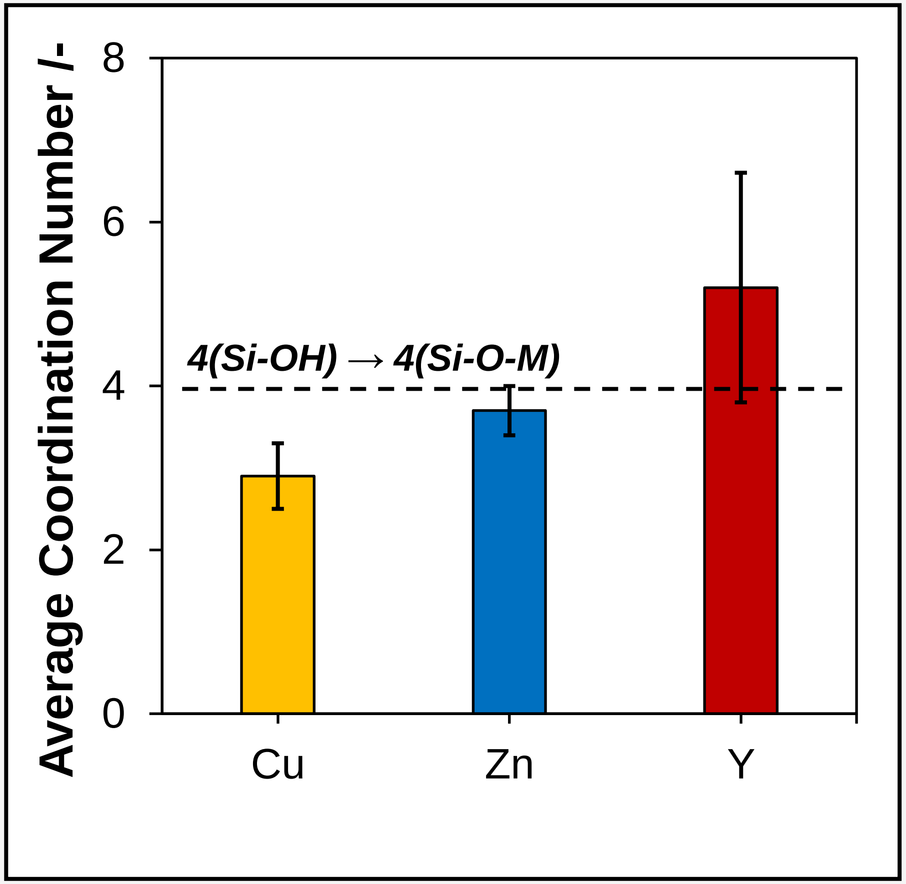
Zhang, Wegener, Samad et al., *ACS Catal.,* 11 (2021) 9885-9897

In-Situ Transmission X-ray Absorption Spectroscopy

XANES



XAFS



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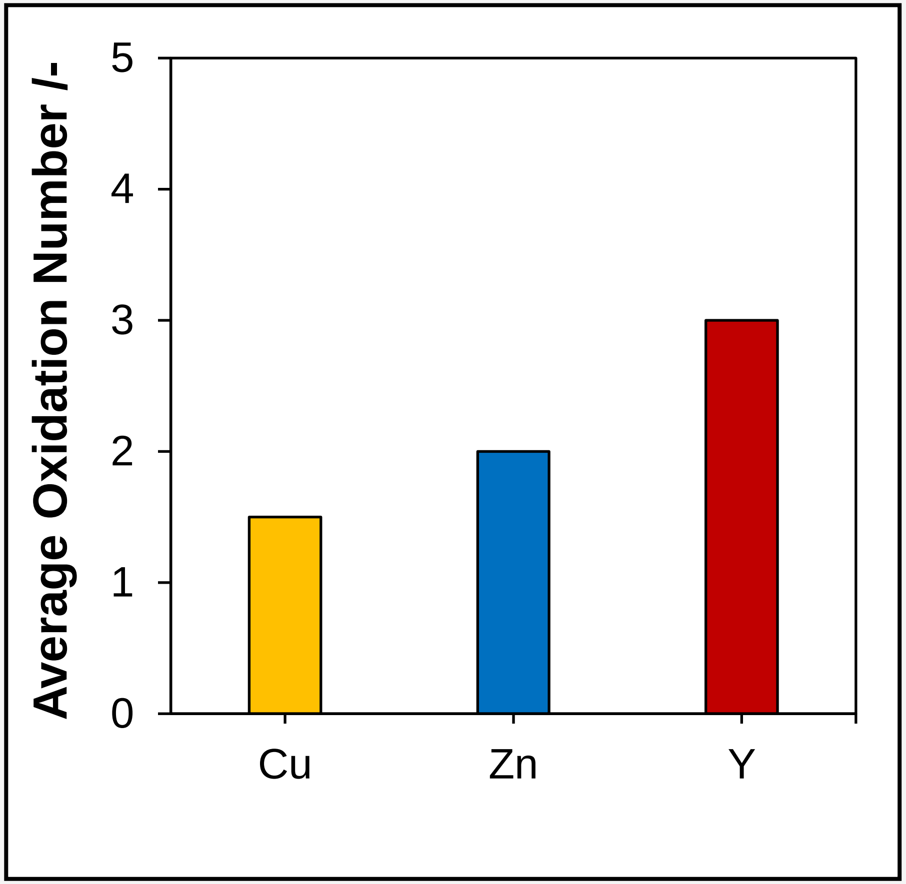
In-Situ Transmission X-ray Absorption Spectroscopy

XANES



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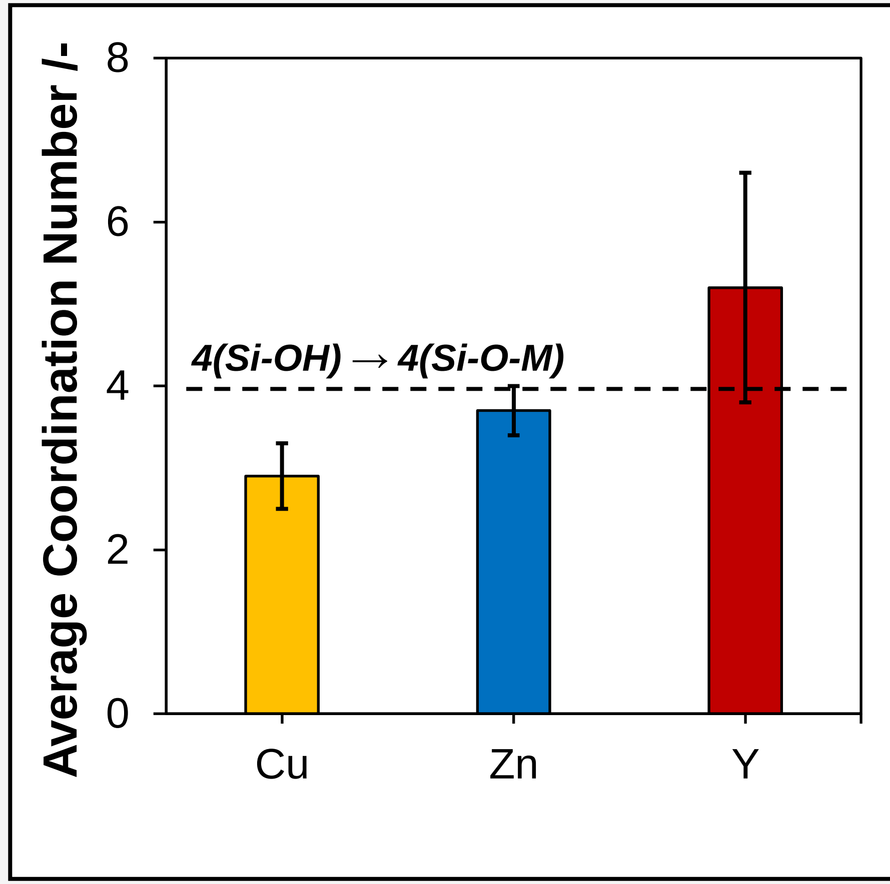
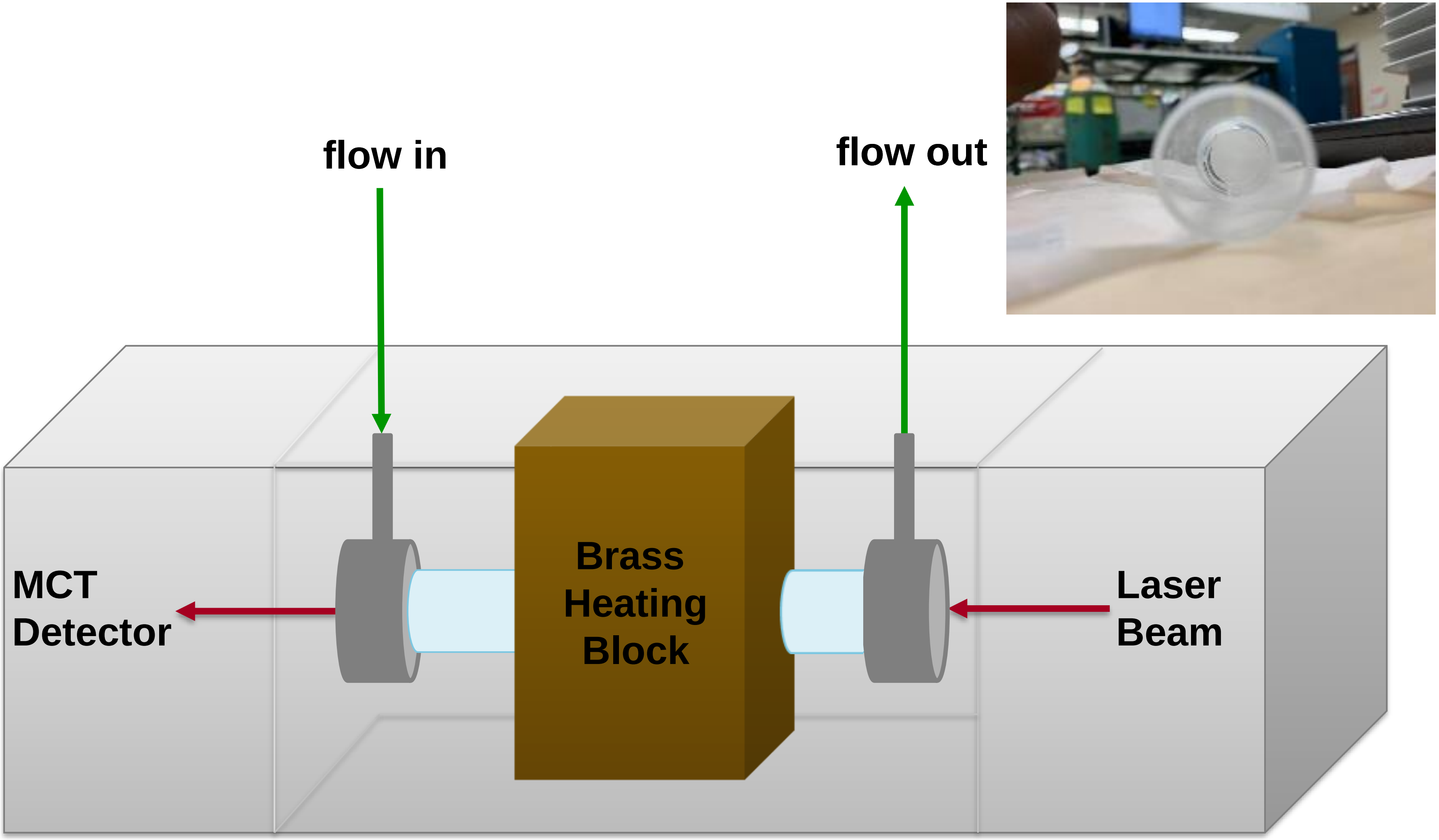


- Mixture of Y_2O_3 oligomers isolated Y sites?
- No Y_xO_y observed by HRTEM or XRD

After treatment in flowing 3.5 kPa H_2, 98 kPa He, for 2 h at 673 K

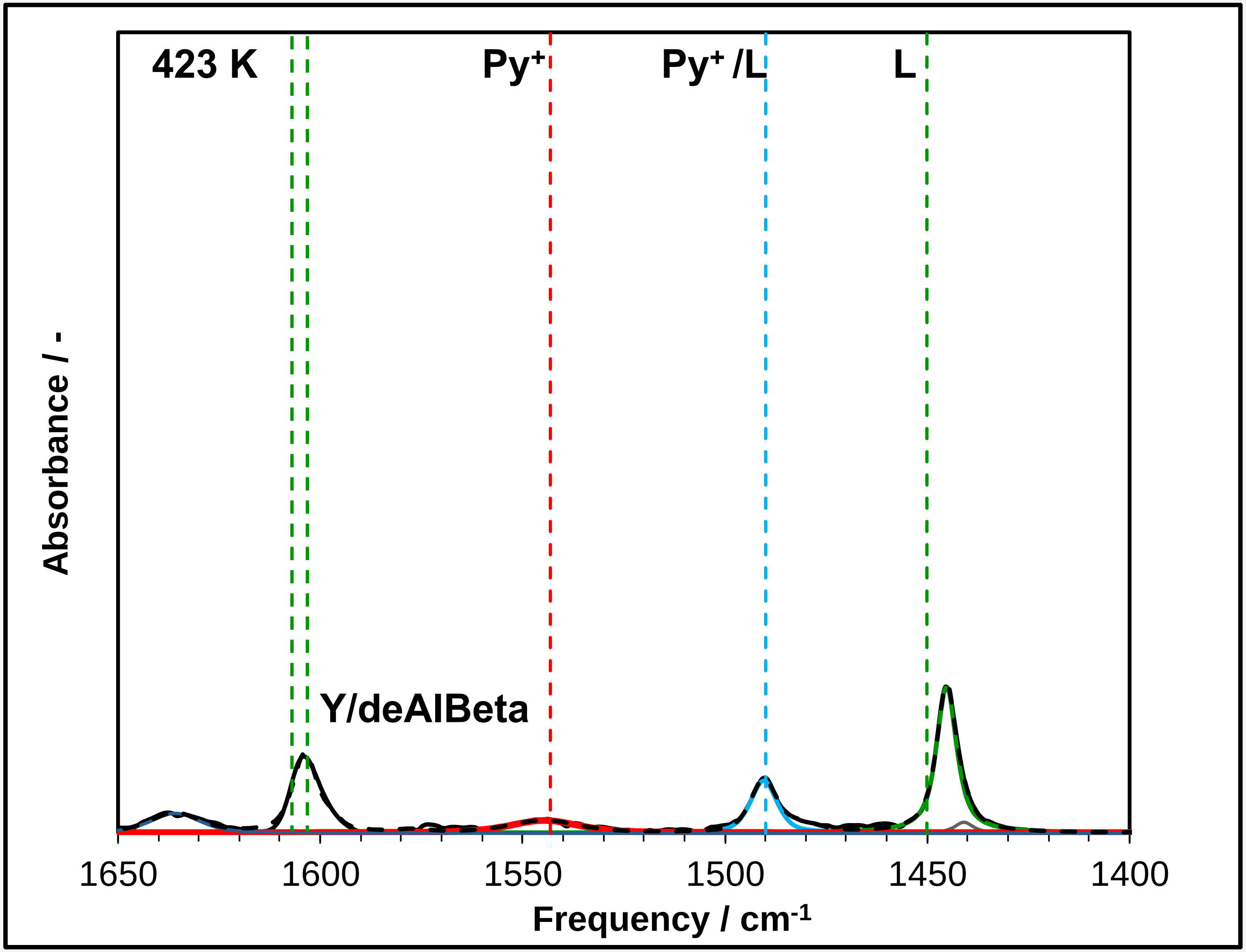
Zhang, Wegener, Samad et al., *ACS Catal.*, 11 (2021) 9885-9897

Fourier Transformed Infrared Spectroscopy

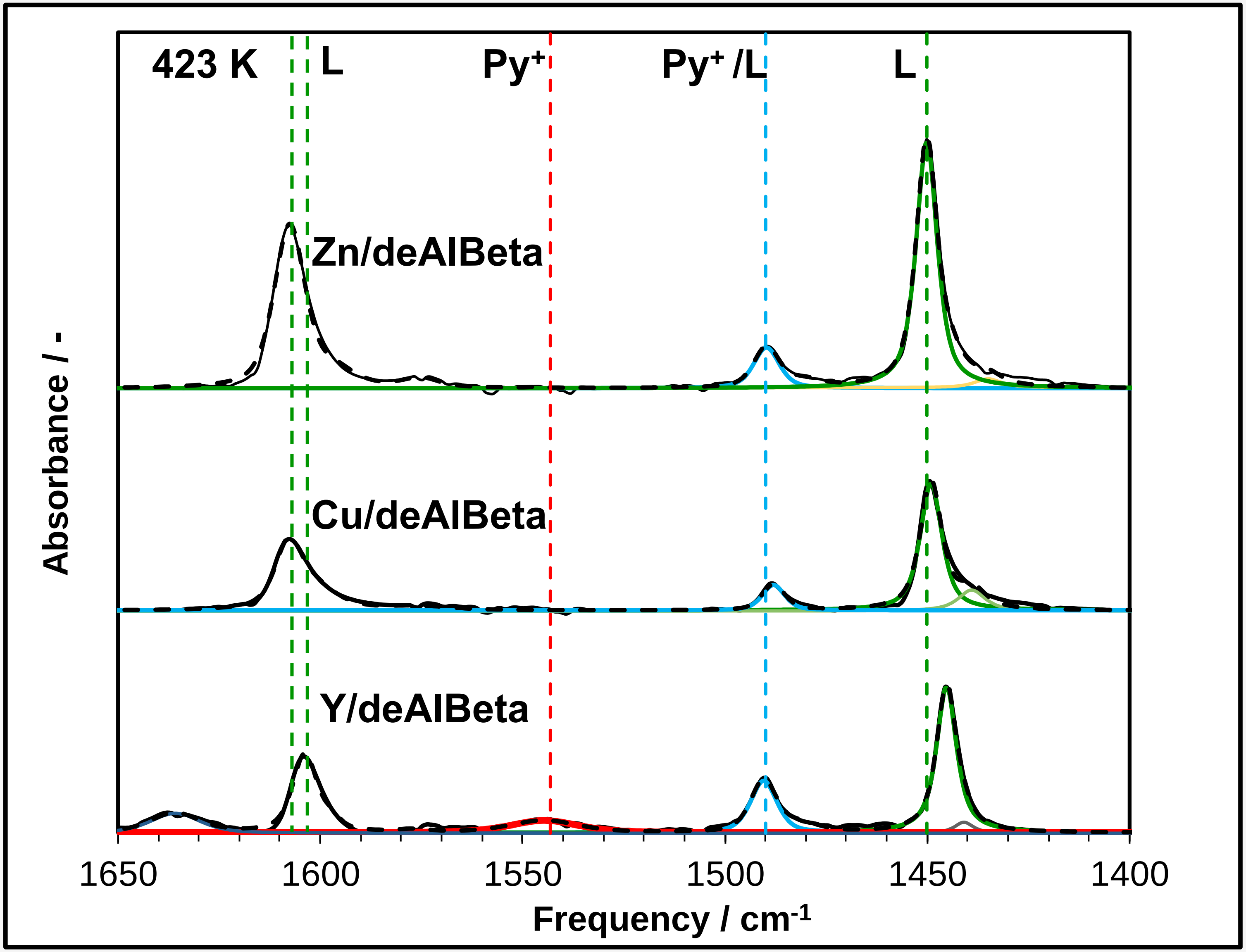


Cybulskis, Harris et al., *Rev. Sci. Inst.*, 87 (2016) 103101

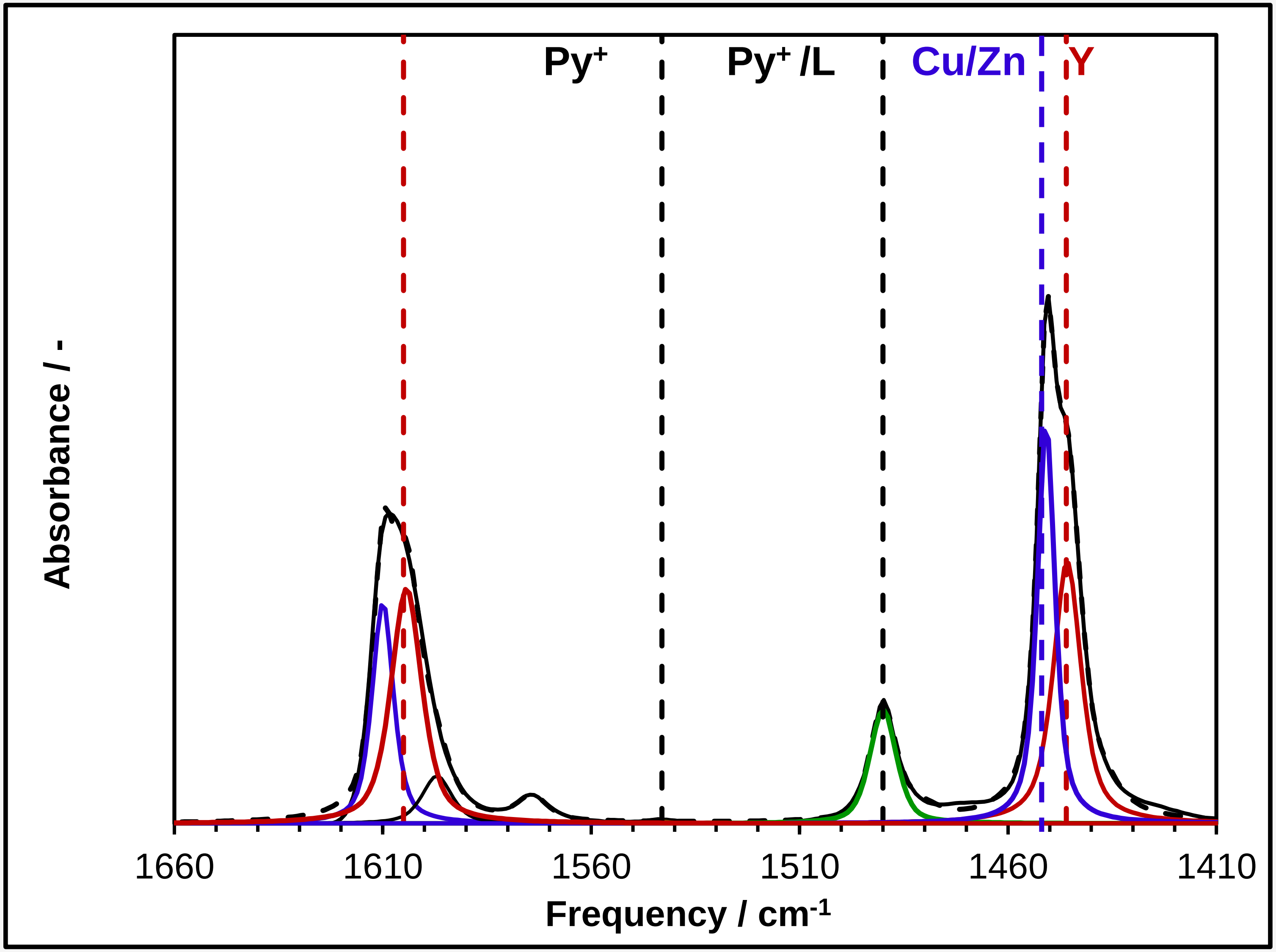
Pyridine IR: M/deAlBeta



Pyridine IR: M/deAlBeta

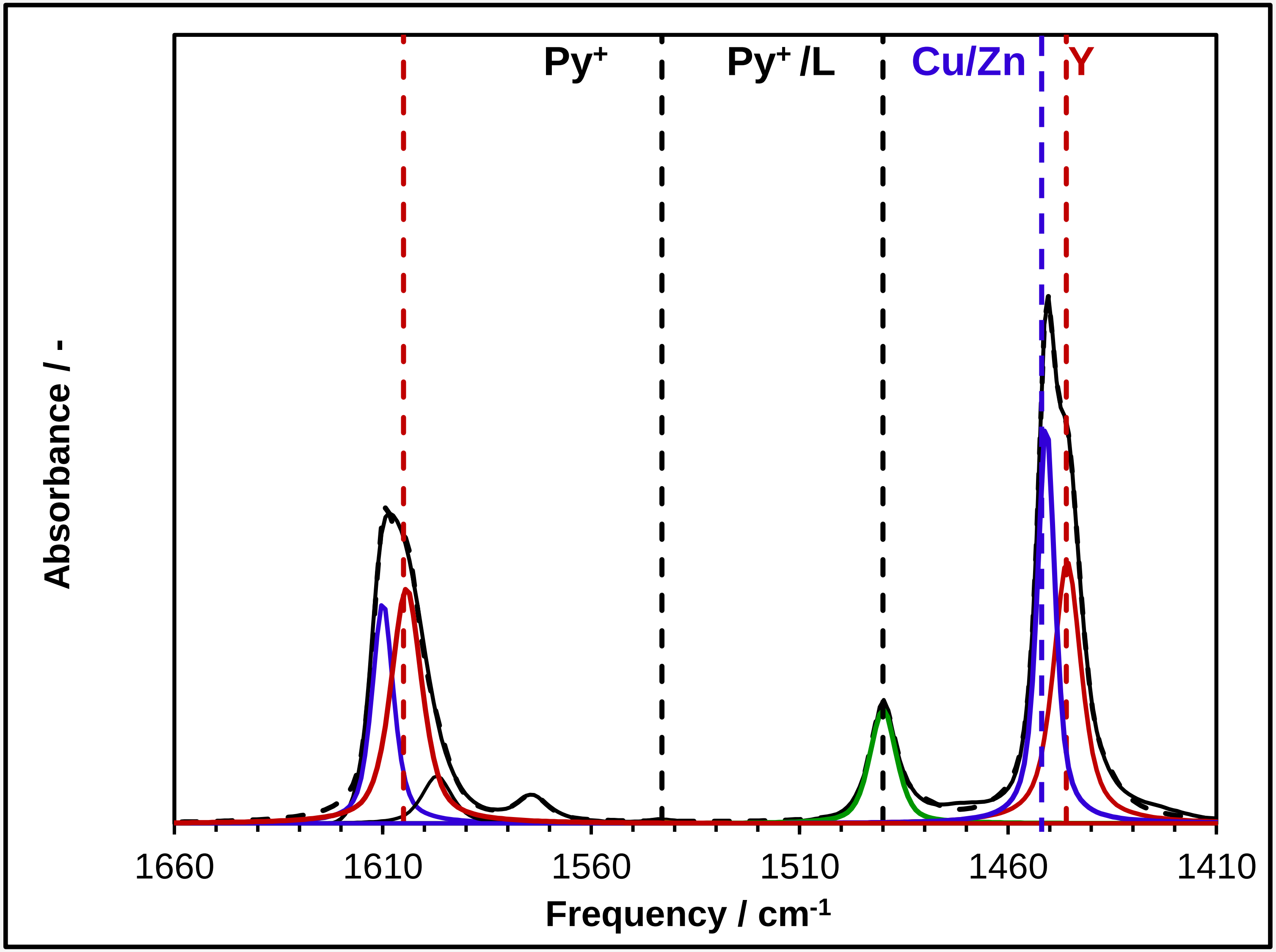


Pyridine IR: CuZnY/deAlBeta



Can distinguish Y LAS sites from Cu & Zn LAS sites…

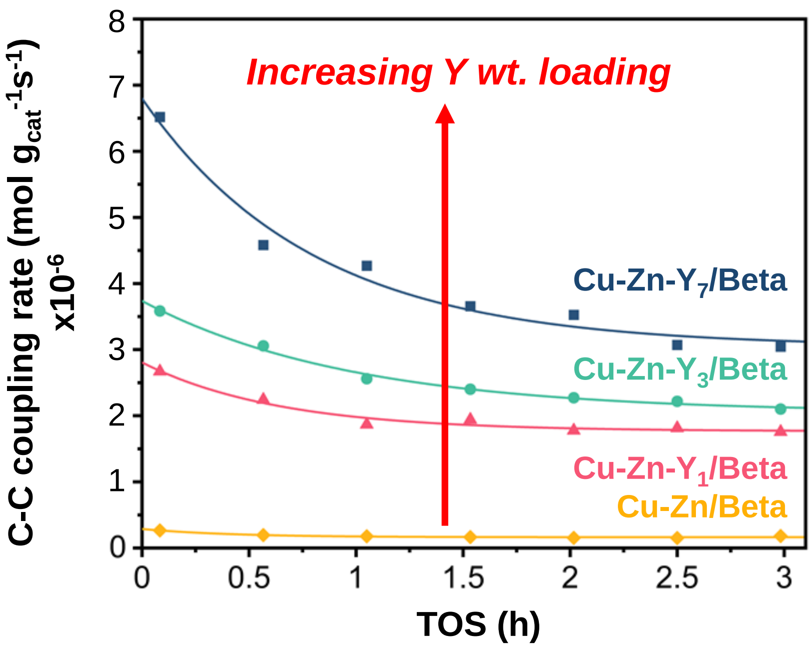
Pyridine IR: CuZnY/deAlBeta



Can distinguish Y LAS sites from Cu & Zn LAS sites… and Py^+ no longer present in CuZnY/Beta

Measurement of product formation rates on CuZnY/deAlBeta

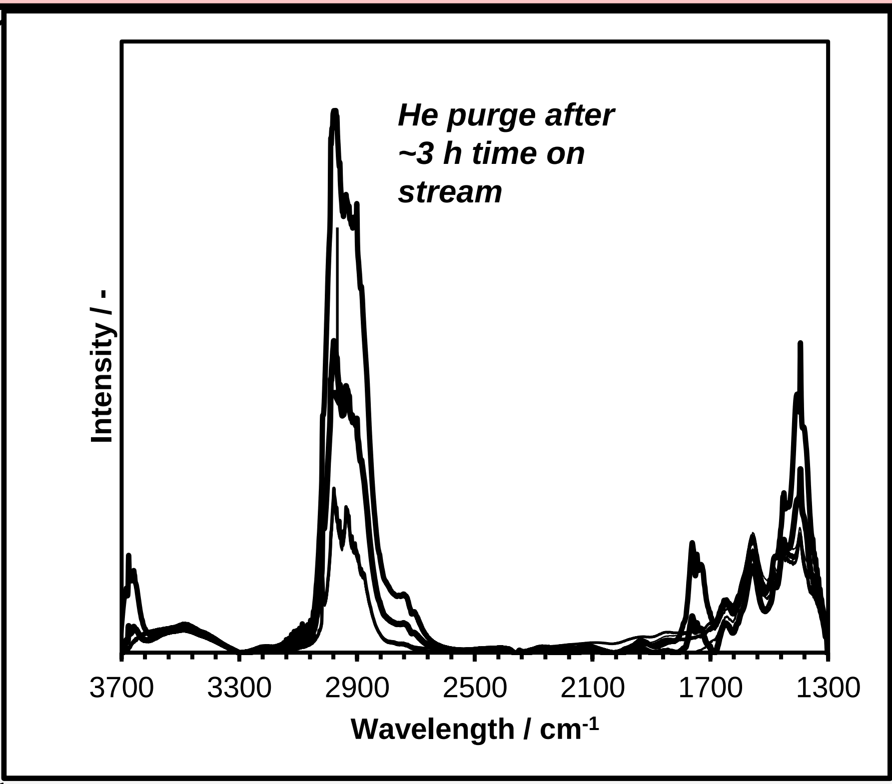
$$r_{C-C\ coupling} = \frac{(r_{butenes} + r_{butadiene} + r_{C4aldehydes} + 2 \times r_{hexenes} + 3 \times r_{octenes})}{m_c}$$

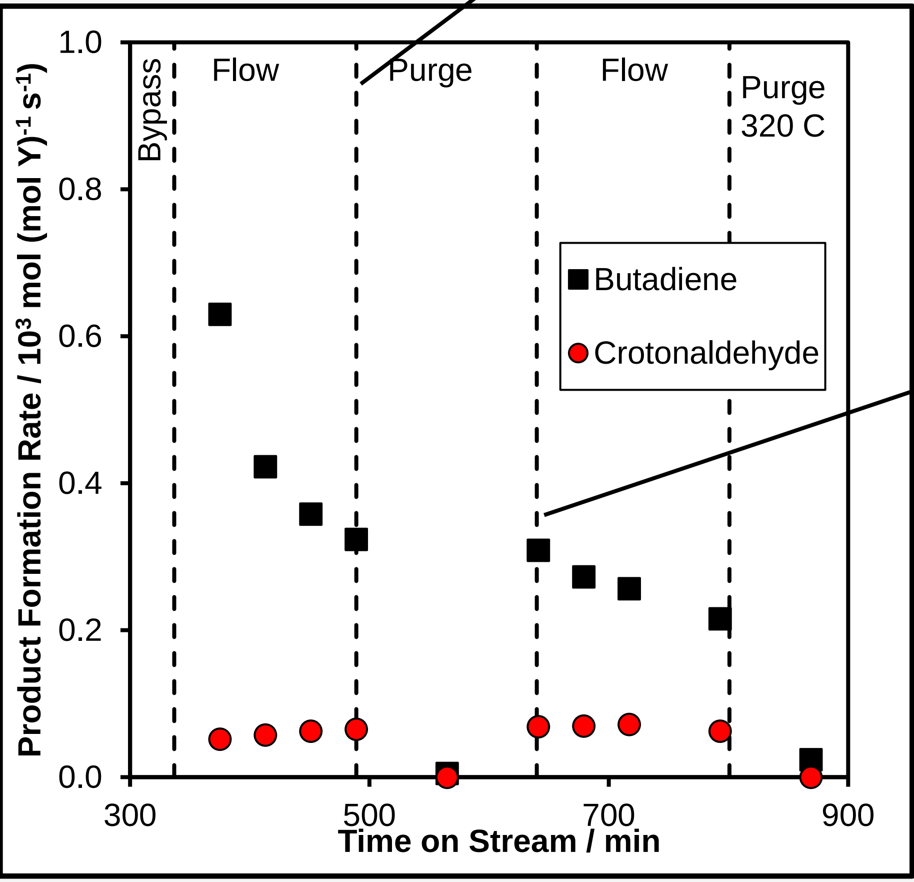


***Data Collected by Junyan Zhang, ORNL**

Zhang, Wegener, Samad et al., *ACS Catal.,* 11 (2021) 9885-9897
See also: Cordon, Samad, et al., *ACS Sus. Chem. Eng.*, 10 (2022) 5702-5707 (CuLa/deAlBeta)

Flow experiment on $Y_{9.8\%}$/Beta in IR cell





$Y_{9.8}$/Beta; T=503 K and 593 K

Flow mode

Total flowrate 100 $cm^3\ min^{-1}$, CH_4 (1.04% in He) as internal standard, reactant partial pressures (p_{AcH} = 0.0048, p_{EtOH} = 0.03) kept constant.

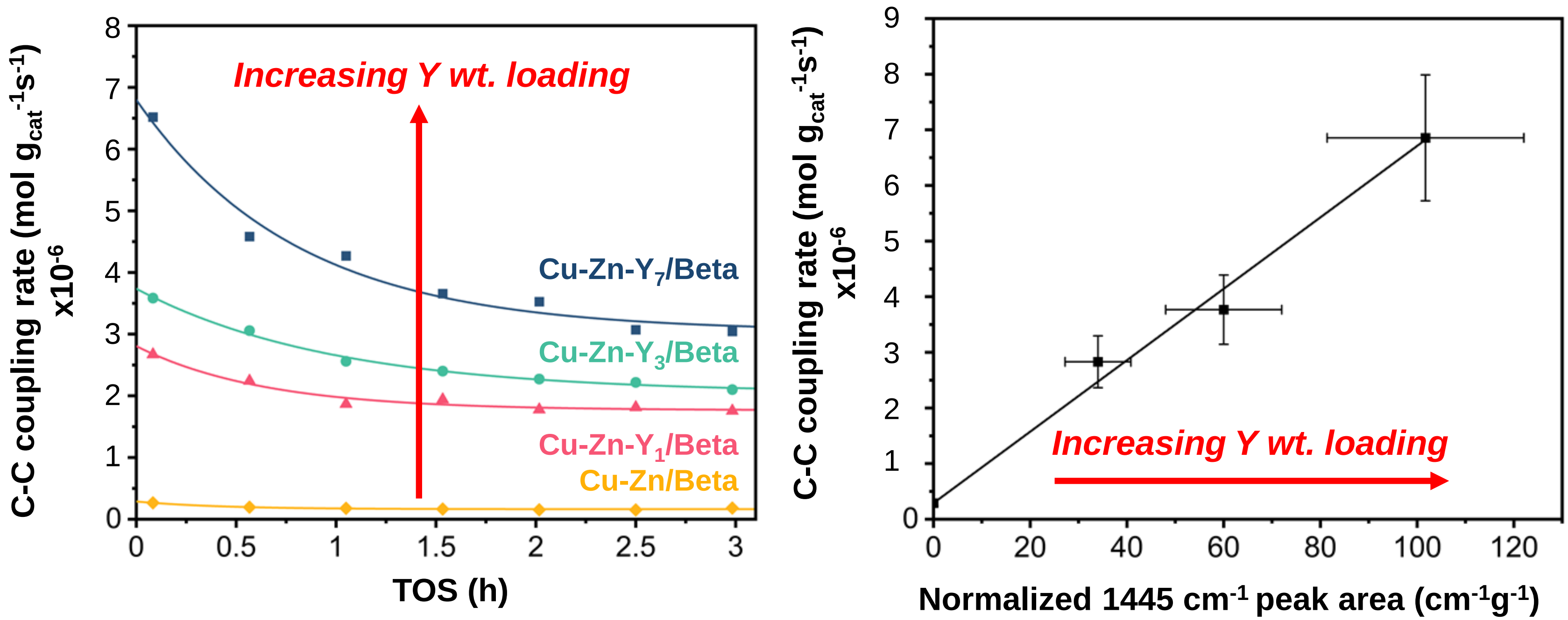
Purge mode

Reactants (EtOH and AcH) switched off during He purge mode. Total flowrate 100 $cm^3\ min^{-1}$, CH_4 (1.04% in He) as internal standard.

Borate et al., *in prep*

Measurement of product formation rates on CuZnY/deAlBeta

$$r_{C-C\ coupling} = \frac{(r_{butenes} + r_{butadiene} + r_{C4aldehydes} + 2 \times r_{hexenes} + 3 \times r_{octenes})}{m_c}$$



*Data Collected by Junyan Zhang, ORNL

Zhang, Wegener, Samad et al., *ACS Catal.,* 11 (2021) 9885-9897
See also: Cordon, Samad, et al., *ACS Sus. Chem. Eng.*, 10 (2022) 5702-5707 (CuLa/deAlBeta)

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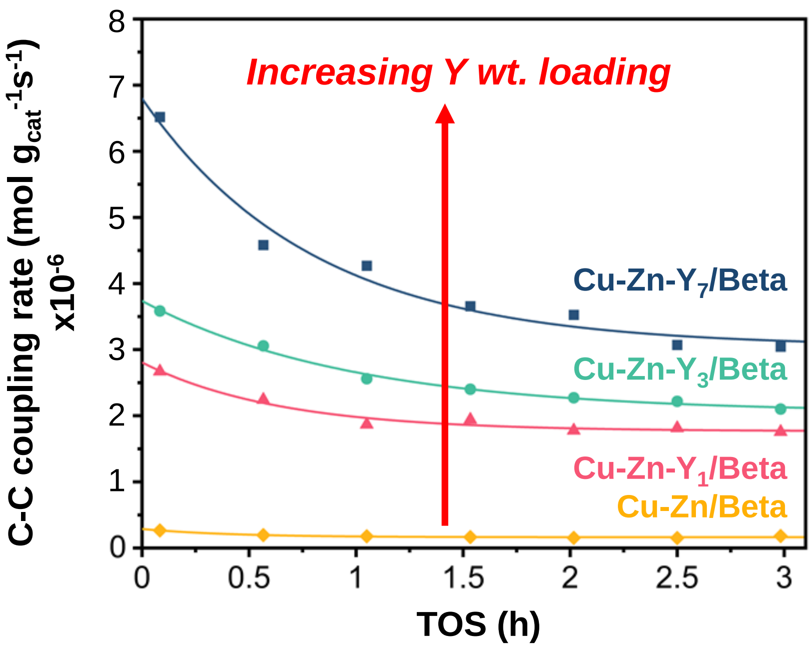

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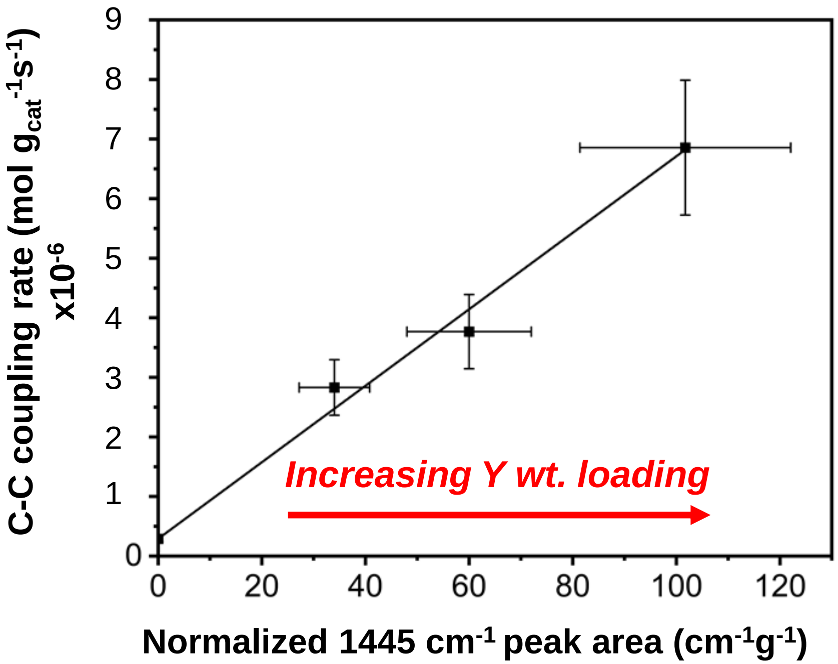

C-C coupling rates correlate linearly with Y_{LAS} density measured by pyridine IR

Zhang, Wegener, Samad et al., *ACS Catal.,* 11 (2021) 9885-9897

See also: Cordon, Samad, et al., *ACS Sus. Chem. Eng.*, 10 (2022) 5702-5707 (CuLa/deAlBeta)

Quantification of IMECS to Enable Quantitative Chemisorption IR

Beer-Lambert law

$$A = \varepsilon \, b \, C$$

A = absorbance
ε = molar extinction coefficient
b = path length
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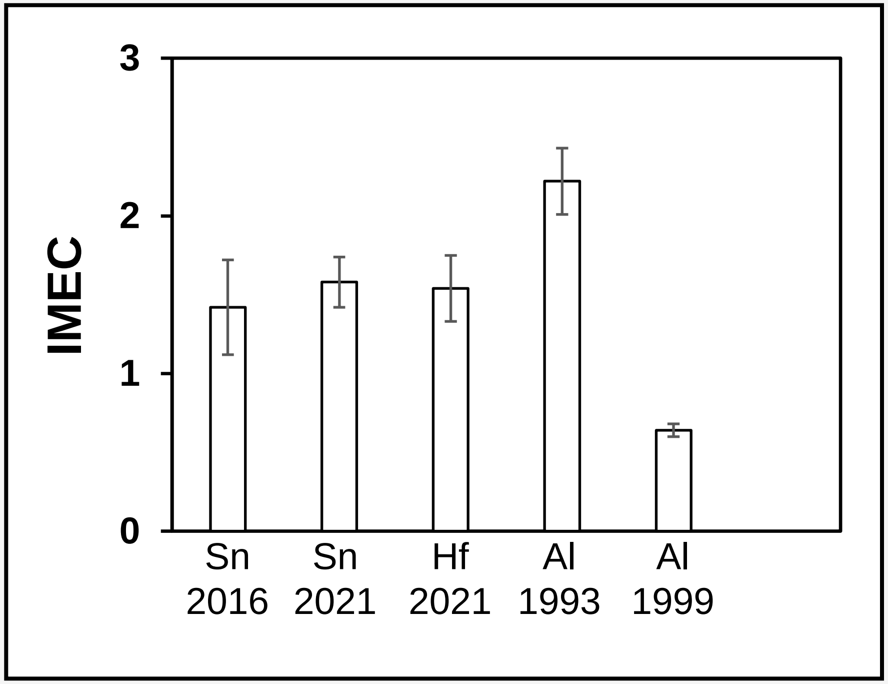

C. A. Emeis., *J Catal*., 141 (1993) 347-354
Selli and Forni, *Micropor. Mesopor. Mat*., 31 (1999) 129 - 140
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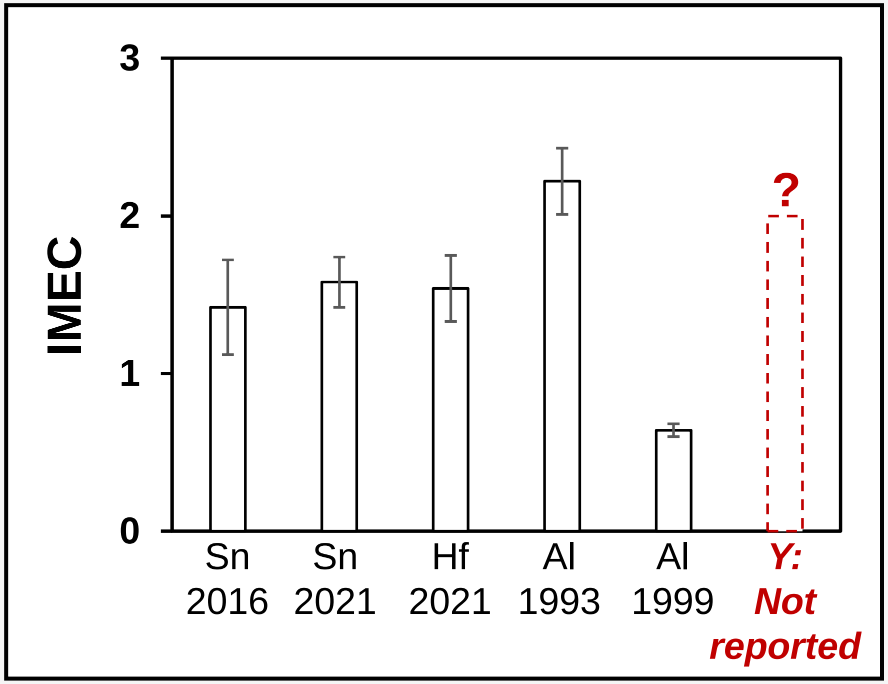

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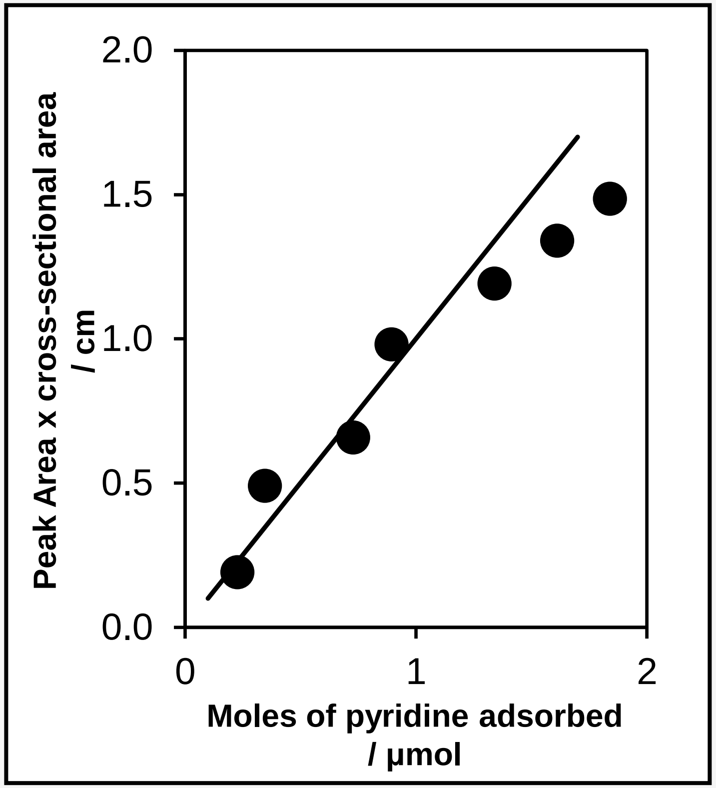

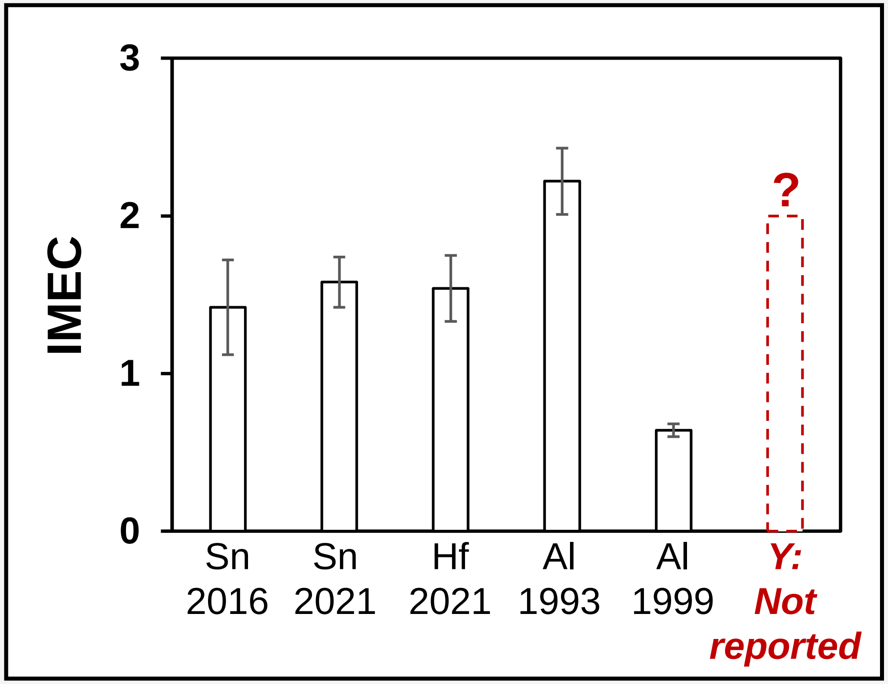

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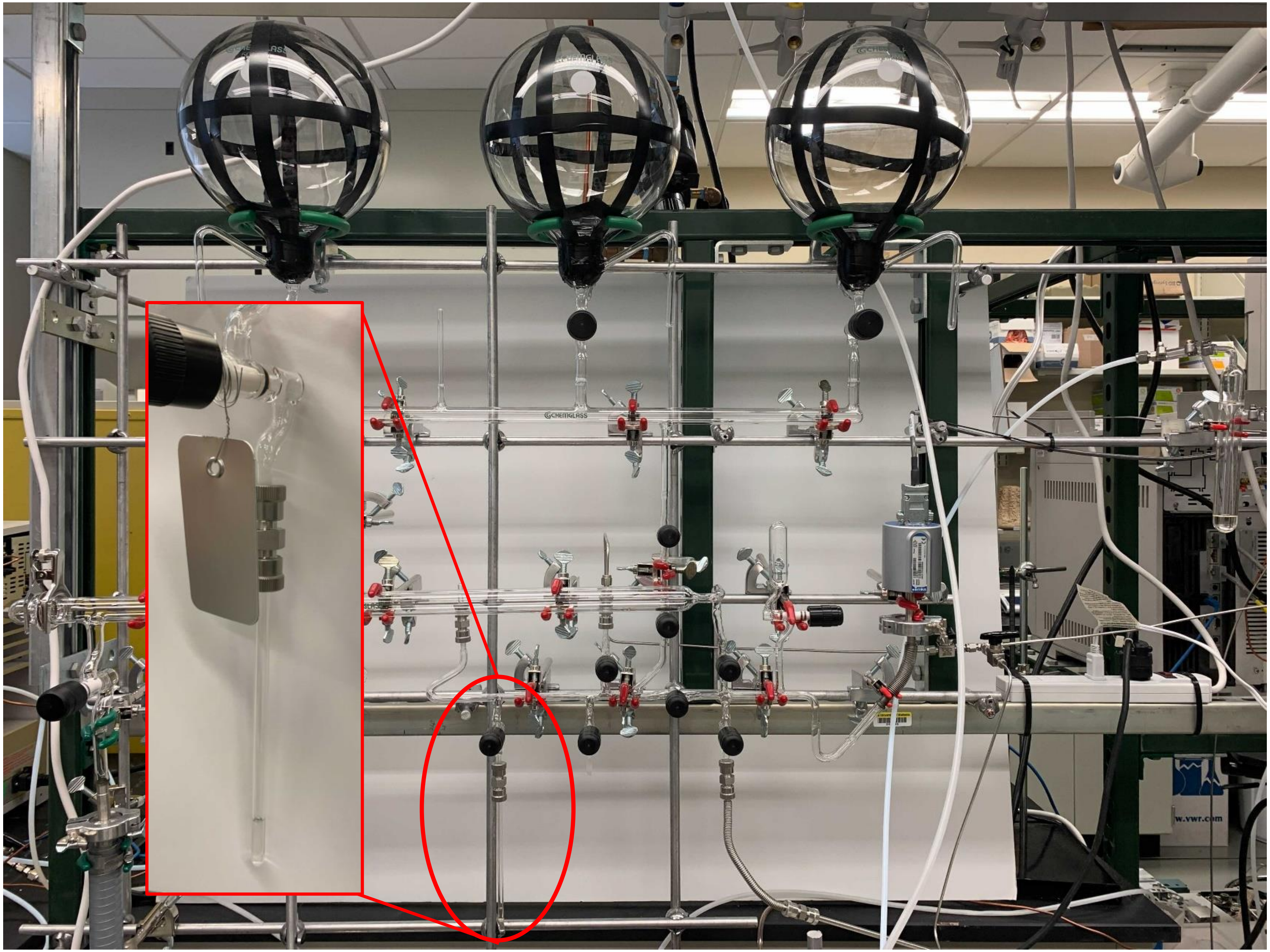
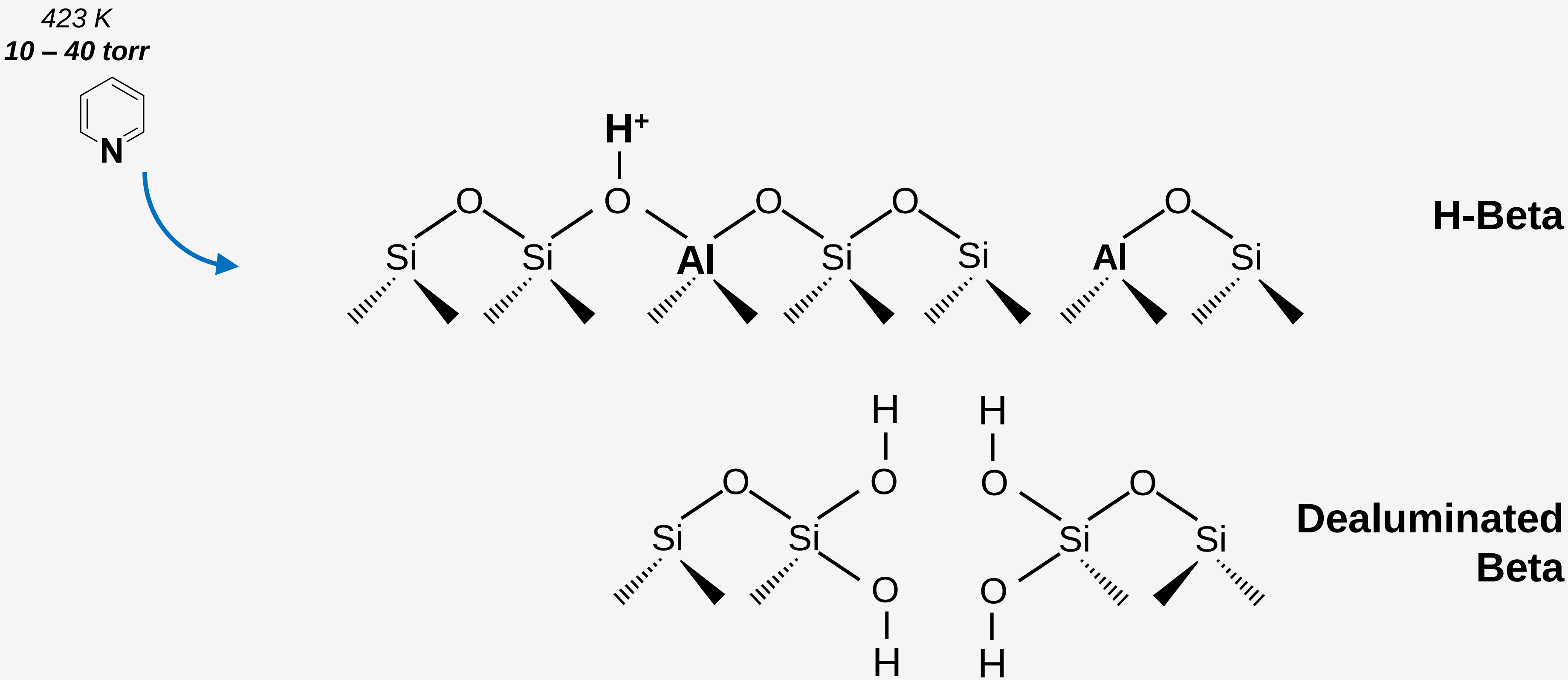
Custom Glass Vacuum Manifold

Custom Glass Vacuum Manifold



Pyridine Adsorption on Dealuminated Beta



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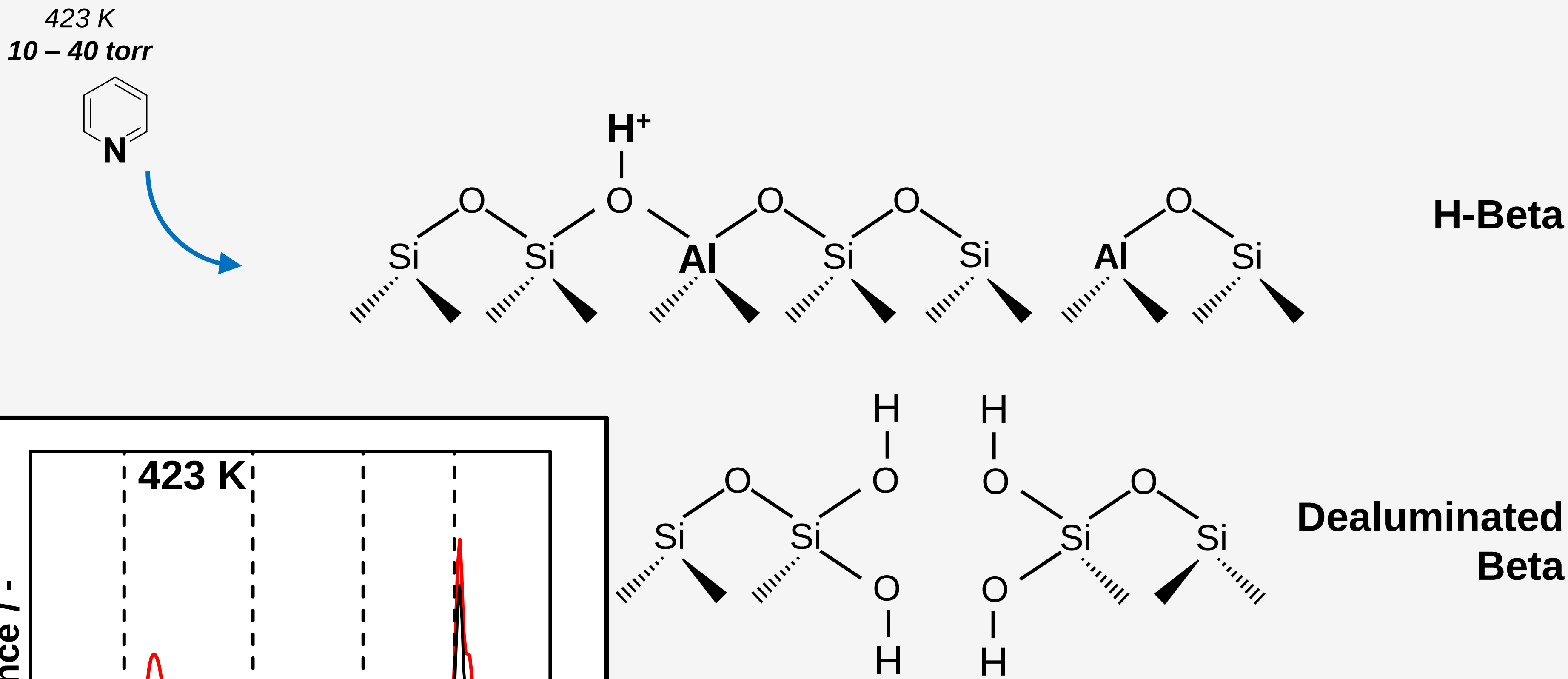
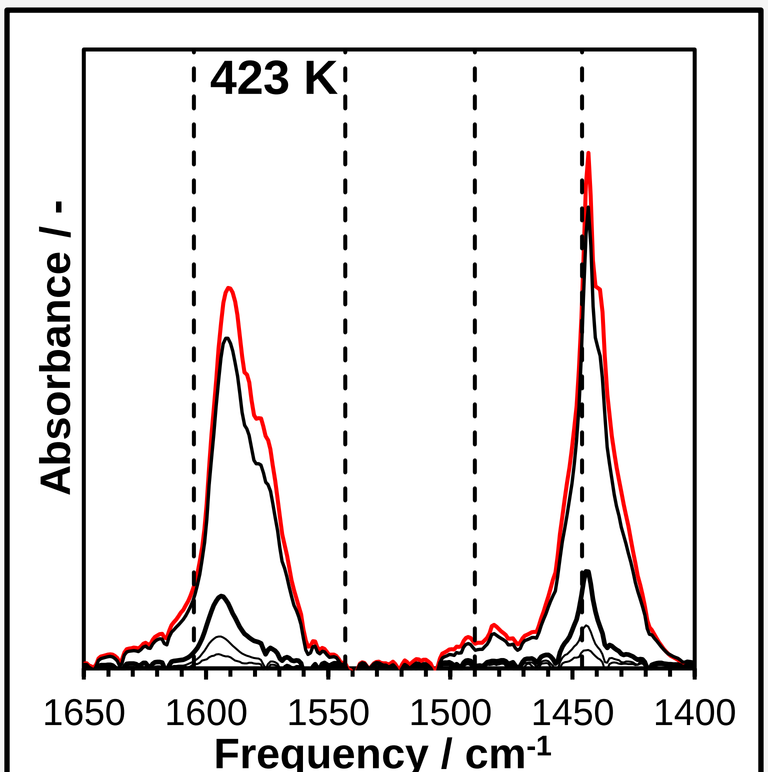
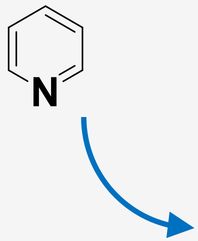


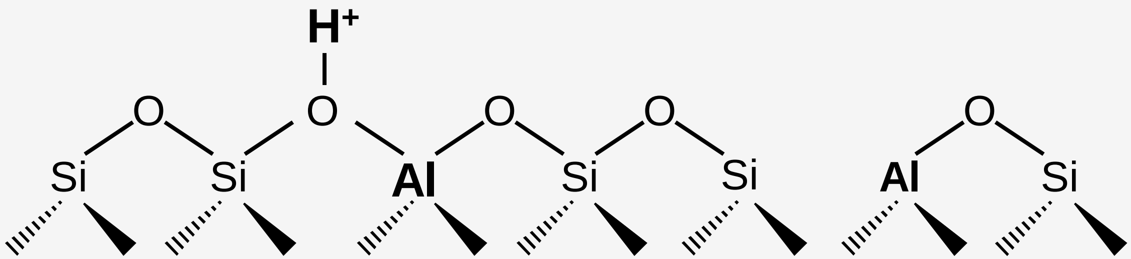


- **Red = pyridine flow**
- Black = He purge

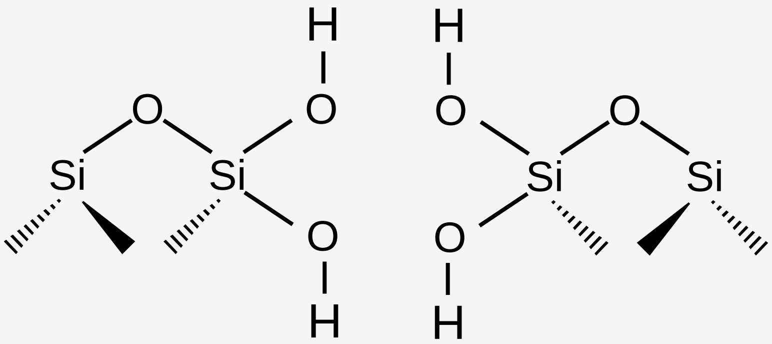
Pyridine Titration of Lewis Acid Sites

423 K
10 – 40 torr



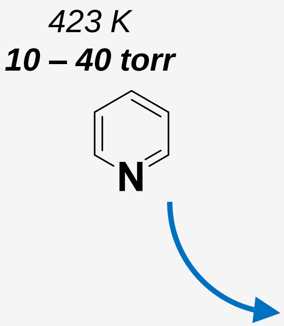


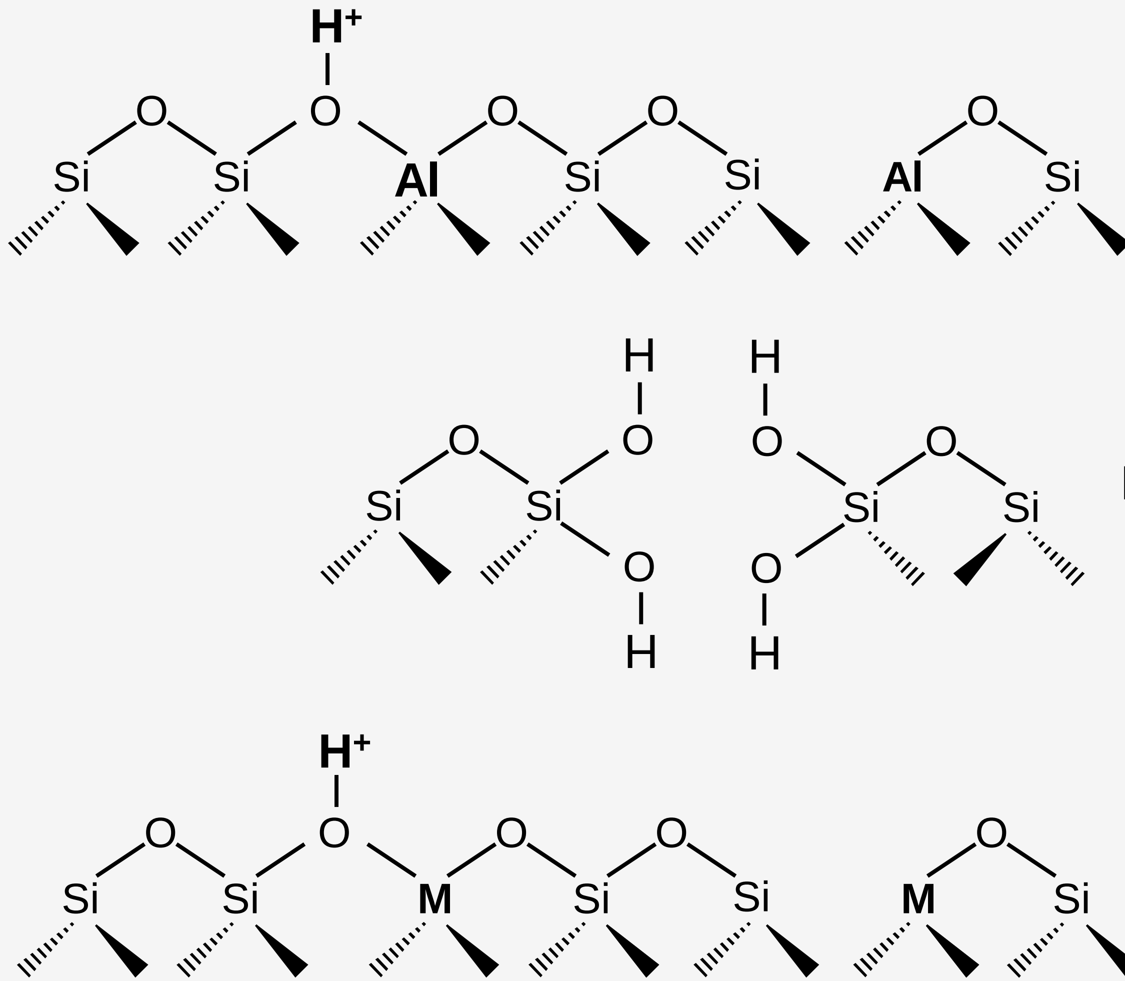
H-Beta



Dealuminated Beta

Pyridine Titration of Lewis Acid Sites





H-Beta

Dealuminated Beta

M Beta

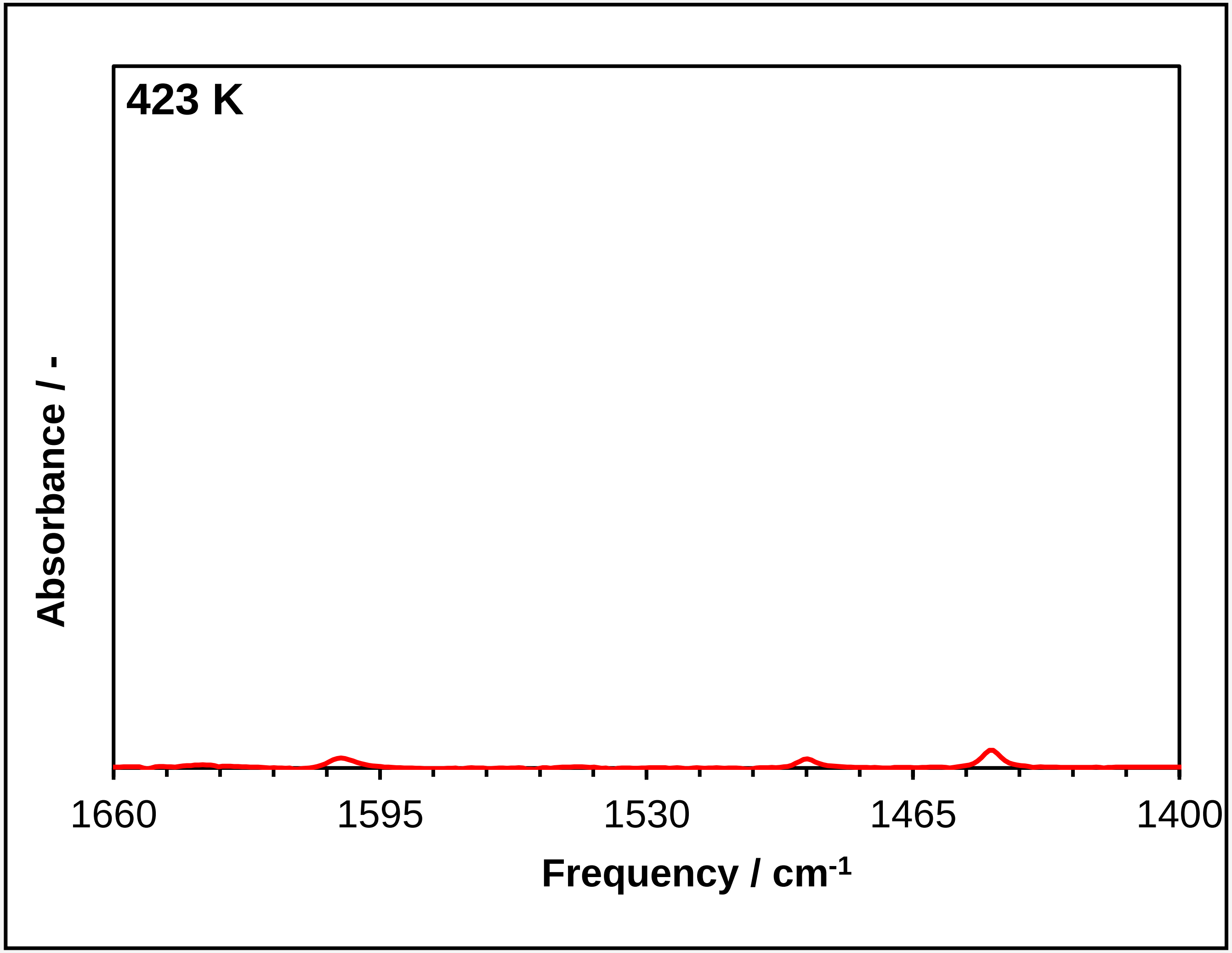
We would expect Y-containing zeolites to have charge balancing protons (akin to aluminosilicate zeolites)

Pyridine Titration on Y/deAlBeta Under Vacuum

Step 1: Dose

Step 2: Saturate

Step 3: Evacuate



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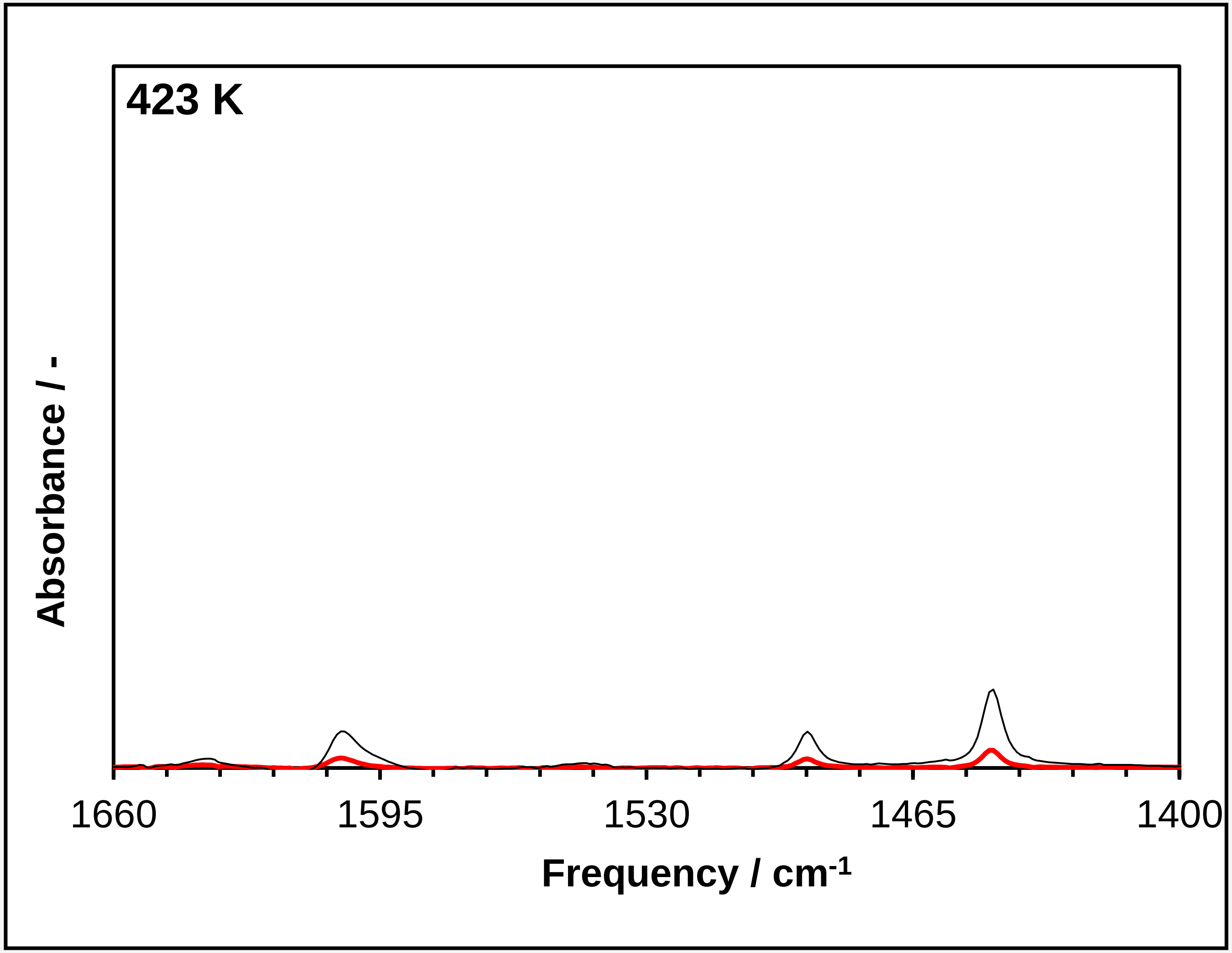

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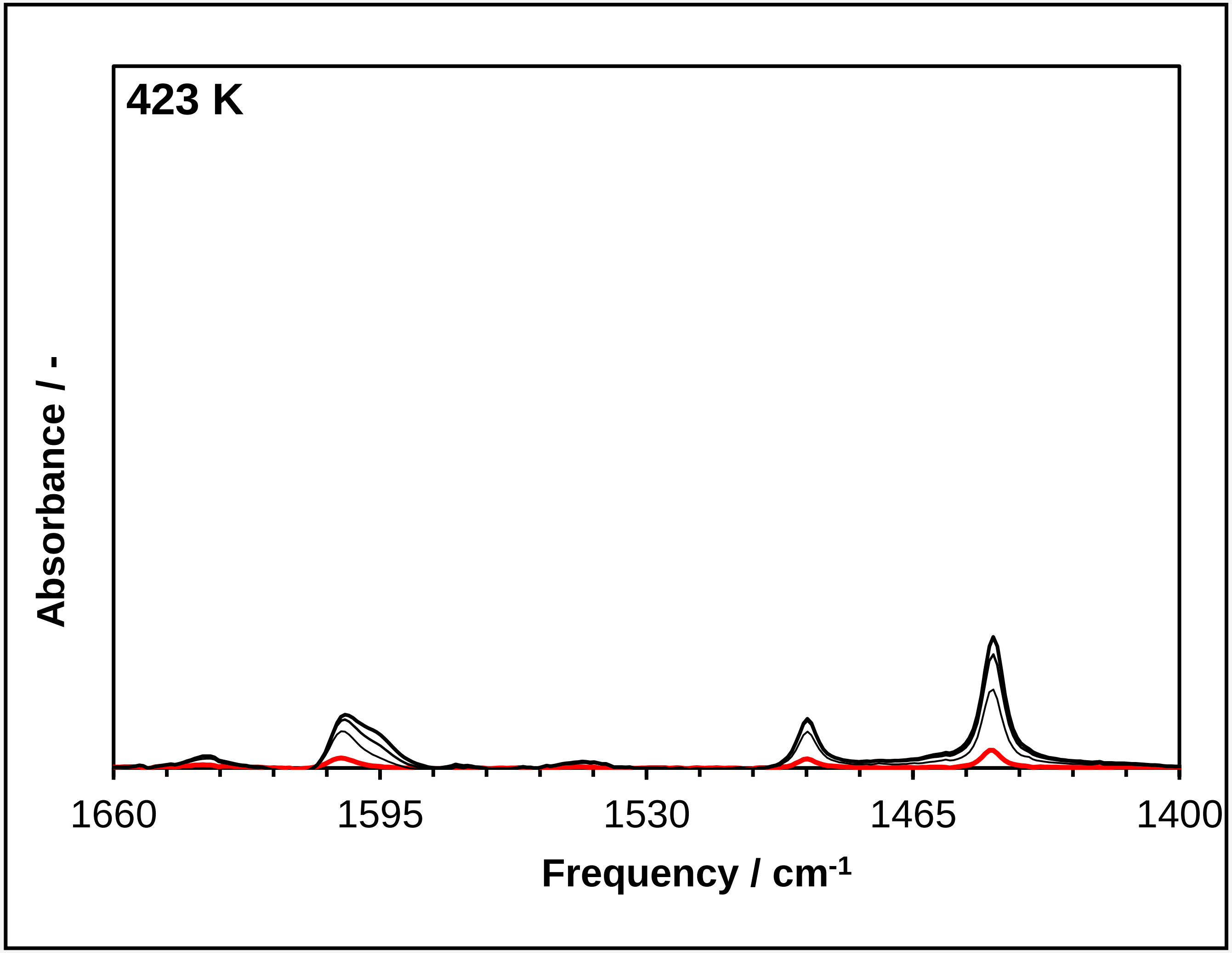

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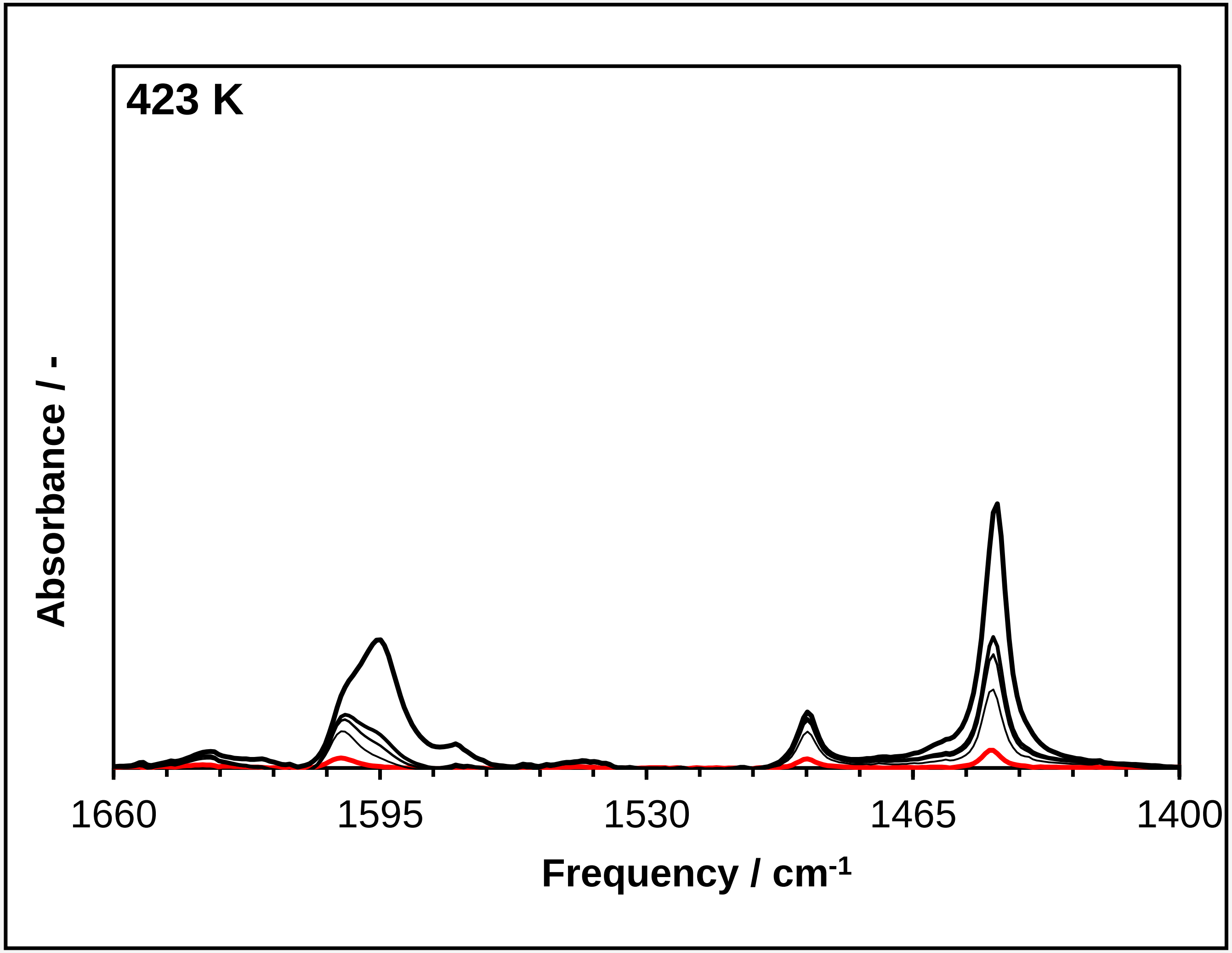

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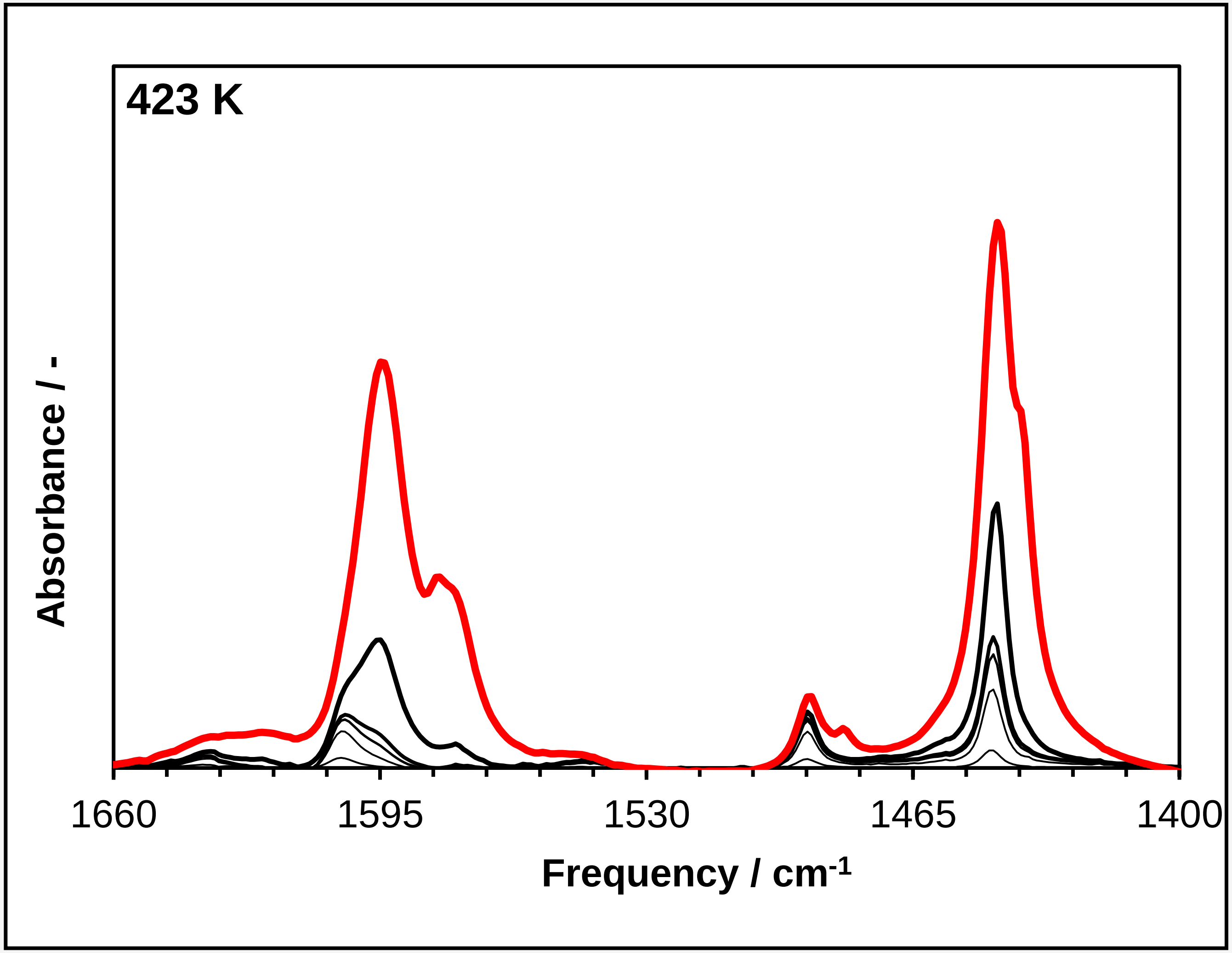

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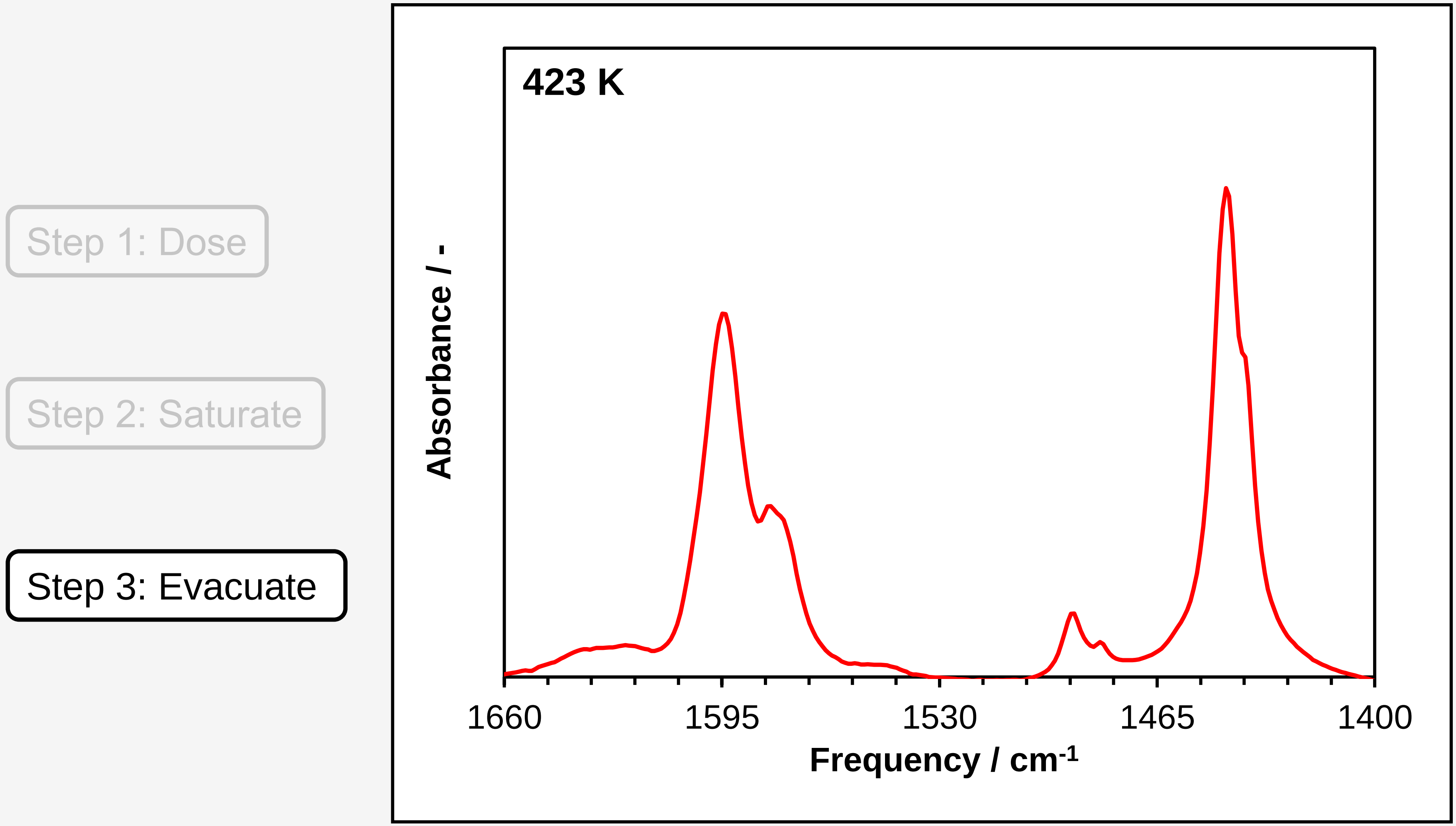

- Red = saturated pyridine dose

Pyridine Titration on Y/deAlBeta Under Vacuum

Step 1: Dose

Step 2: Saturate

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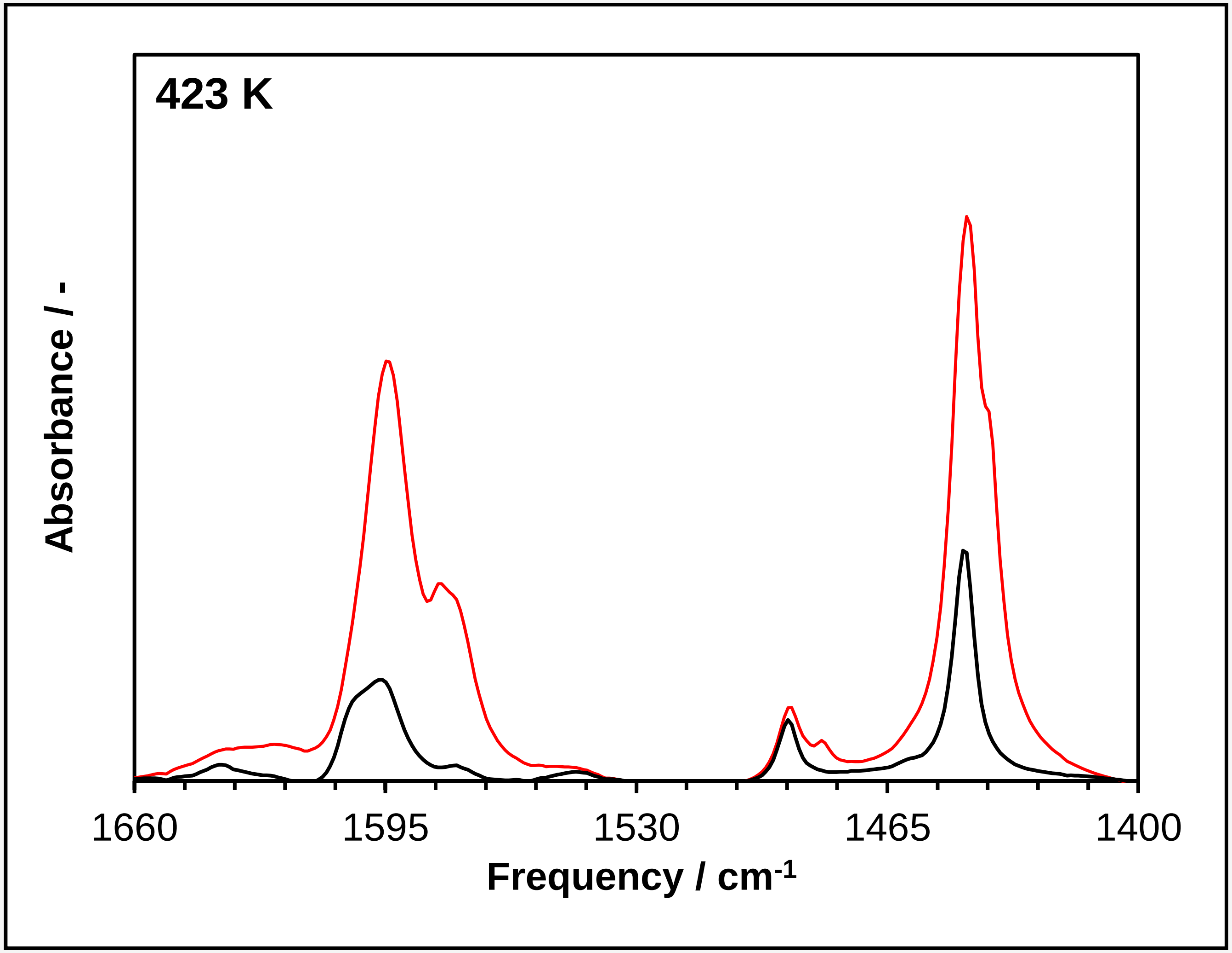

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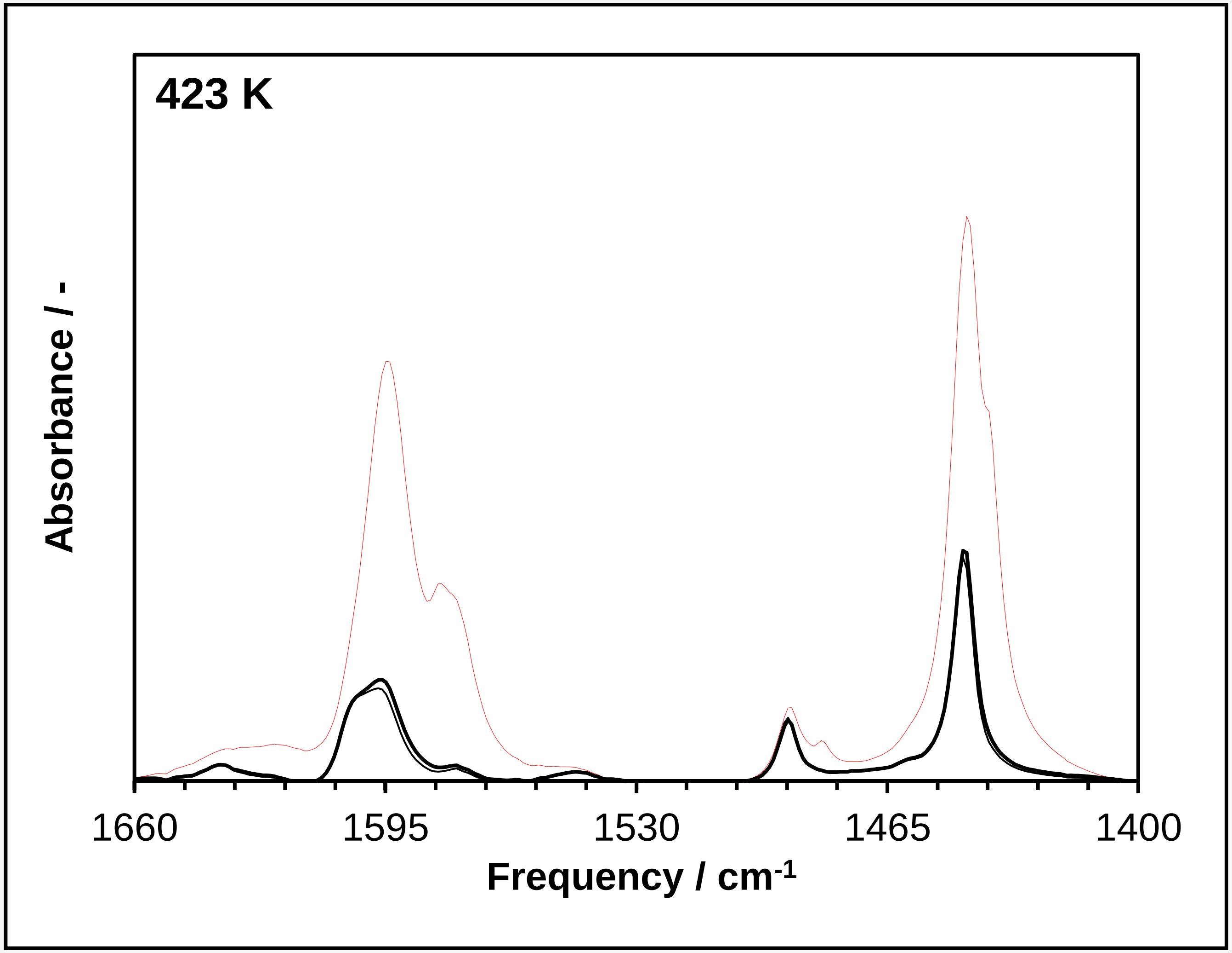

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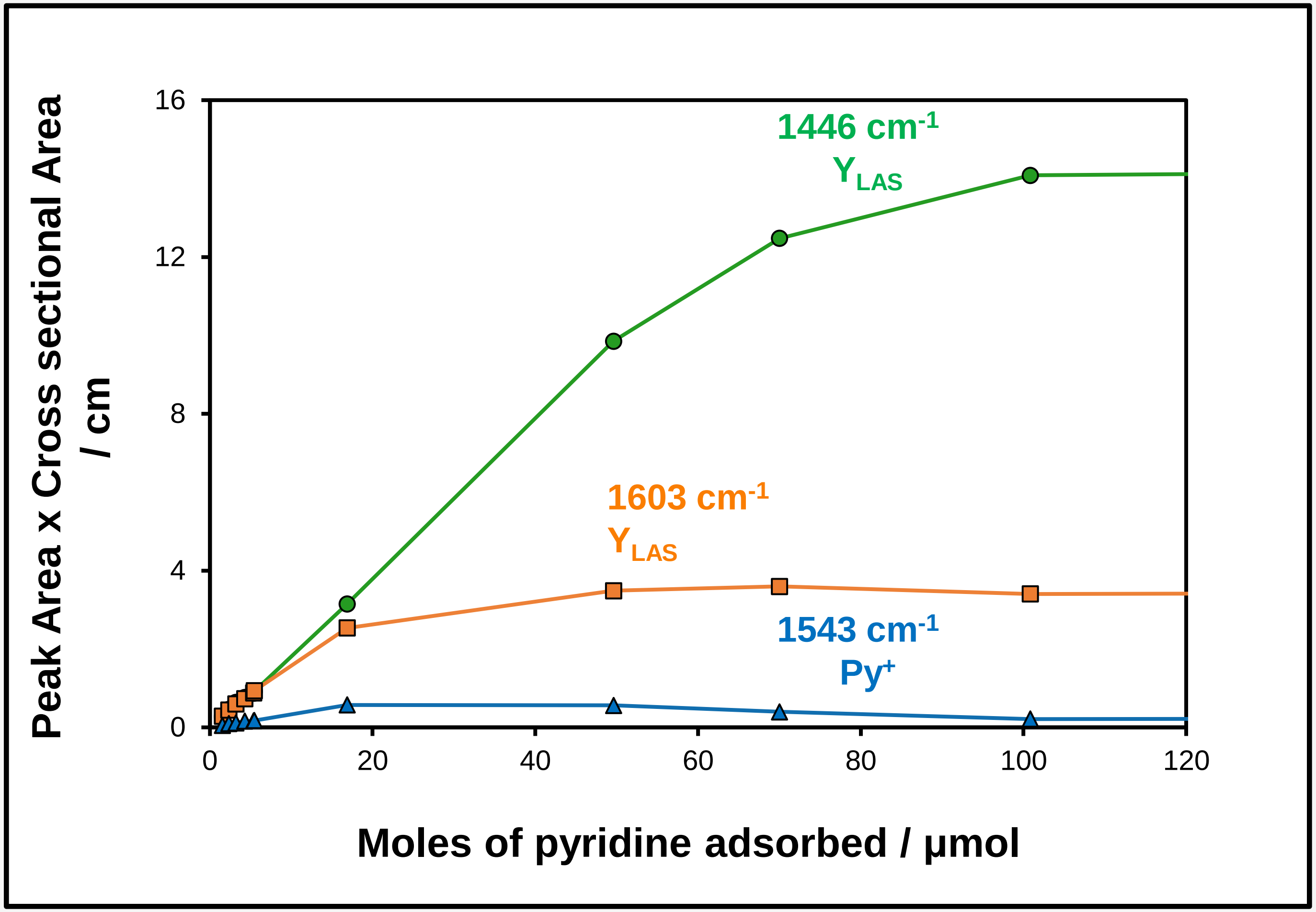
IMEC for Pyridine Bound to Lewis Acidic Y sites (Y_{10}/deAlBeta)



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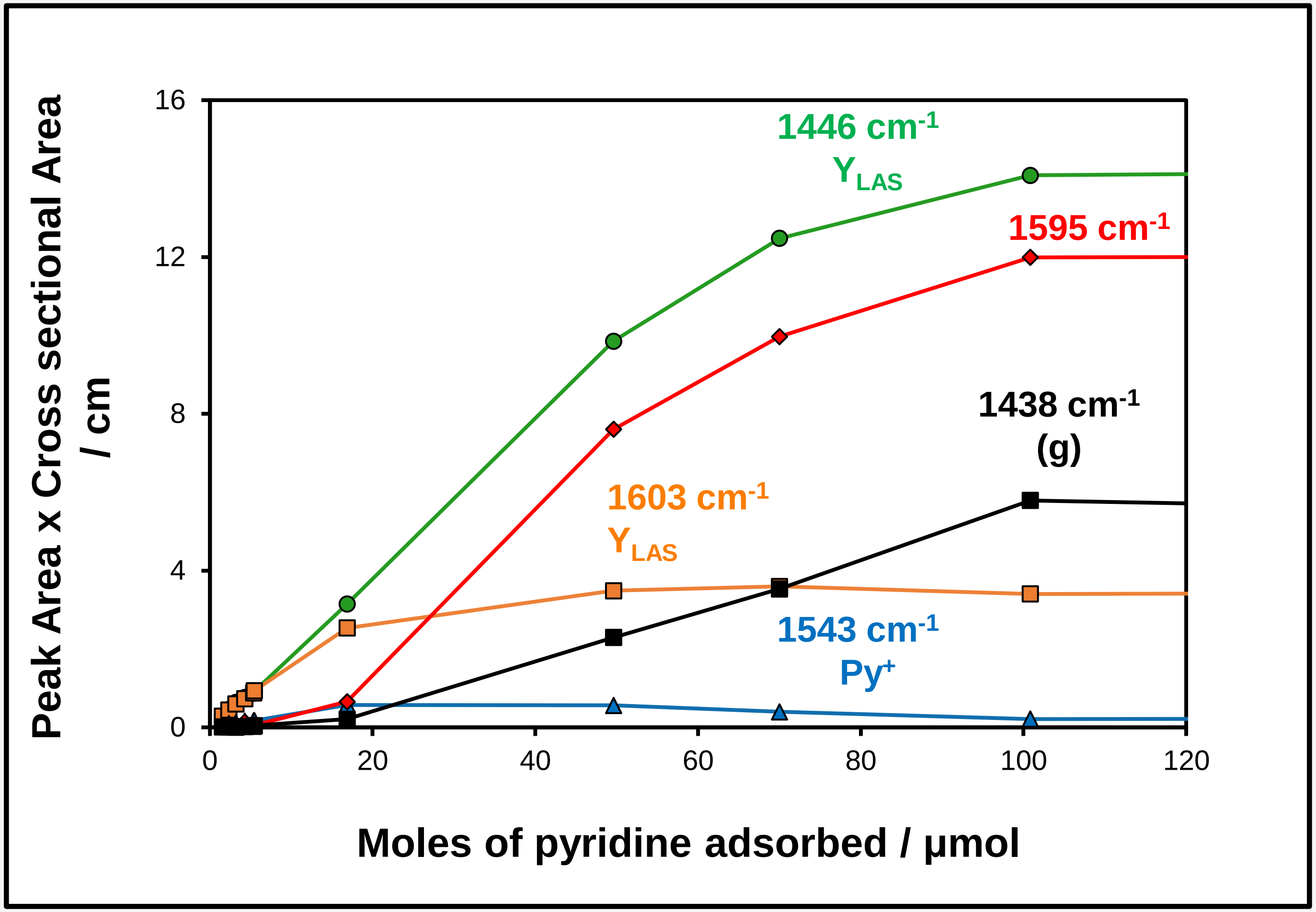
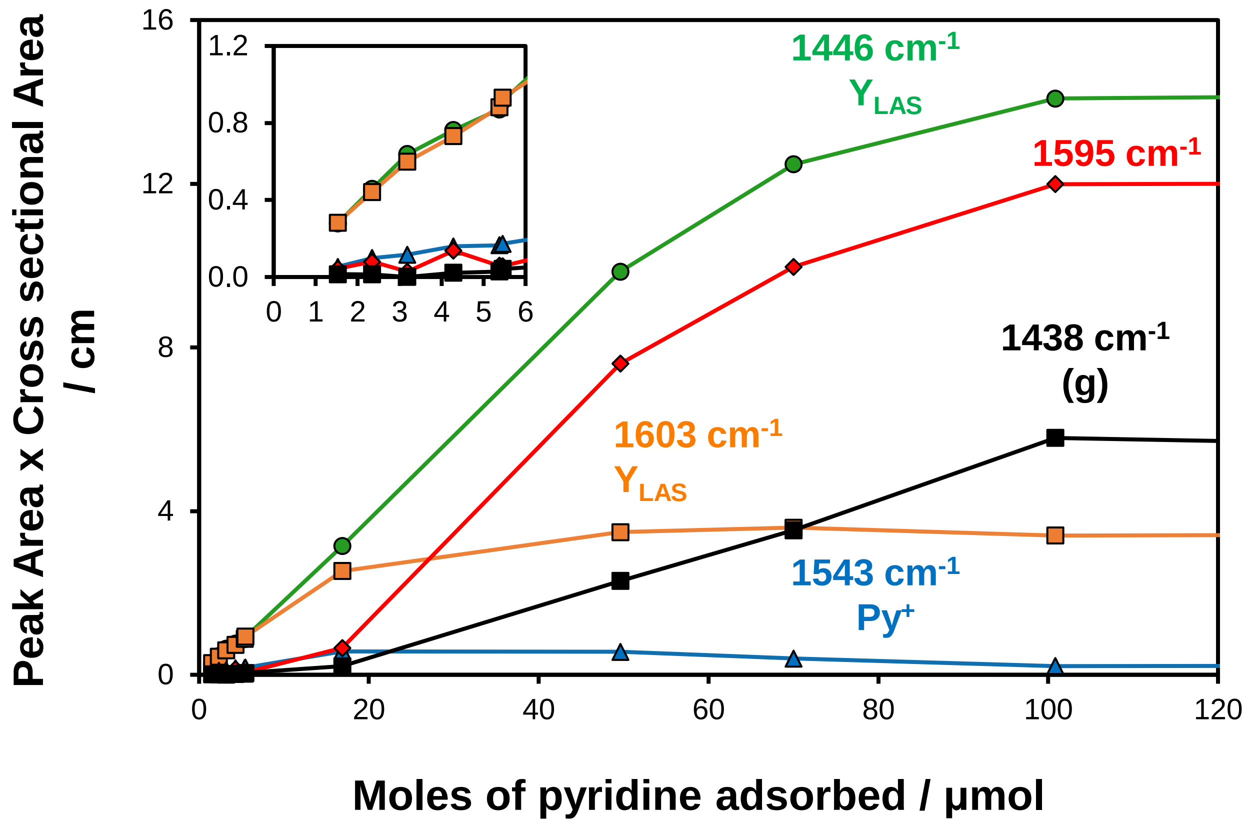


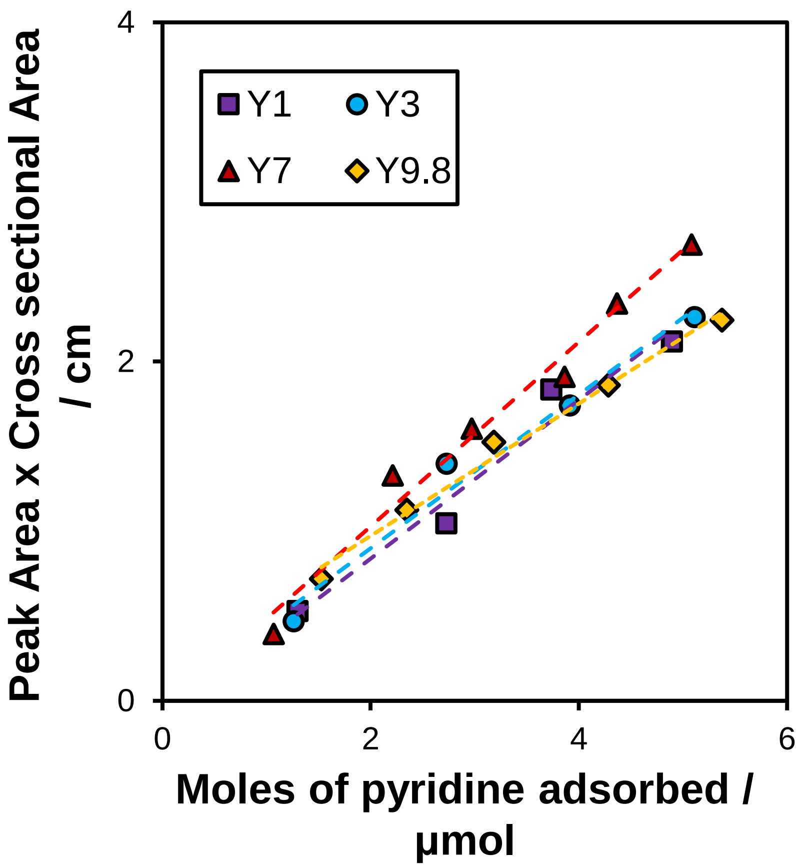
IMEC for Pyridine Bound to Lewis Acidic Y sites (Y_{10}/deAlBeta)

Slope = **ε**



A = ε b C

Comparison of Initial Slopes – Various Y/deAlBeta Samples



Borate, Samad, Harris et al., *in prep*

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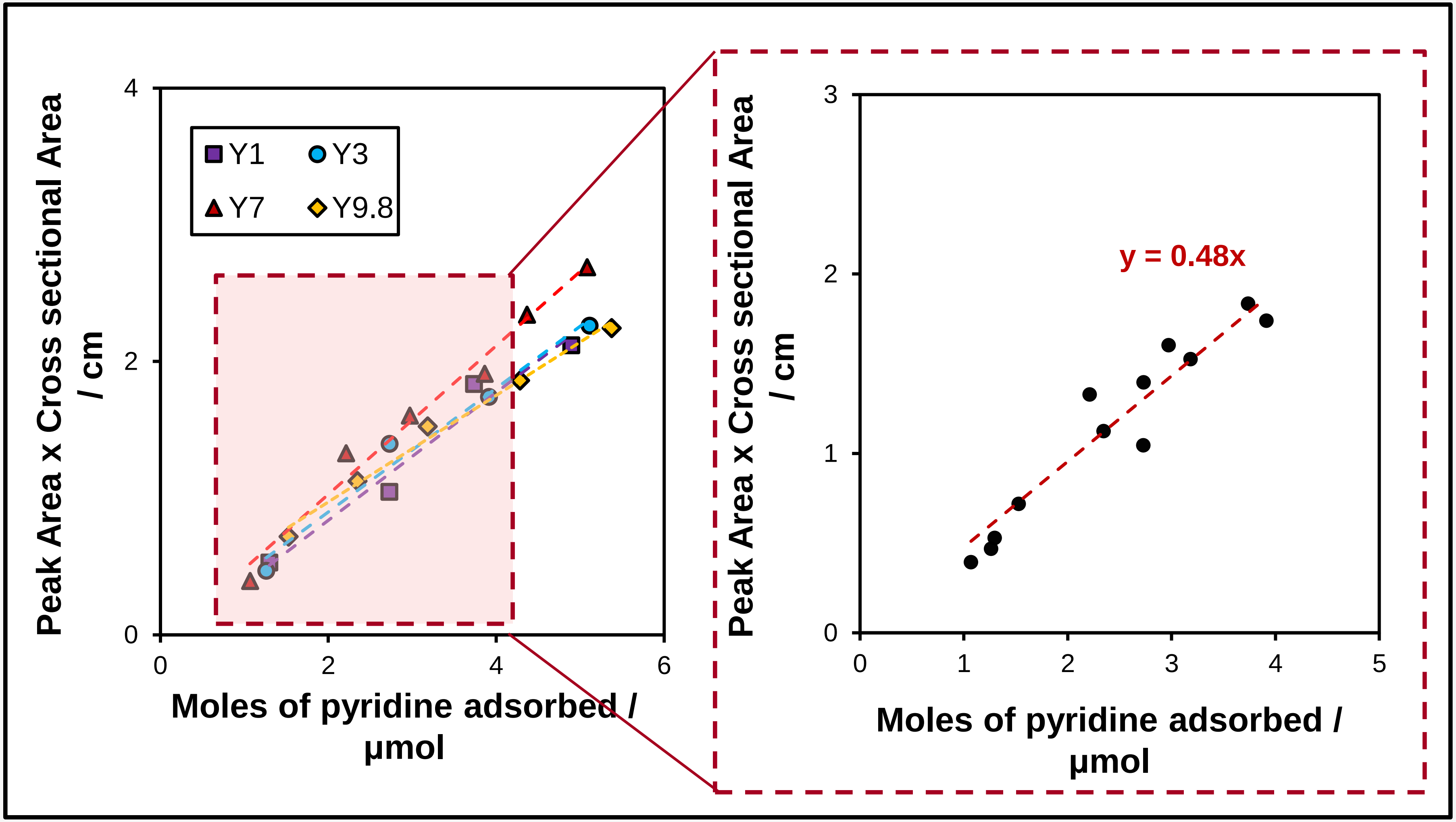

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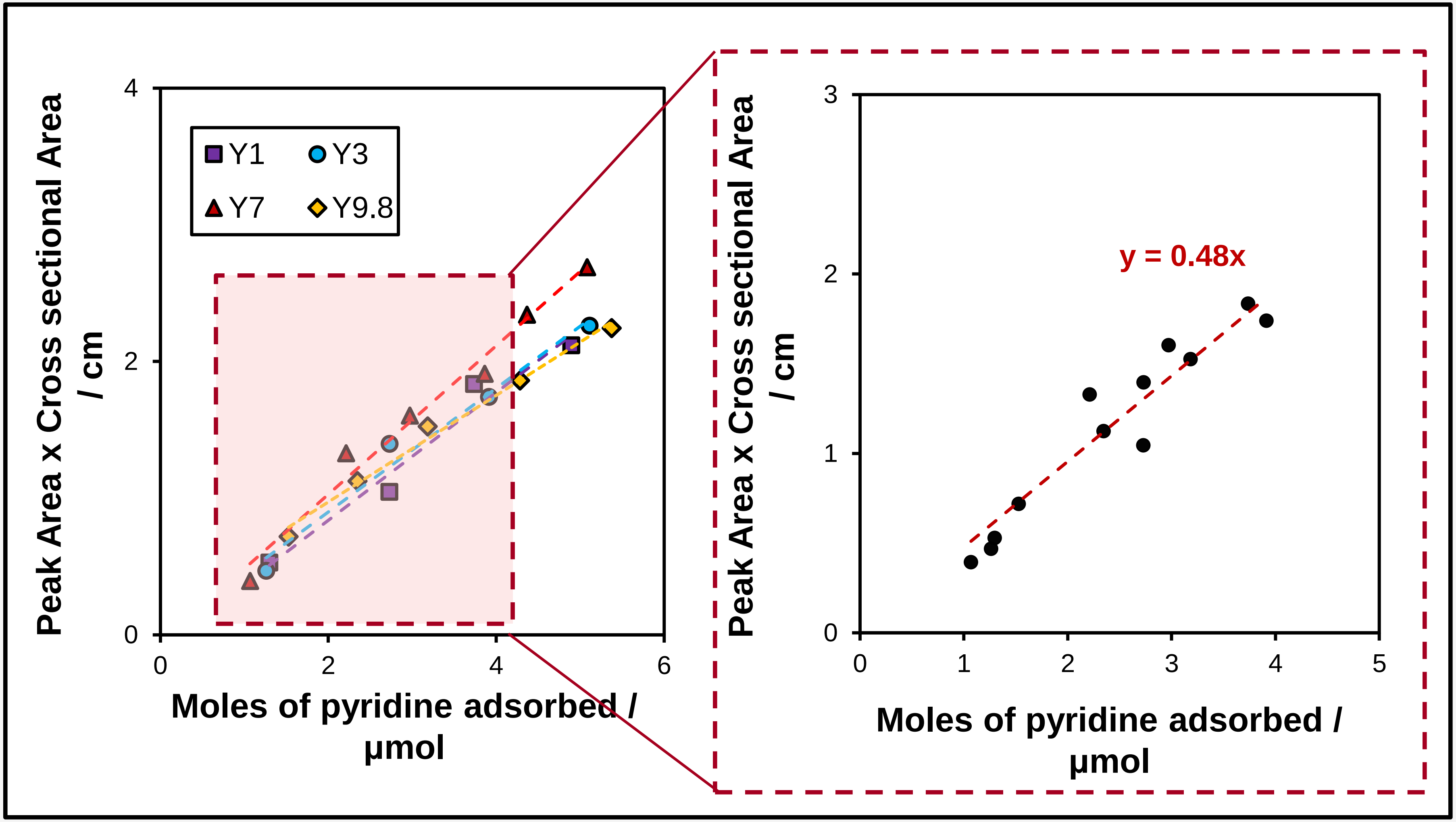
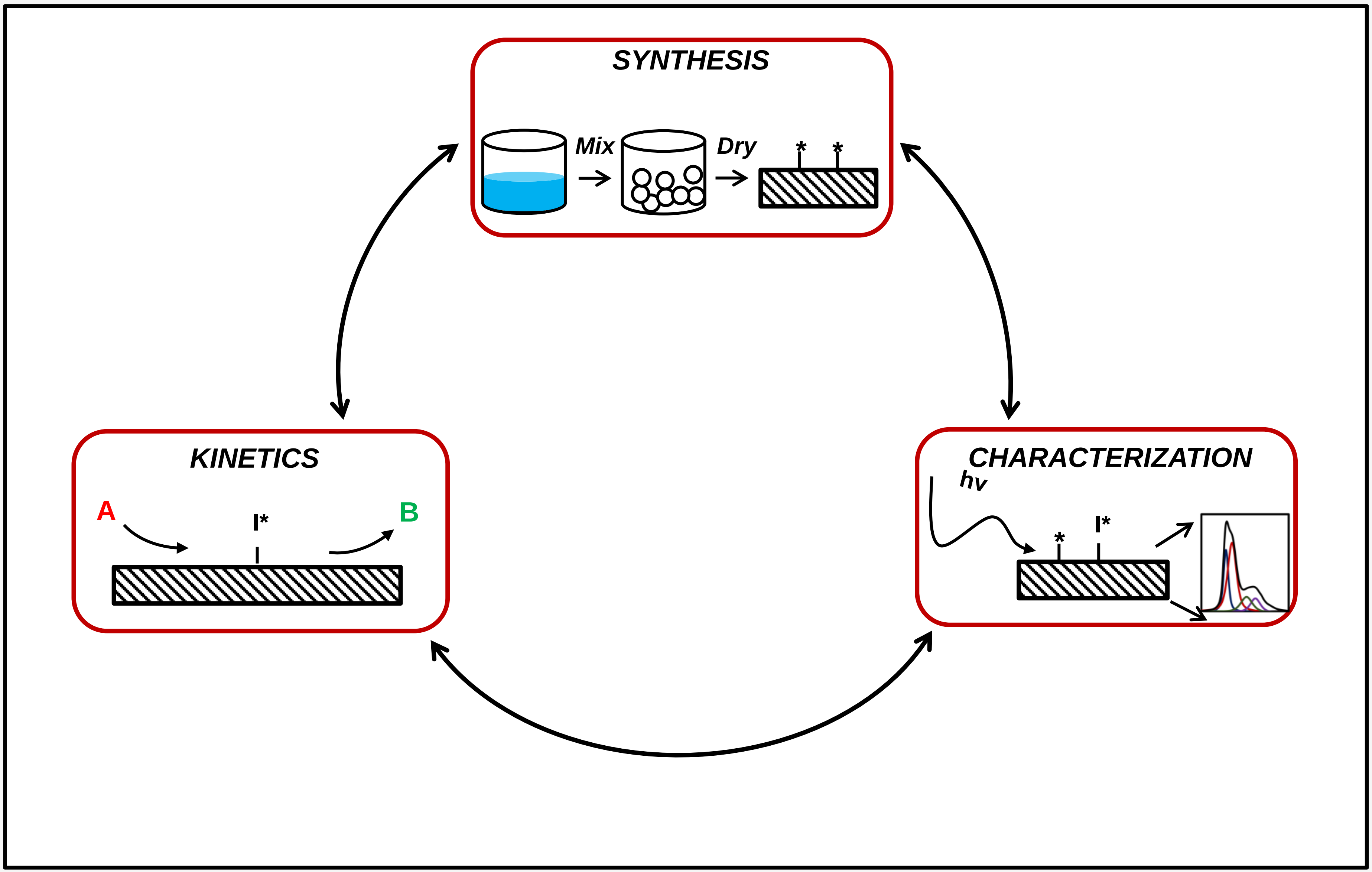


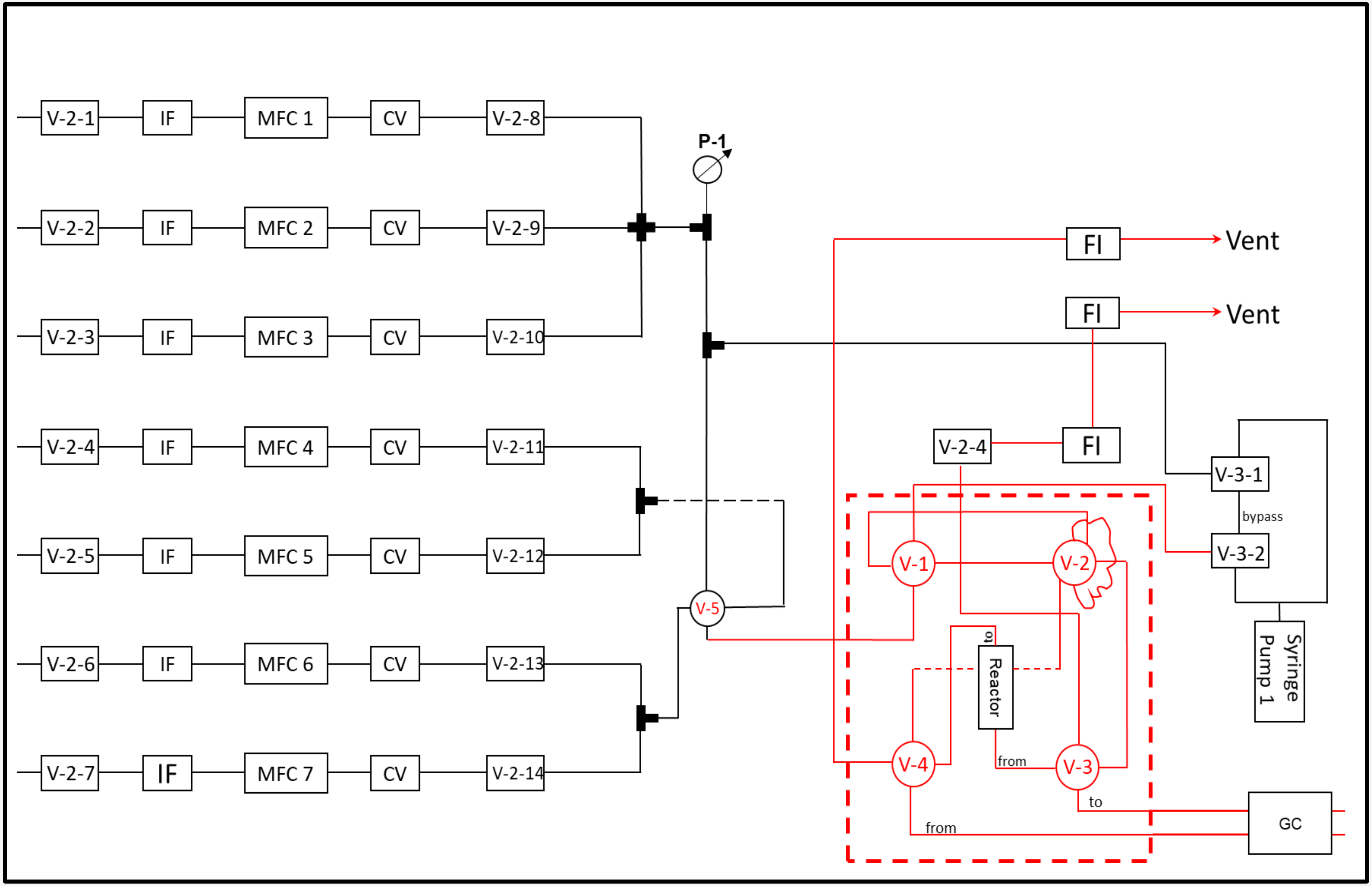
We can quantify YLAS by ex situ pyridine IR, but is that a relevant quantity?

Borate, Samad, Harris et al., *in prep*

Kinetic measurements



Process Flow Diagram of Reactor Setup



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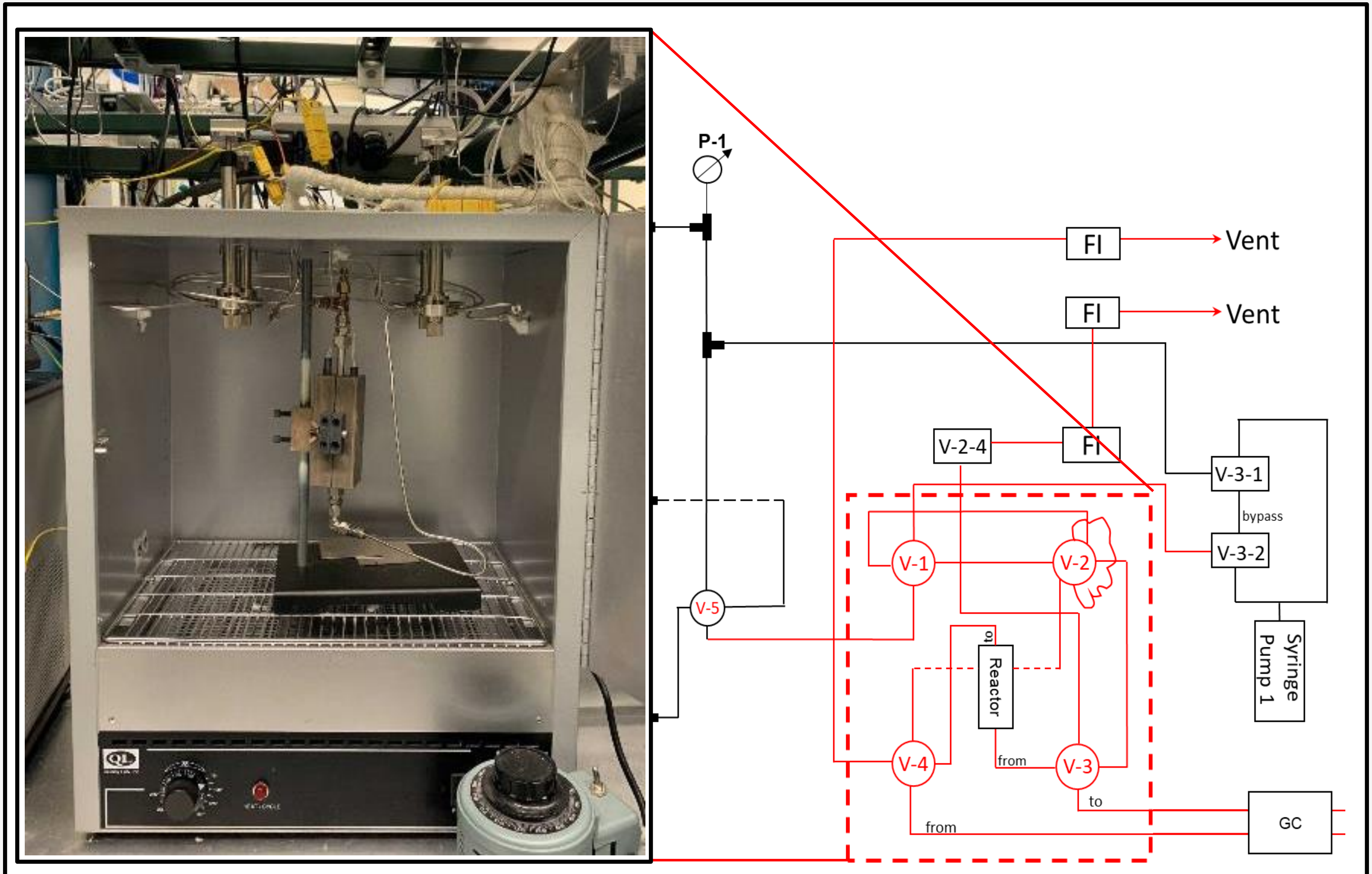
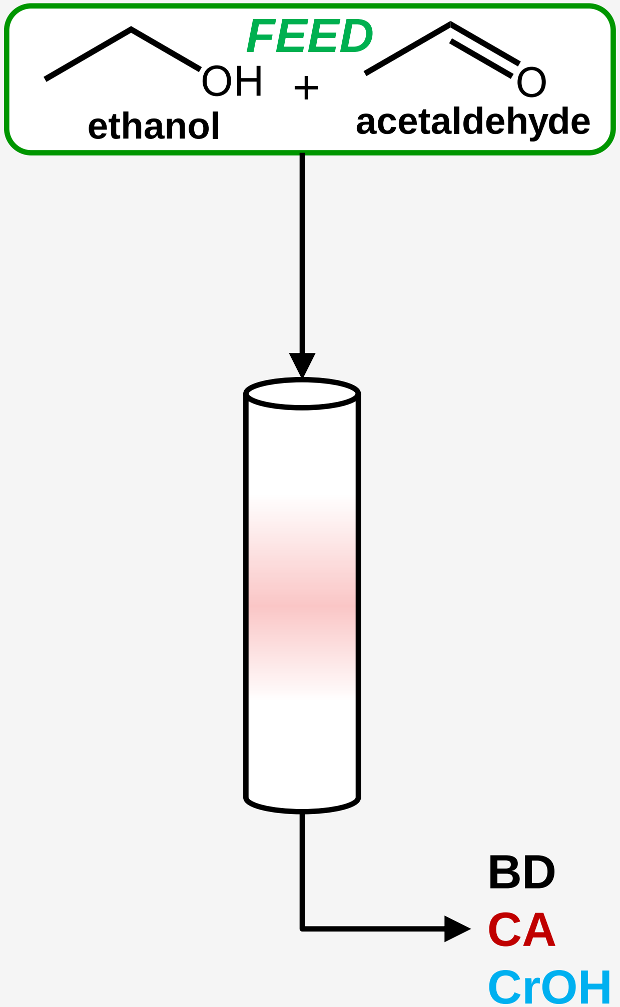
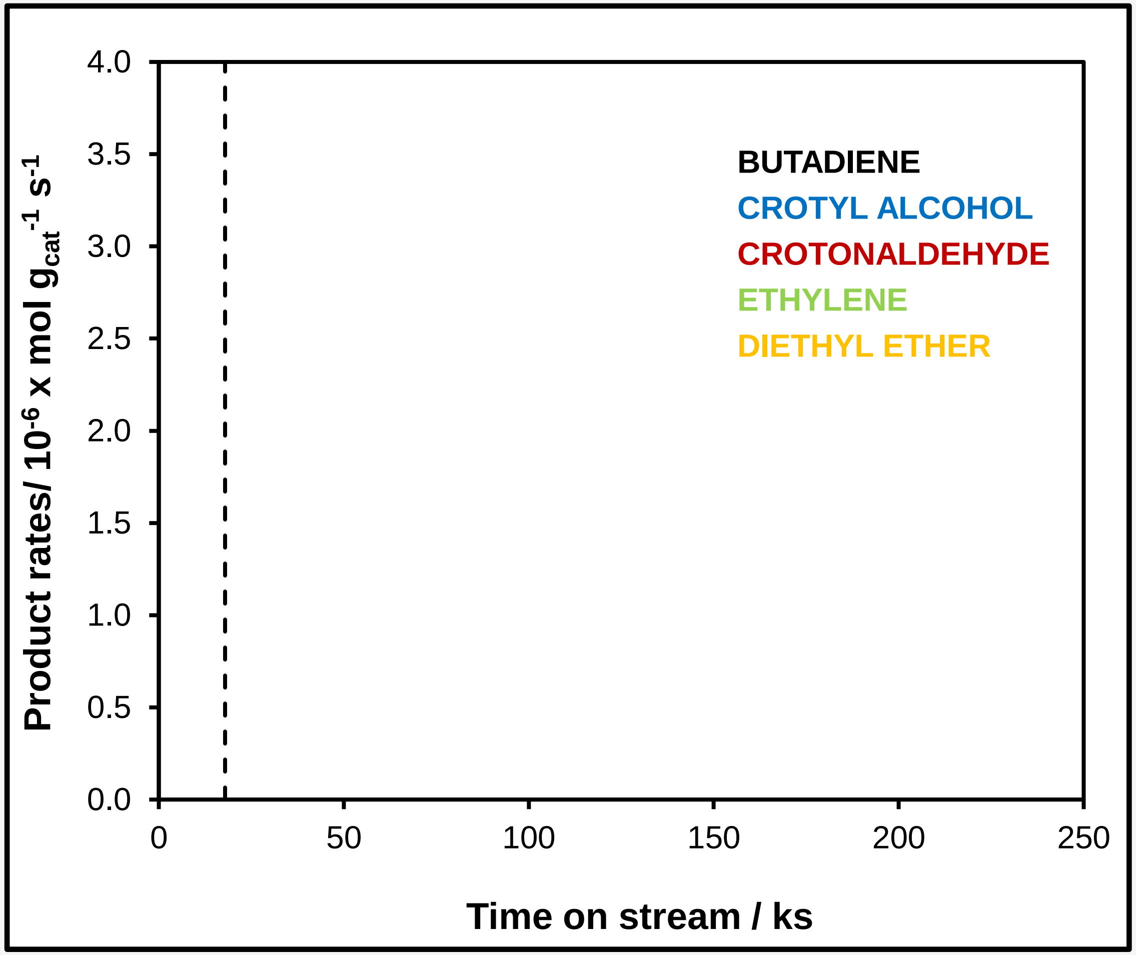


Quantification of Y Active Sites via In Situ Titrations





Reaction conditions: T= 503 K; P = 124 kPa;
Gas Flows: 0.4 kPa AcH, 0.000148 kPa Py (0.01% in EtOH), 3 kPa EtOH, 0.98 kPa CH_4, bal He; Total flow 100 $cm^3.min^{-1}$;
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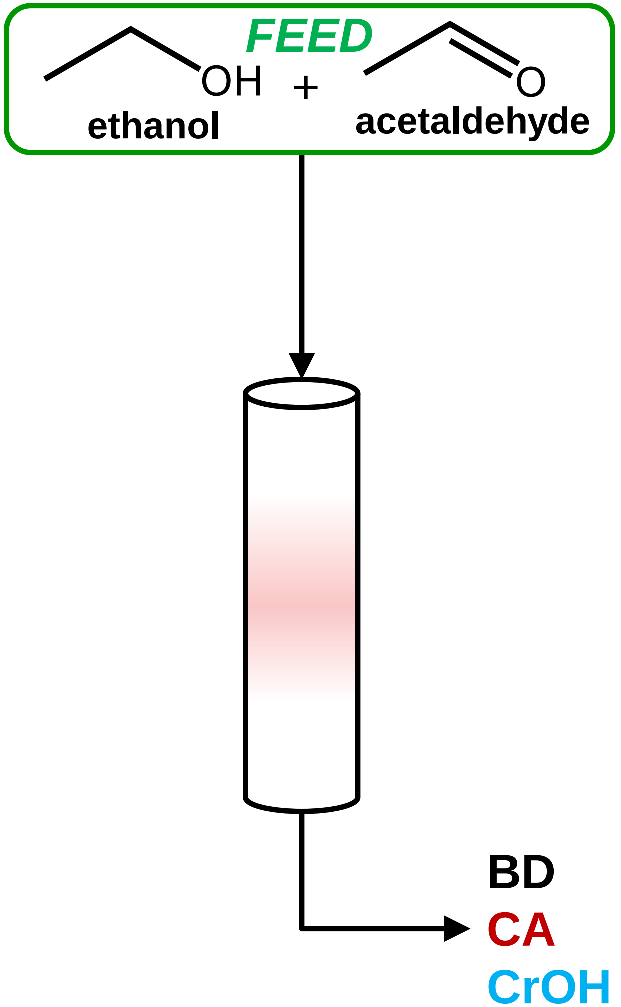

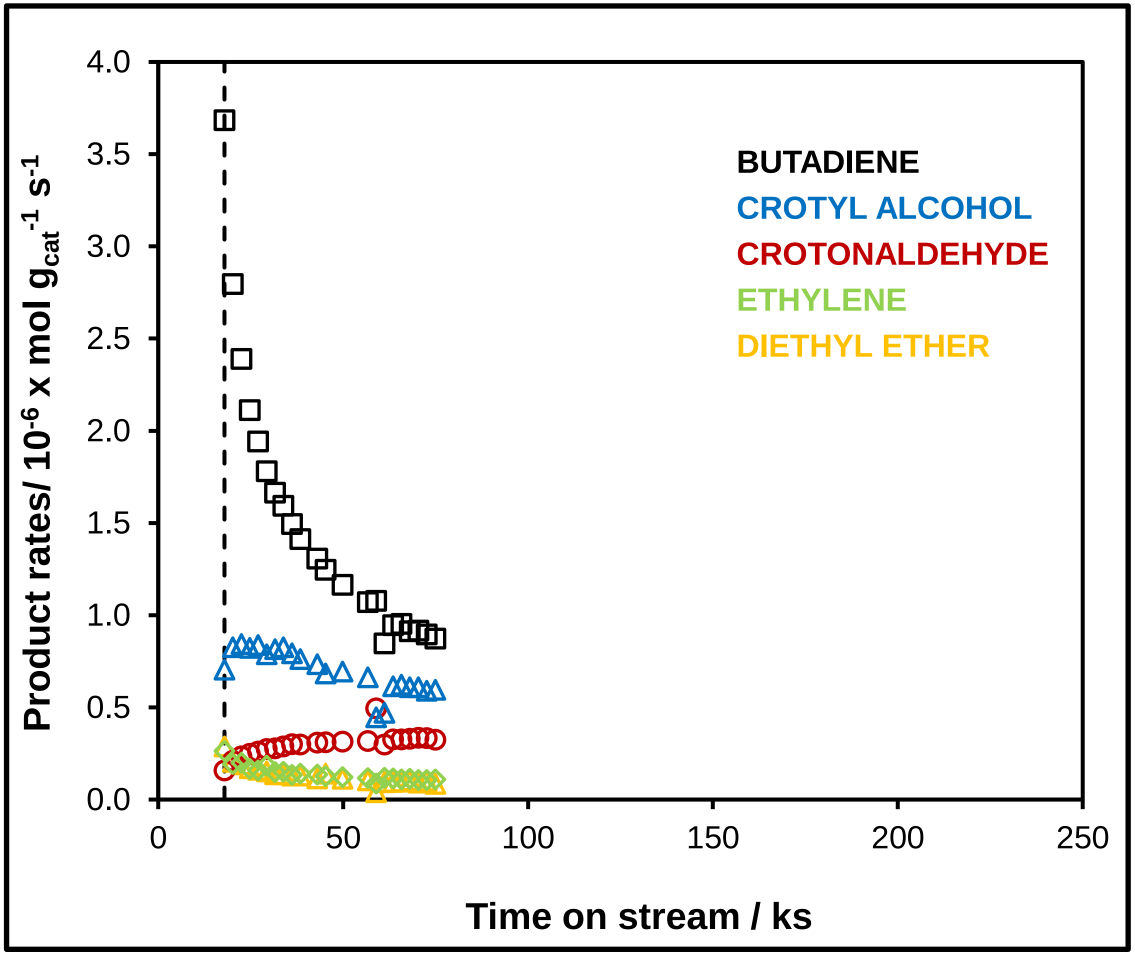

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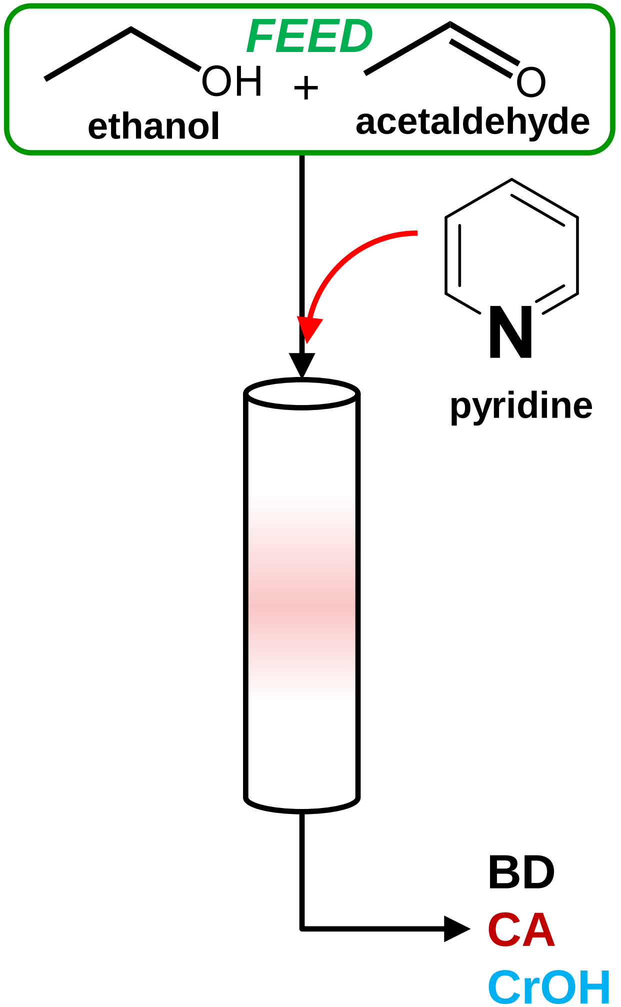

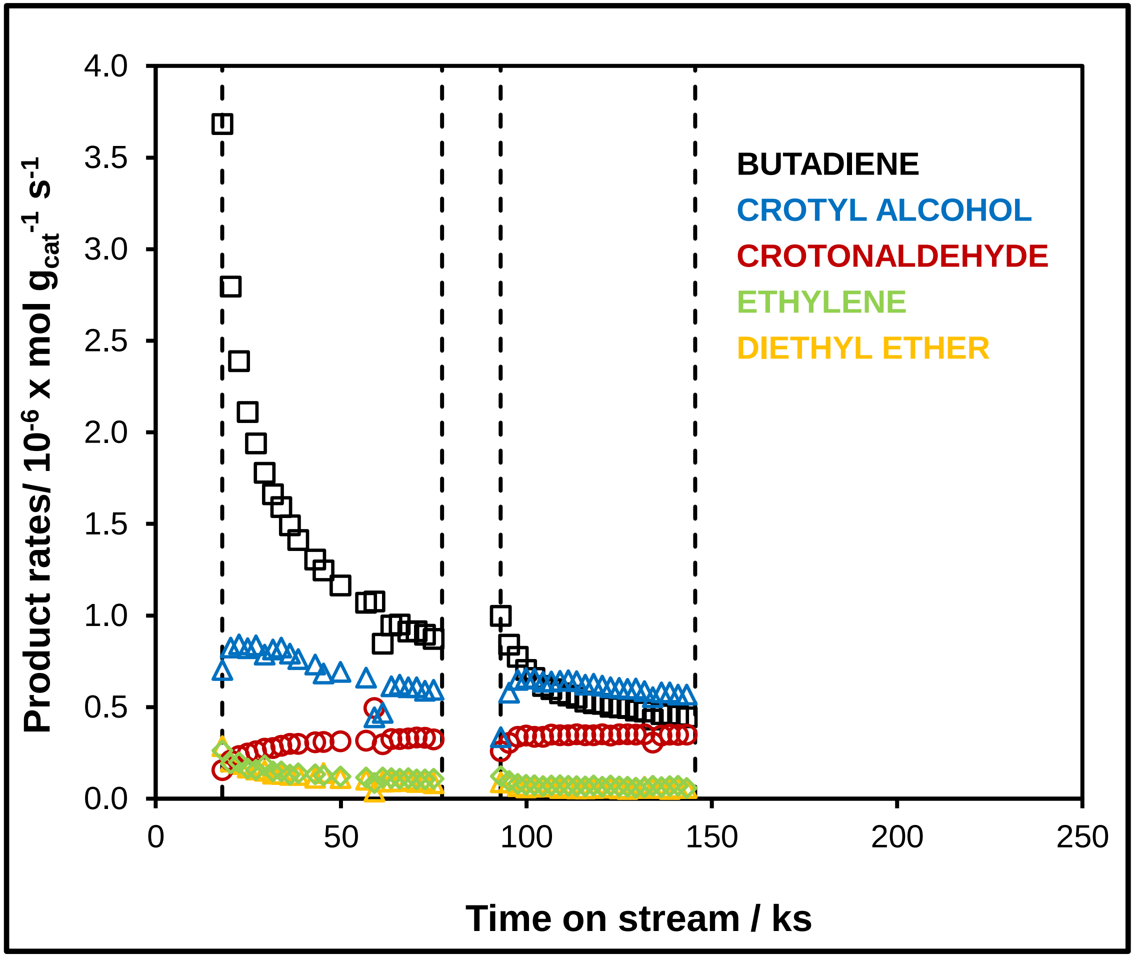

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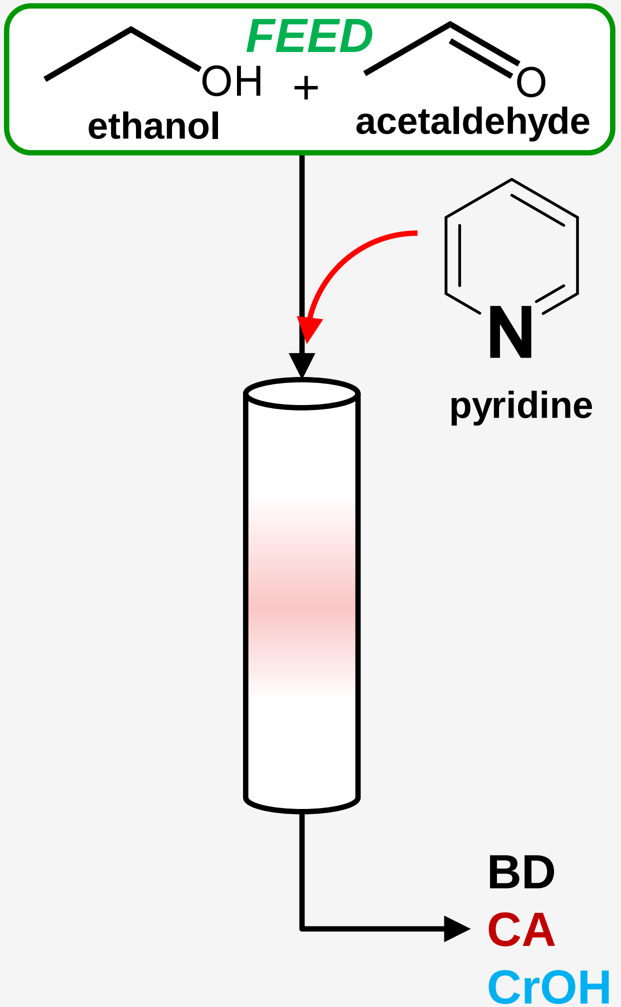

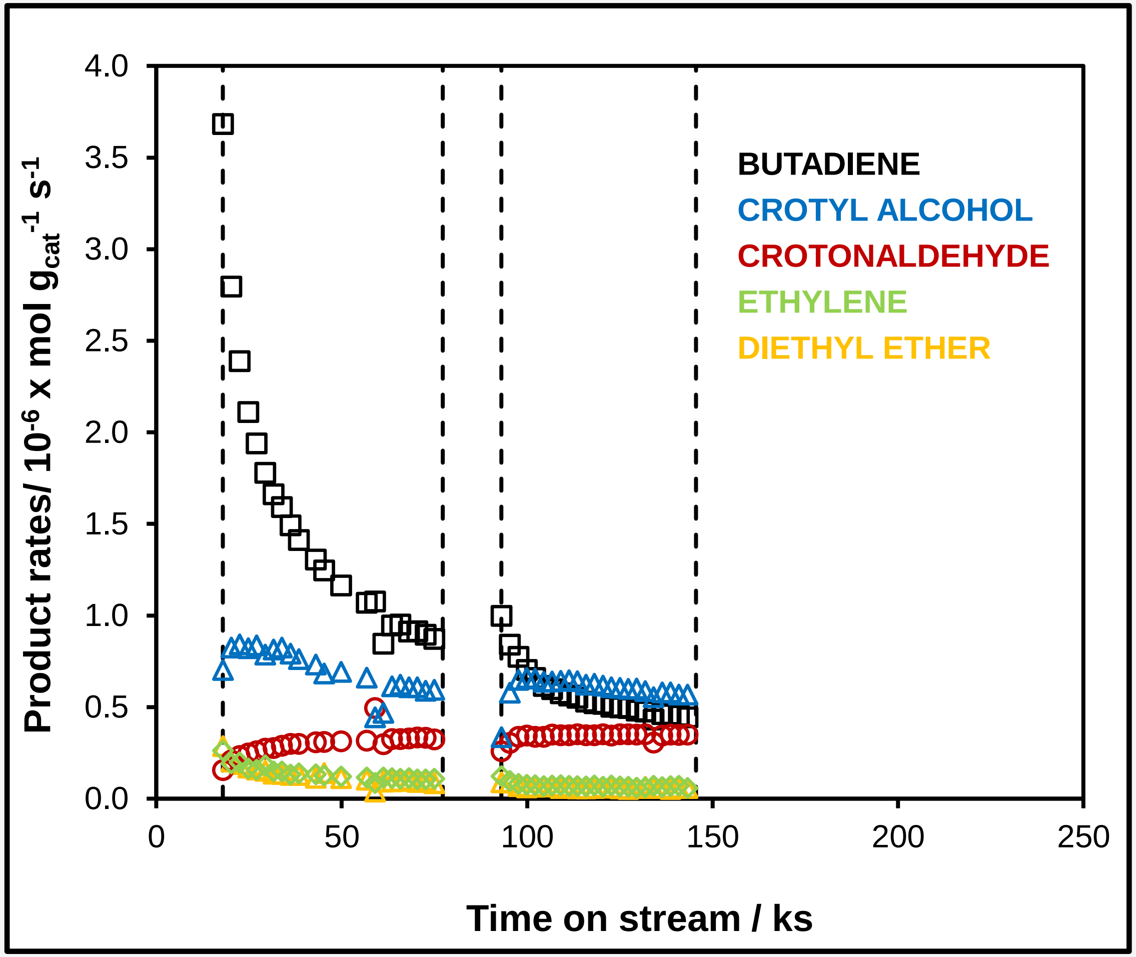

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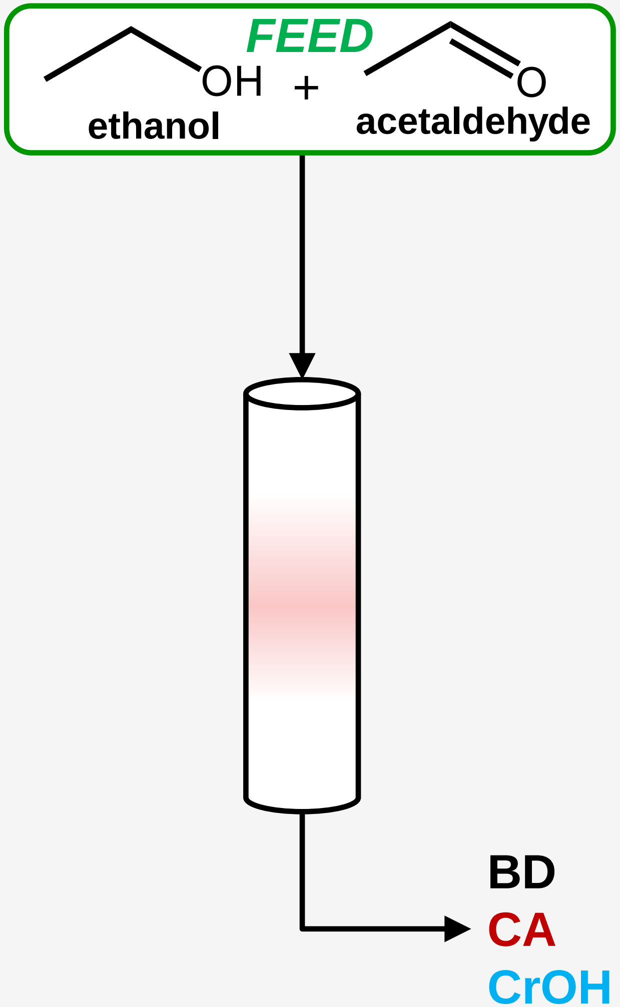

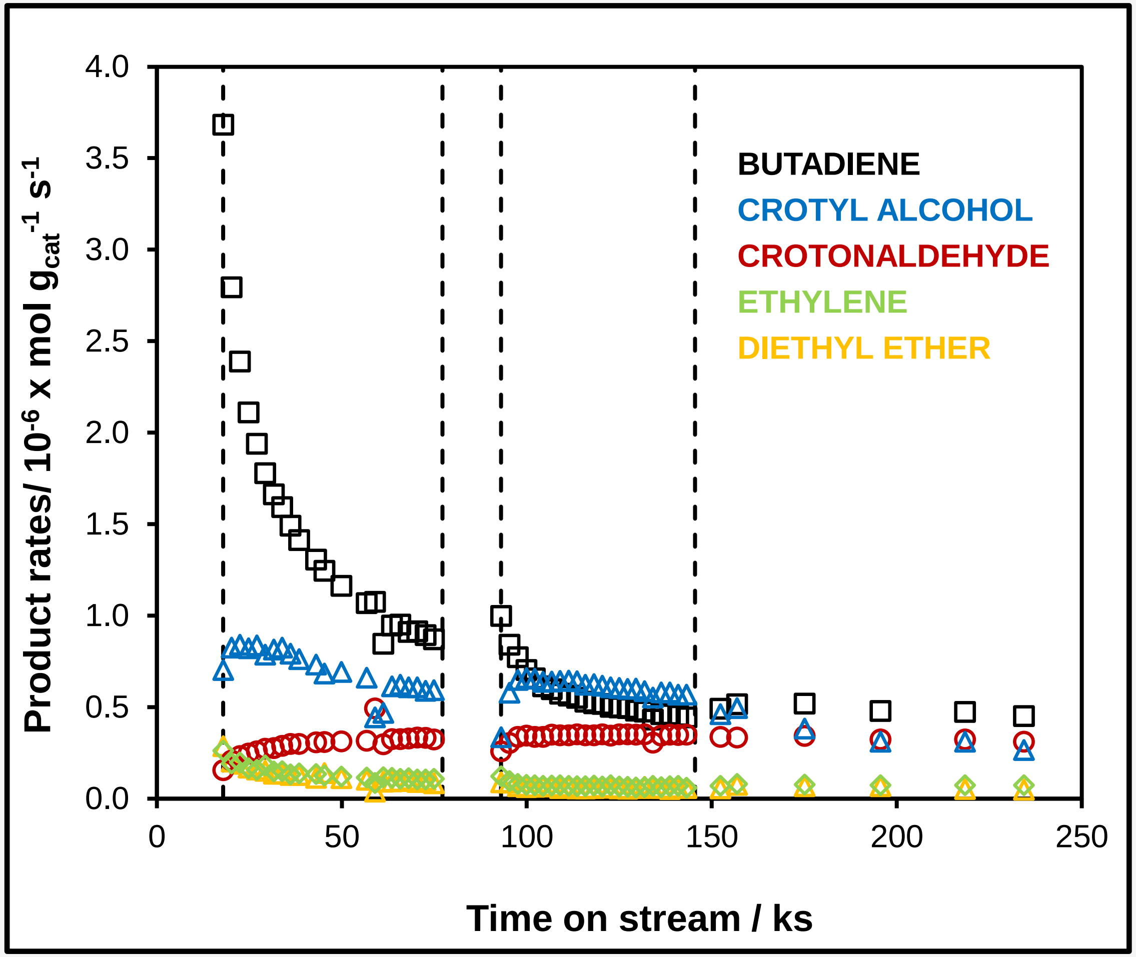

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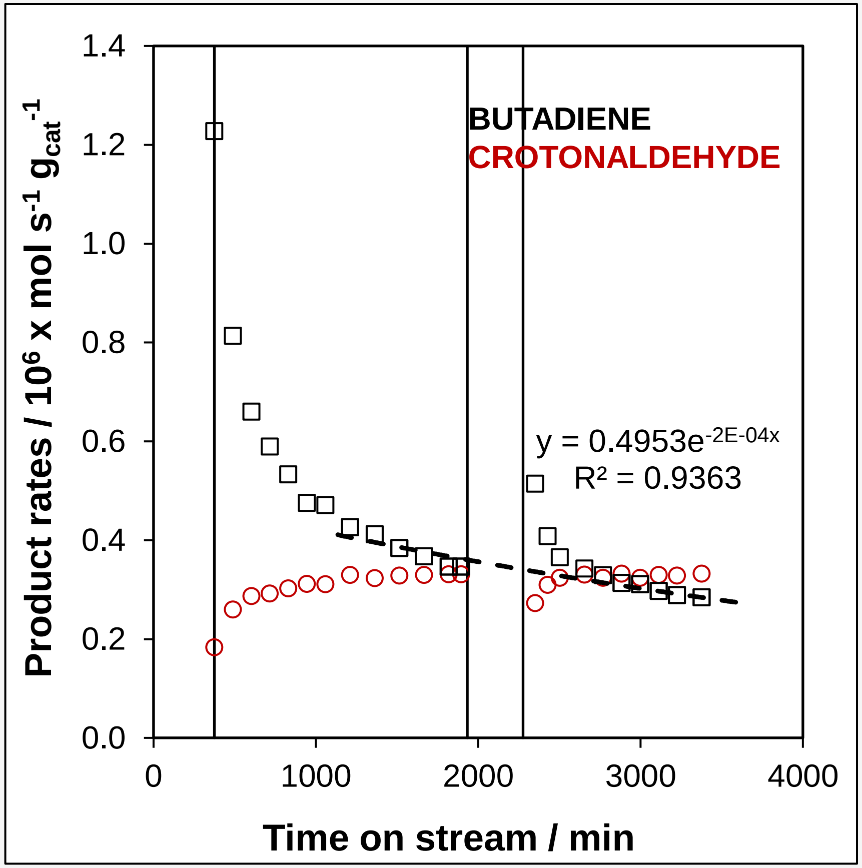
Borate, Samad, Harris et al., *in prep*

EtOH-AcH co feed on $Y_{0.5}$/deAlBeta

TOS data <u>without</u> pyridine titration



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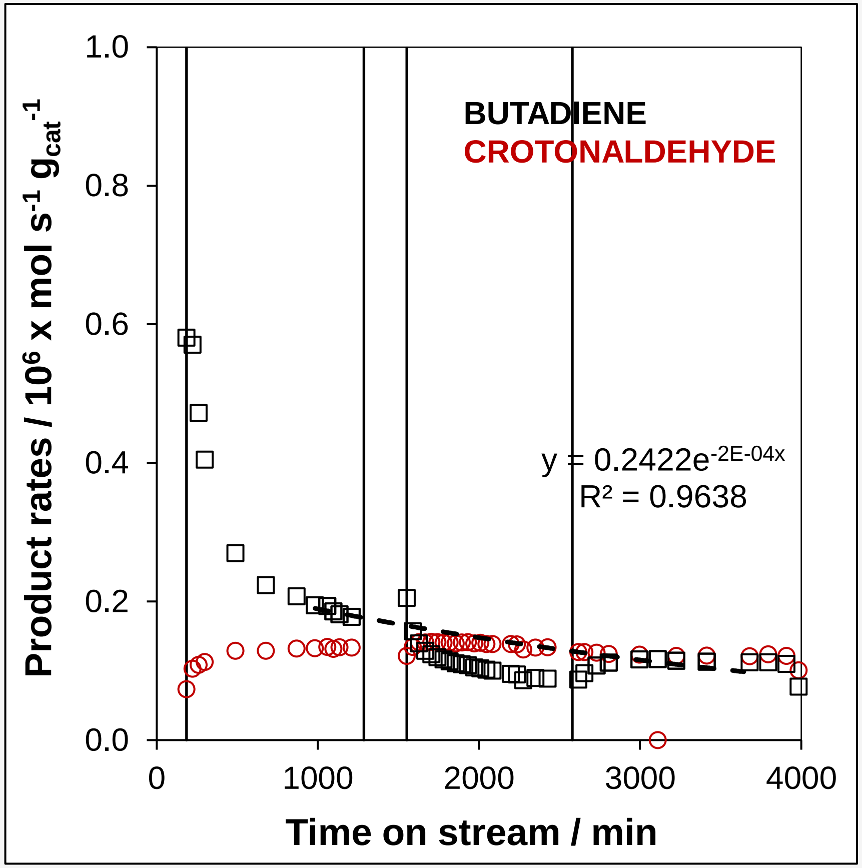
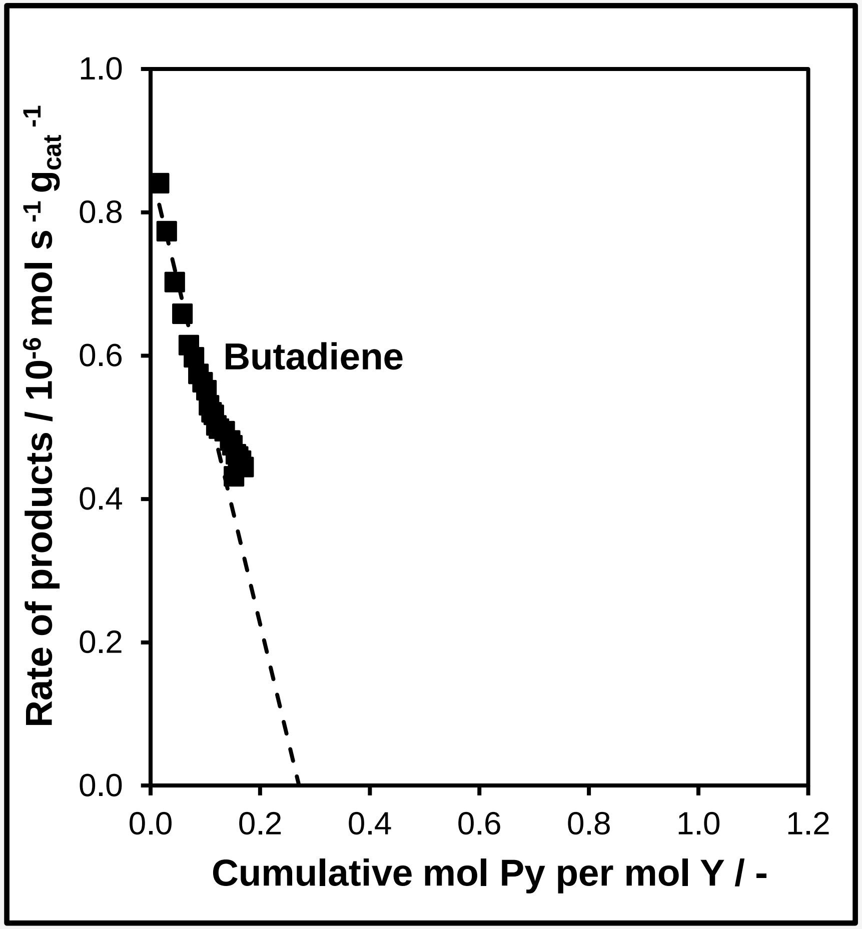


Reaction conditions: T= 503 K, P=124 kPa
Gas flows: without Py titration- 0.7 kPa AcH, 3 kPa EtOH
with Py titration- 0.5 kPa AcH, 0.000148 kPa Py (0.01% in EtOH), 3 kPa EtOH
0.98 kPa CH4, bal He. Total flow: 100 cm^3 min^{-1}
Catalyst: 0.01 g $Y_{0.5}$/deAlBeta diluted with SiC or SiO_2

Quantification of Active Sites via In Situ Titrations

Y_3 /deAlBeta



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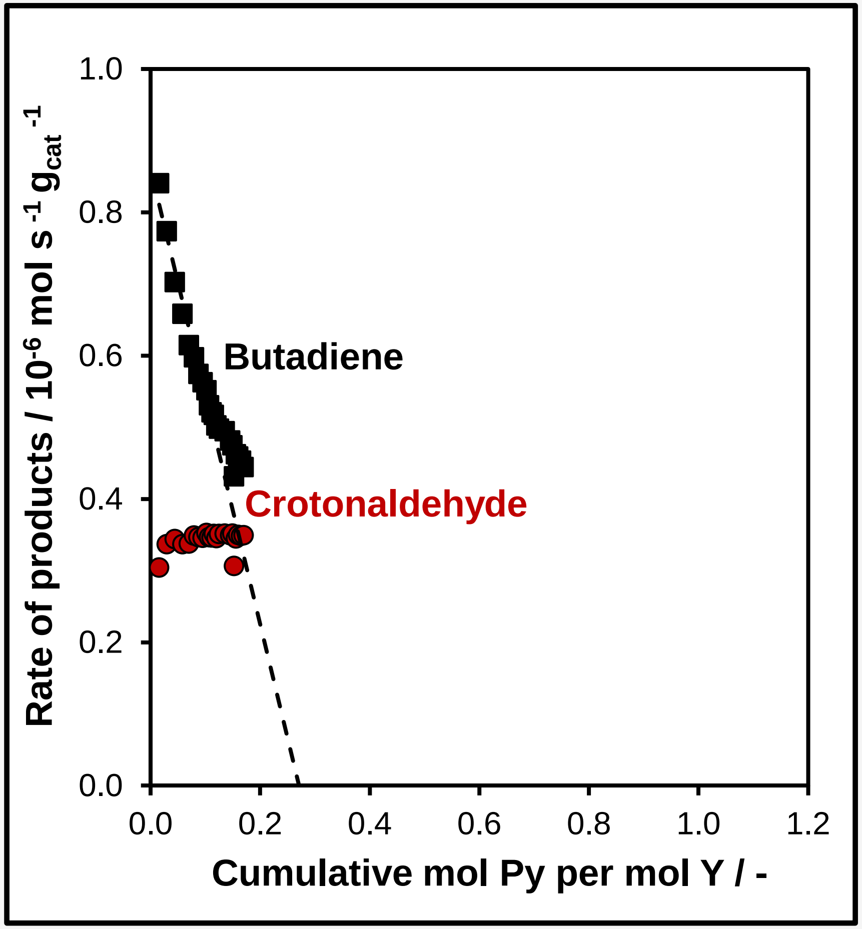
Borate, Samad, Harris et al., *in prep*

Quantification of Active Sites via In Situ Titrations

Y_3/deAlBeta



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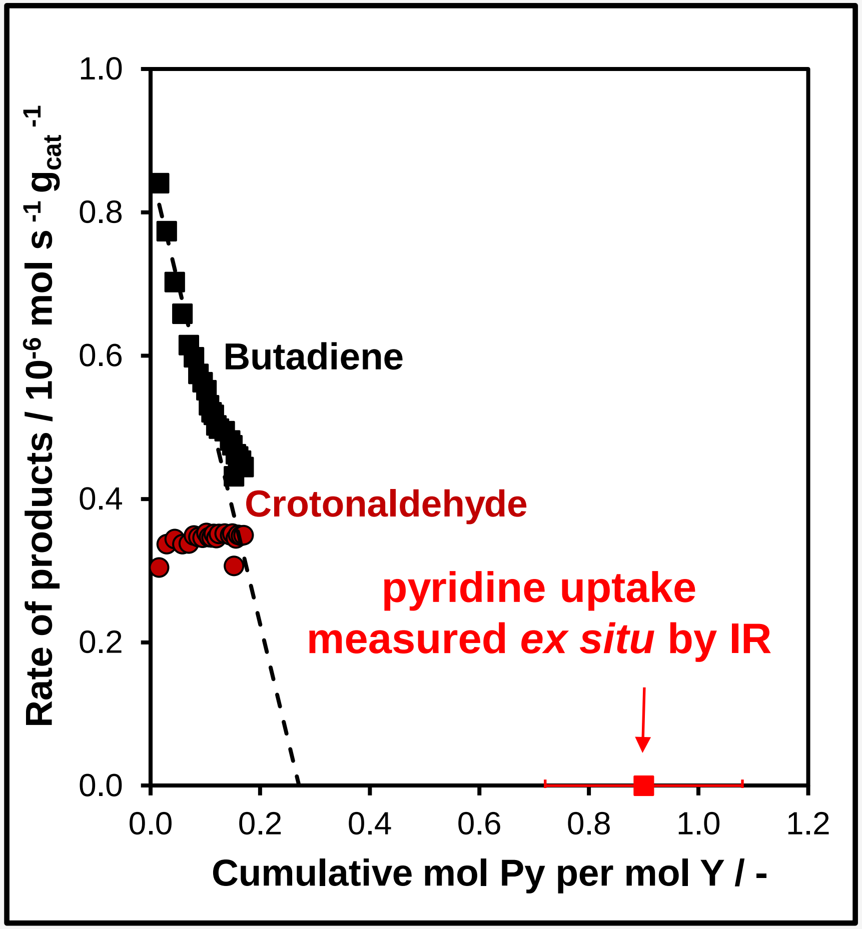

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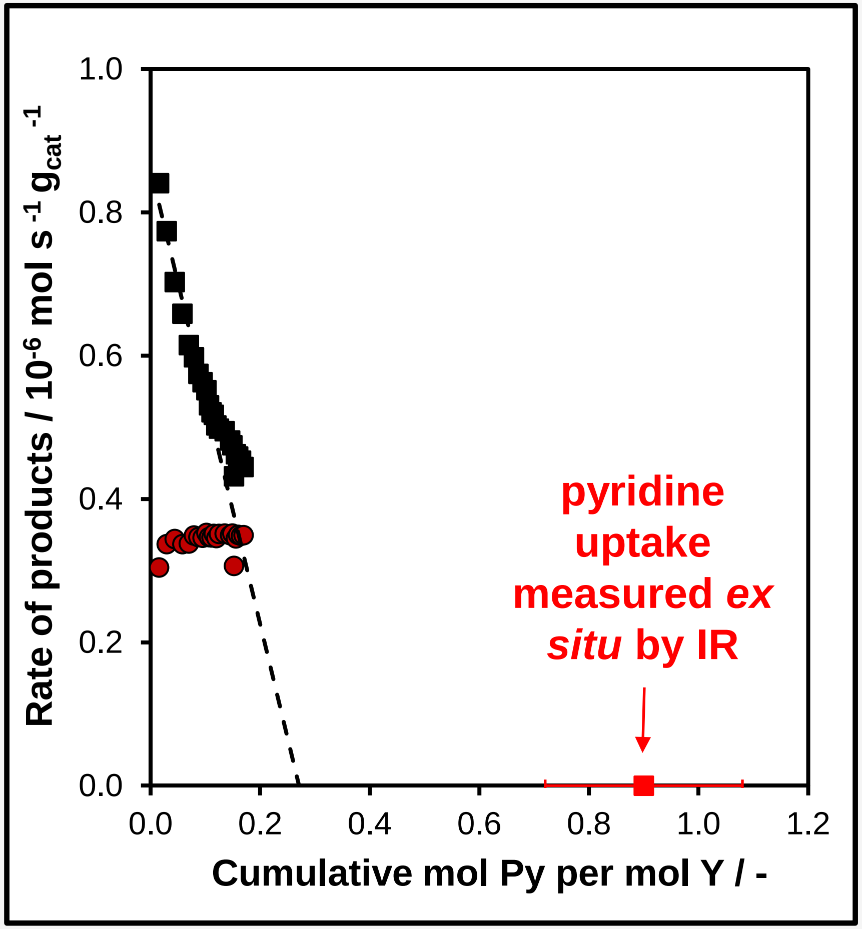
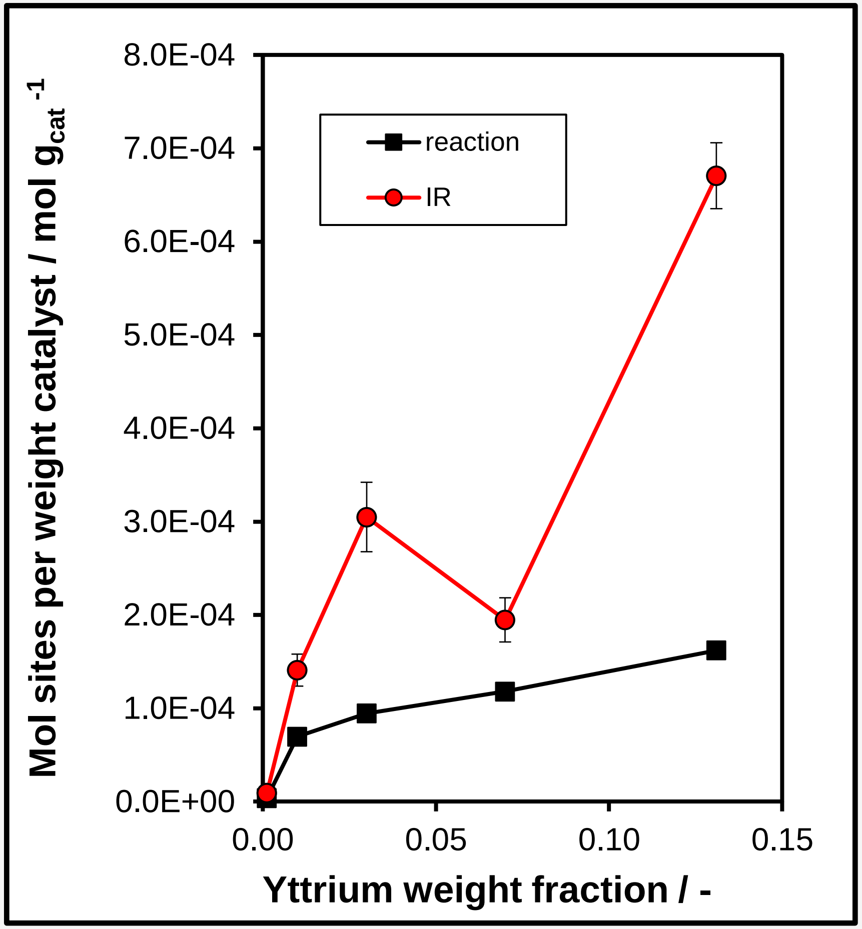
Borate, Samad, Harris et al., *in prep*

Comparison of in situ and ex situ site titrations

Y_3 /deAlBeta





Reaction conditions: T= 503 K; P = 124 kPa;
Gas Flows: 0.4 kPa AcH, 0.000148 kPa Py, 3 kPa EtOH, 0.98 kPa CH_4, bal He; Total flow 100 $cm^3.min^{-1}$;
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Borate, Samad, Harris et al., *in prep*

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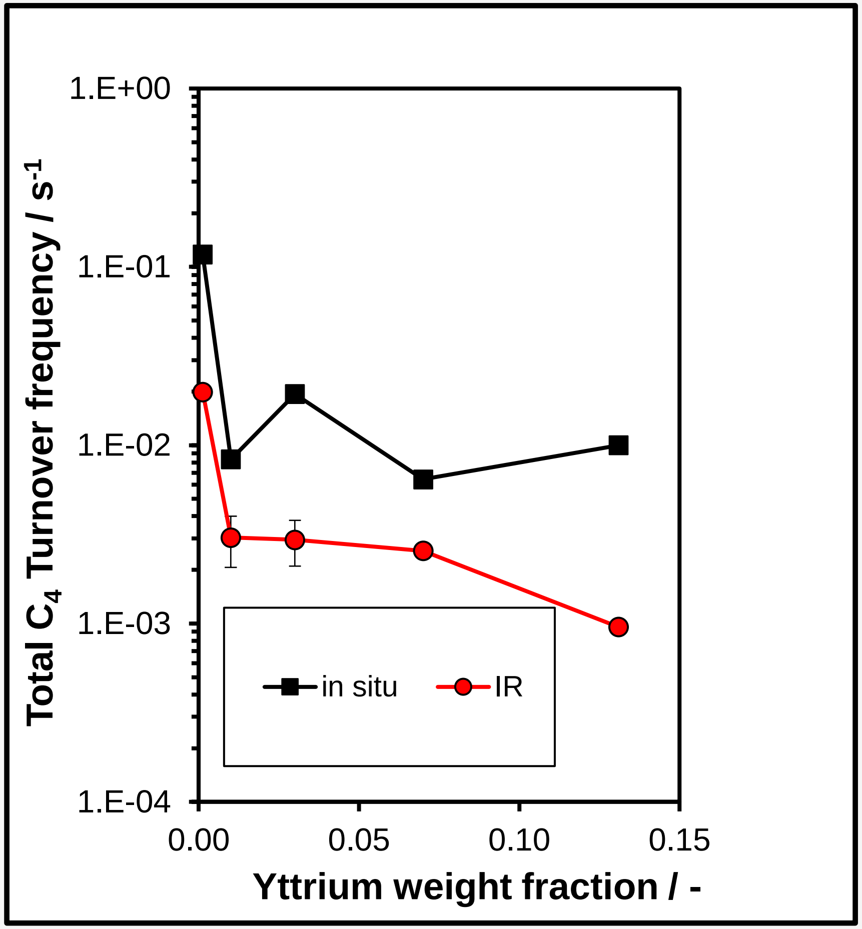

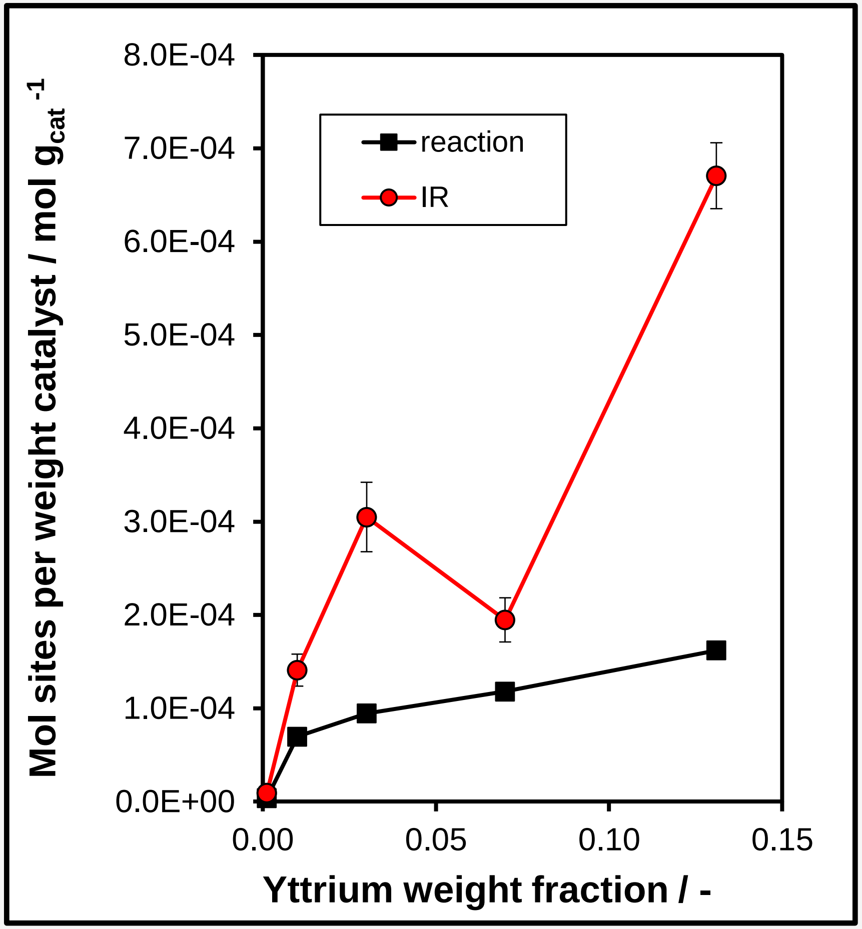

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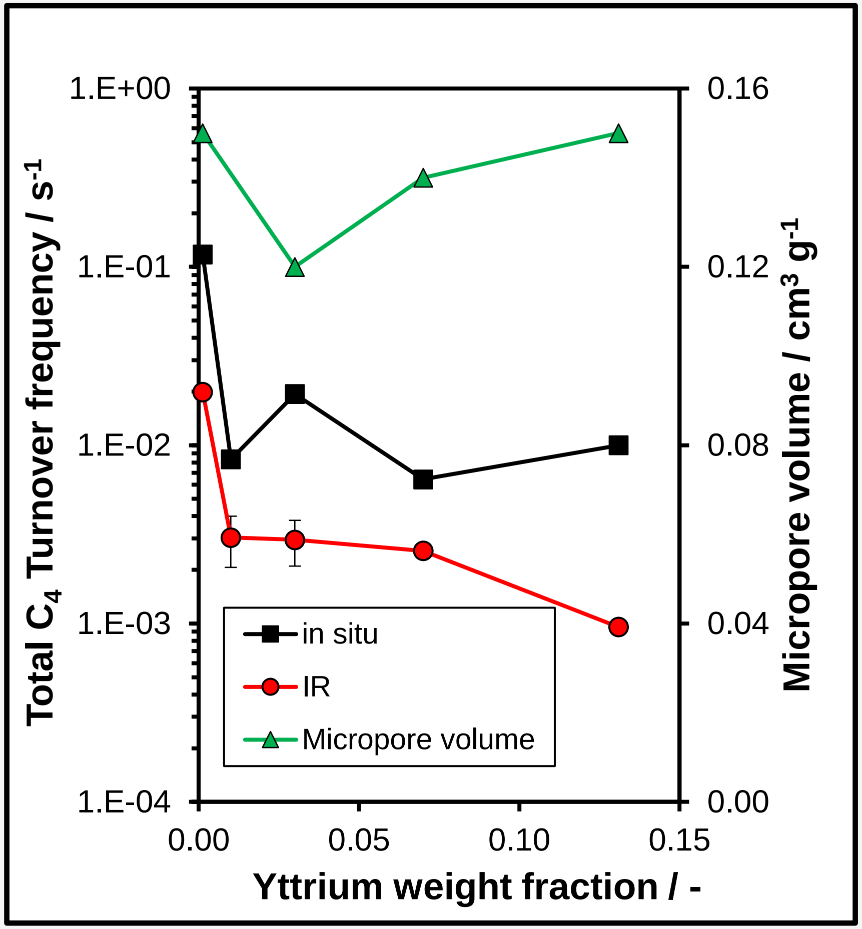

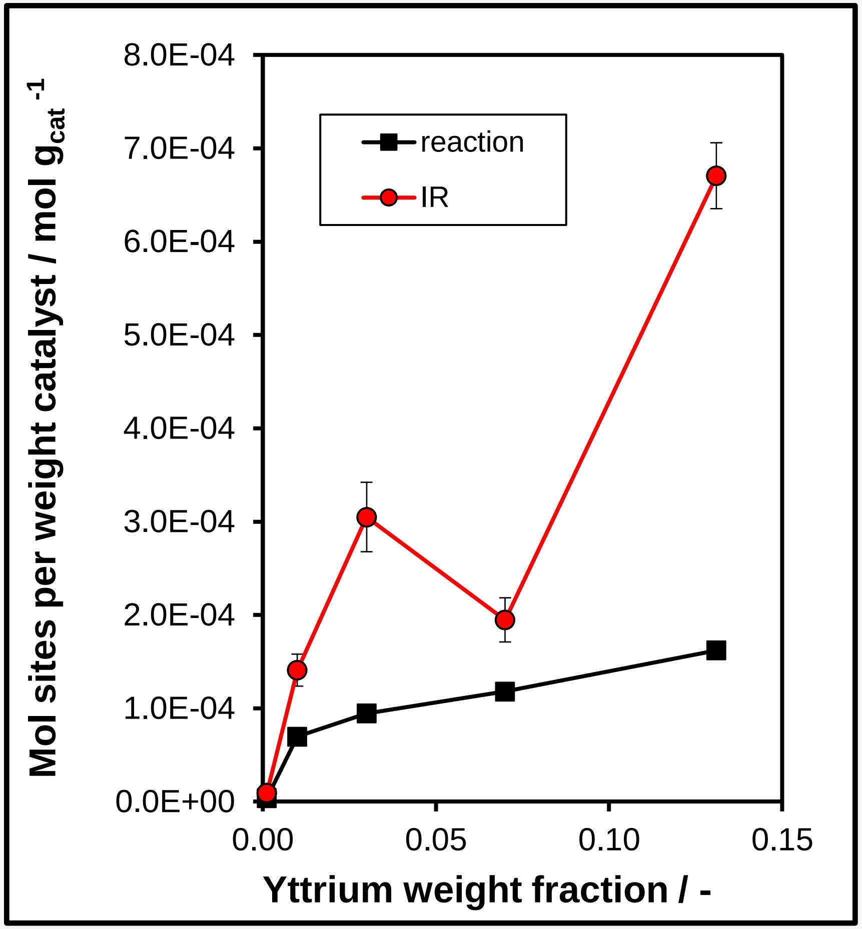

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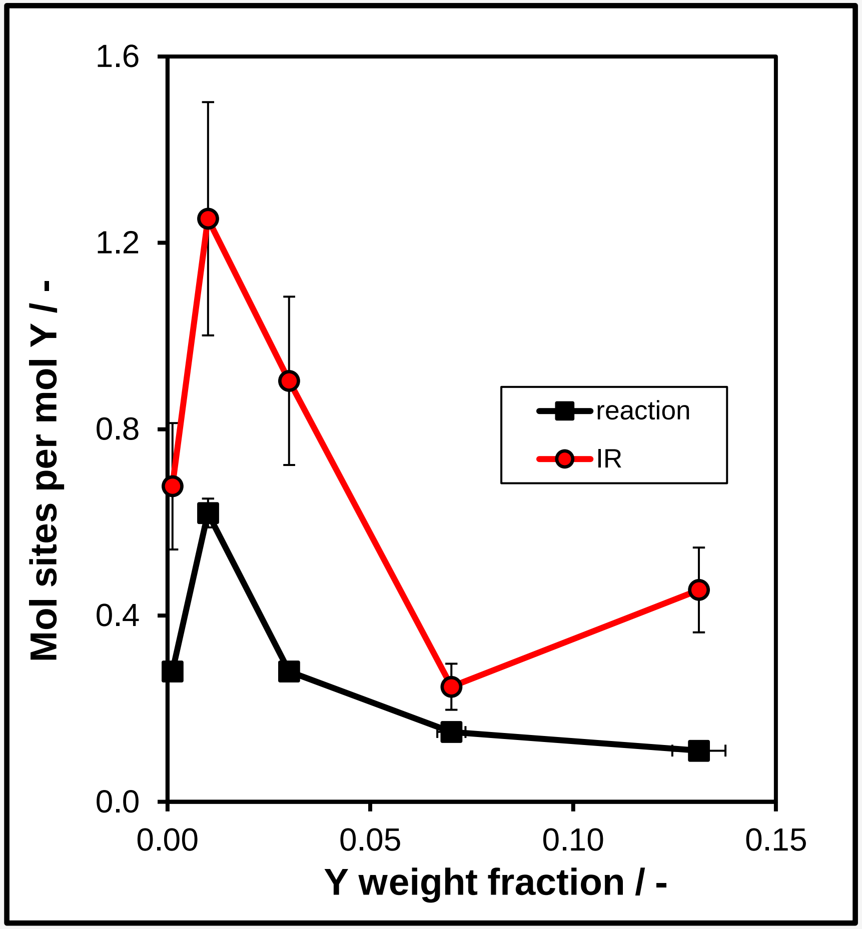

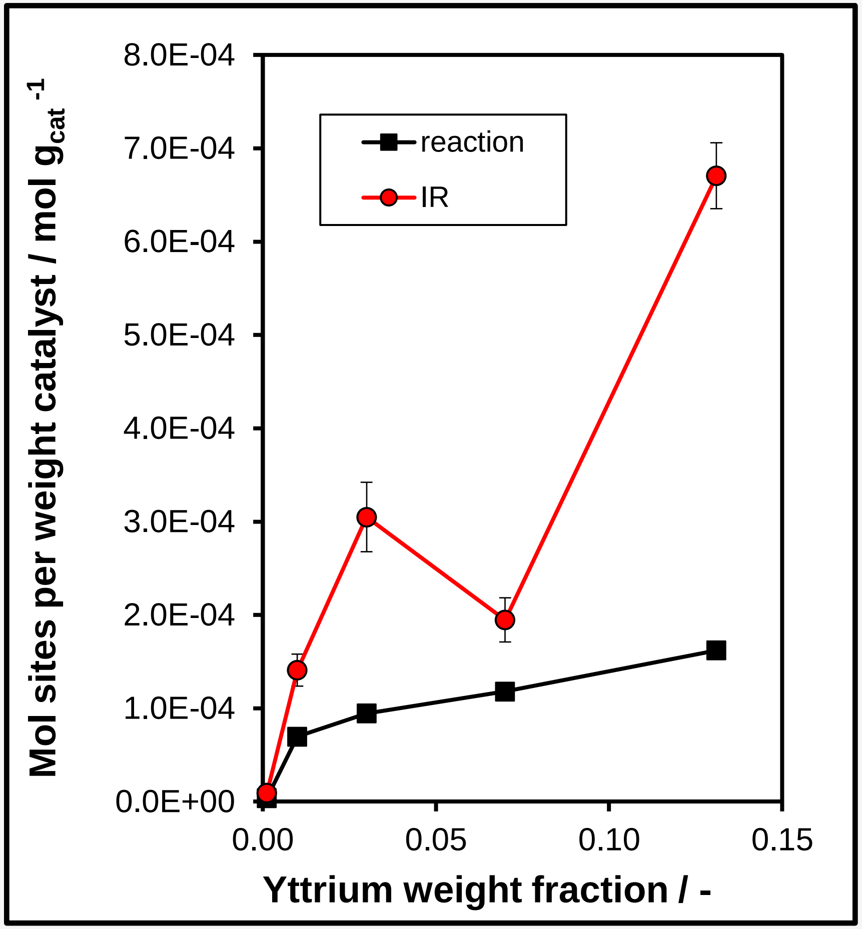

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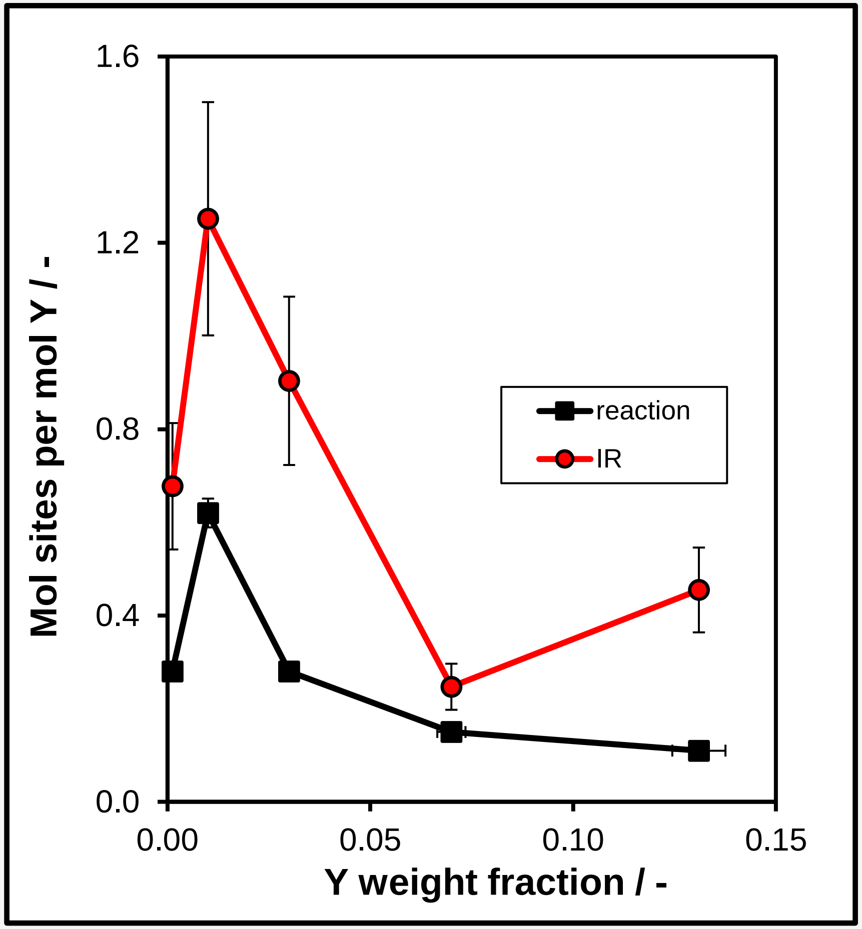
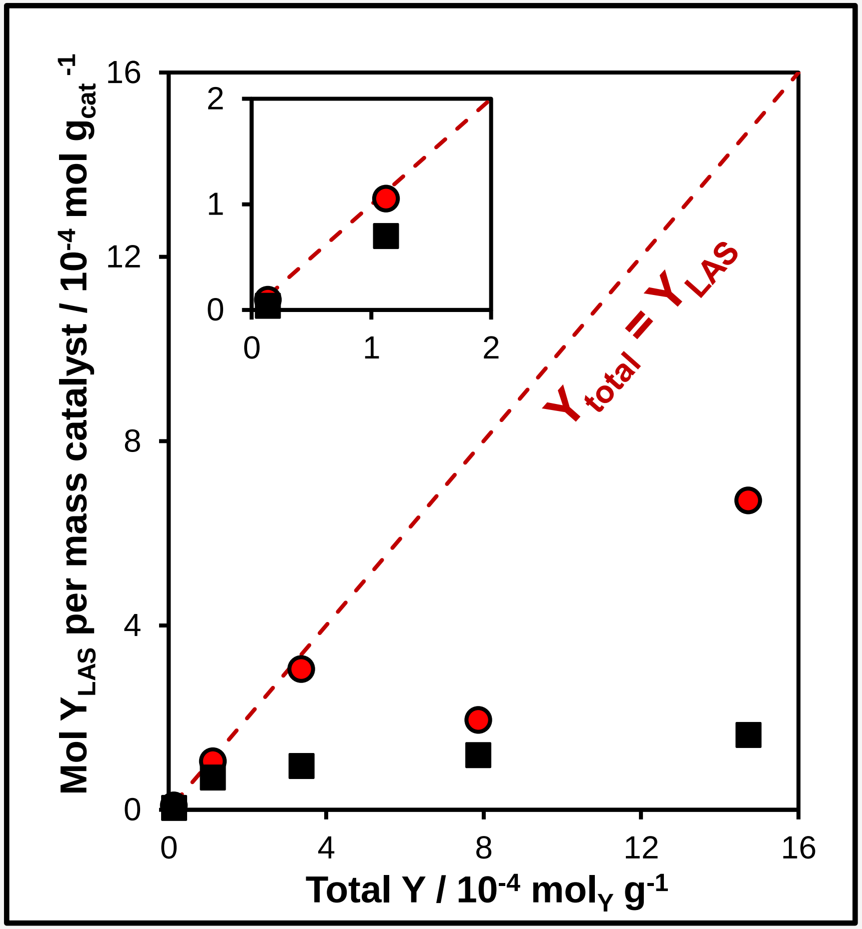
Borate, Samad, Harris et al., *in prep*

A minority of the total Y binds pyridine during reaction or under vacuum





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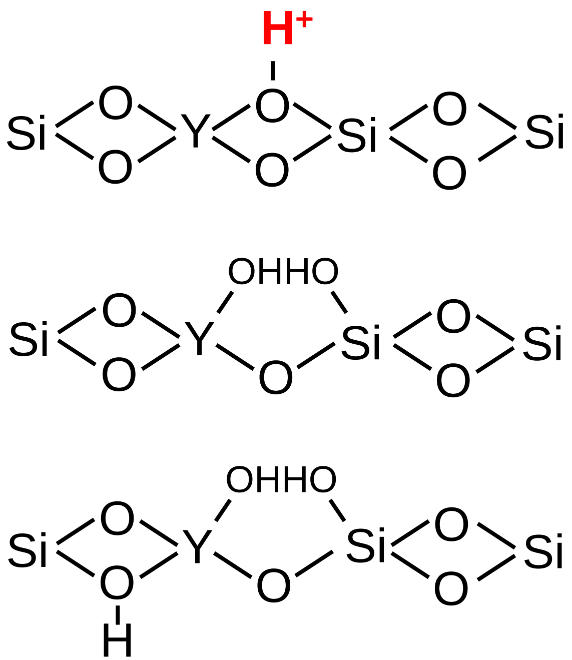
Borate, Samad, Harris et al., *in prep*

What sites are present in Y/deAlBeta samples?

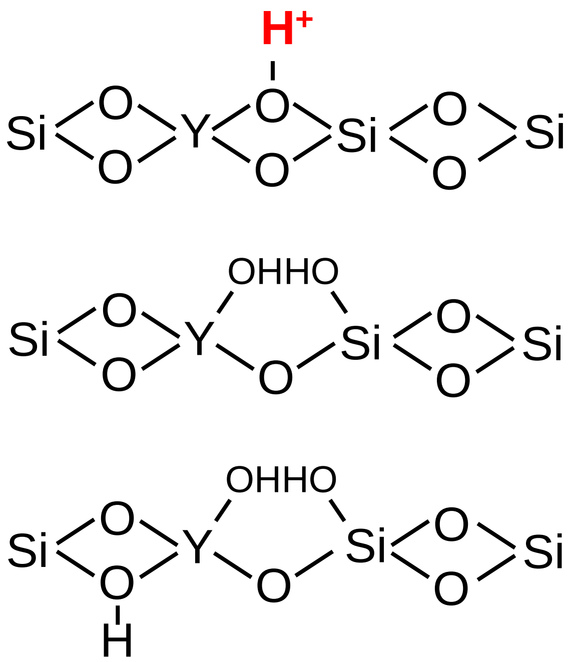
What are the active sites and how many are there?



- ***Minimal H^+ in Y/deAlBeta***
- ***BD forming sites ≠ sites titrated in IR***
- ***Crotonal forming sites unaffected by pyridine***

How do we get from A to D (or E…)?

What are the active sites and how many are there?



- *Minimal H^+ in Y/deAlBeta*
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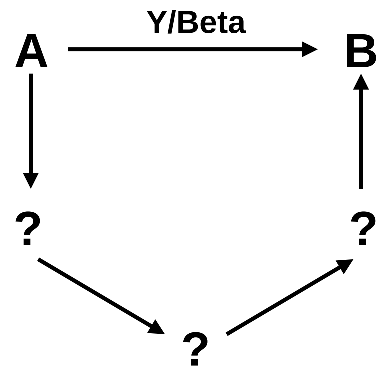
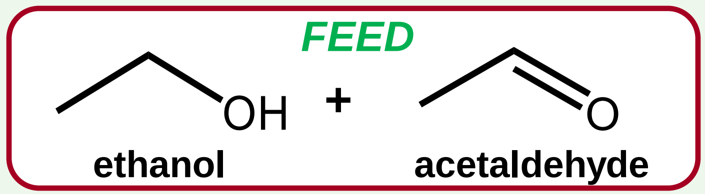
What is the reaction pathway?



What intermediates?

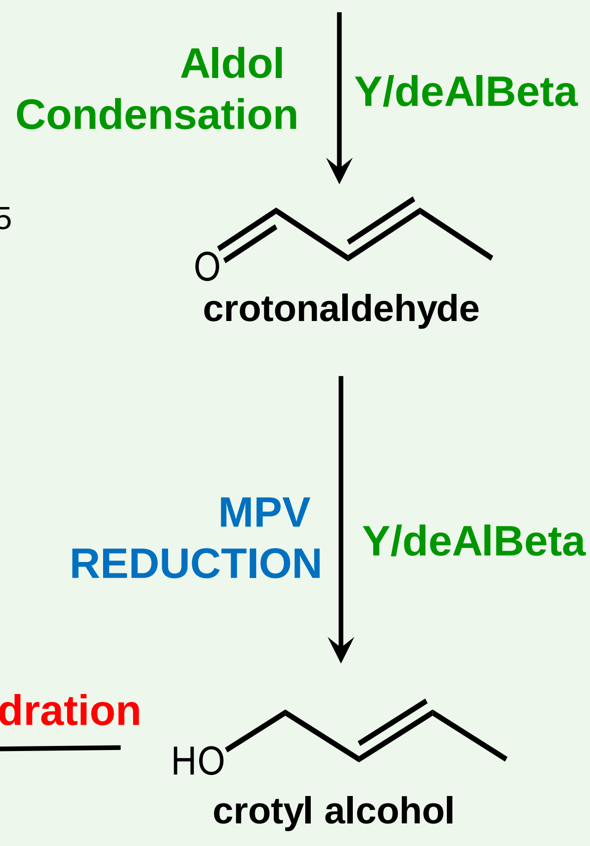
Proposed Ethanol to Butadiene Reaction Pathway on Y/deAlBeta

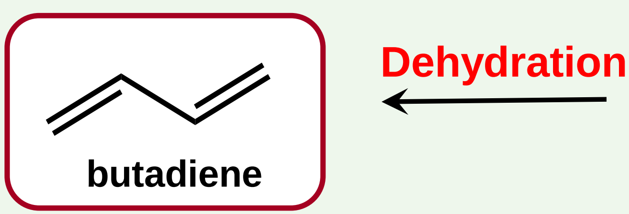
Inert environment



Ag-Zr catalysts
Sushkevich et al., *ChemSusChem*, 7 (2014) 2527-2536
Dagle et al., *Appl. Catal. B*., 236 (2018) 576-587
Miyake et al., *ACS Sus. Chem. Eng*., 10 (2022) 1020-1035

Zn and/or Y catalysts
Yan et al., *ACS Catal*., 8 (2018) 2760-2773
Qi et al., *J. Am. Chem. Soc.,* 34 (2020) 14674-14687

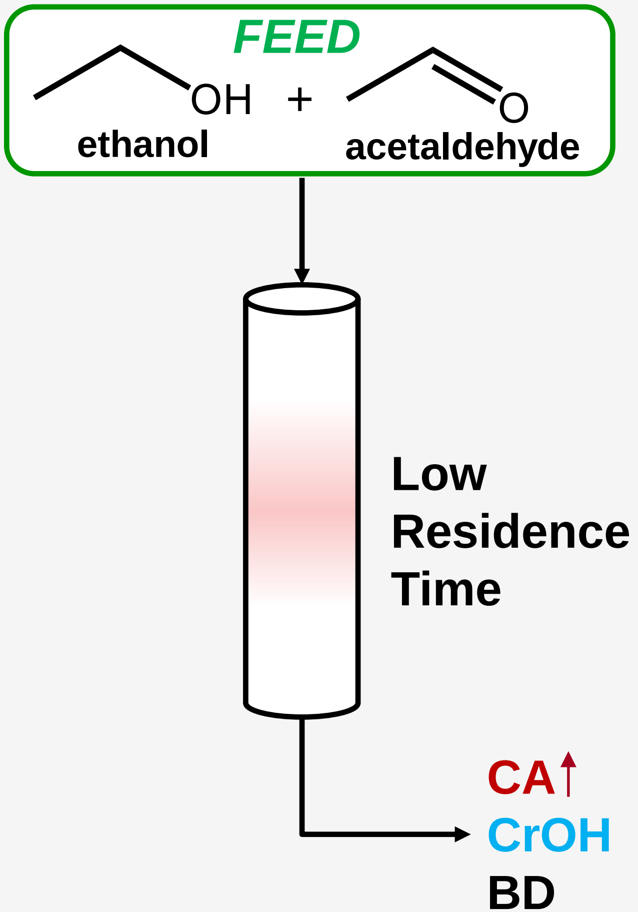


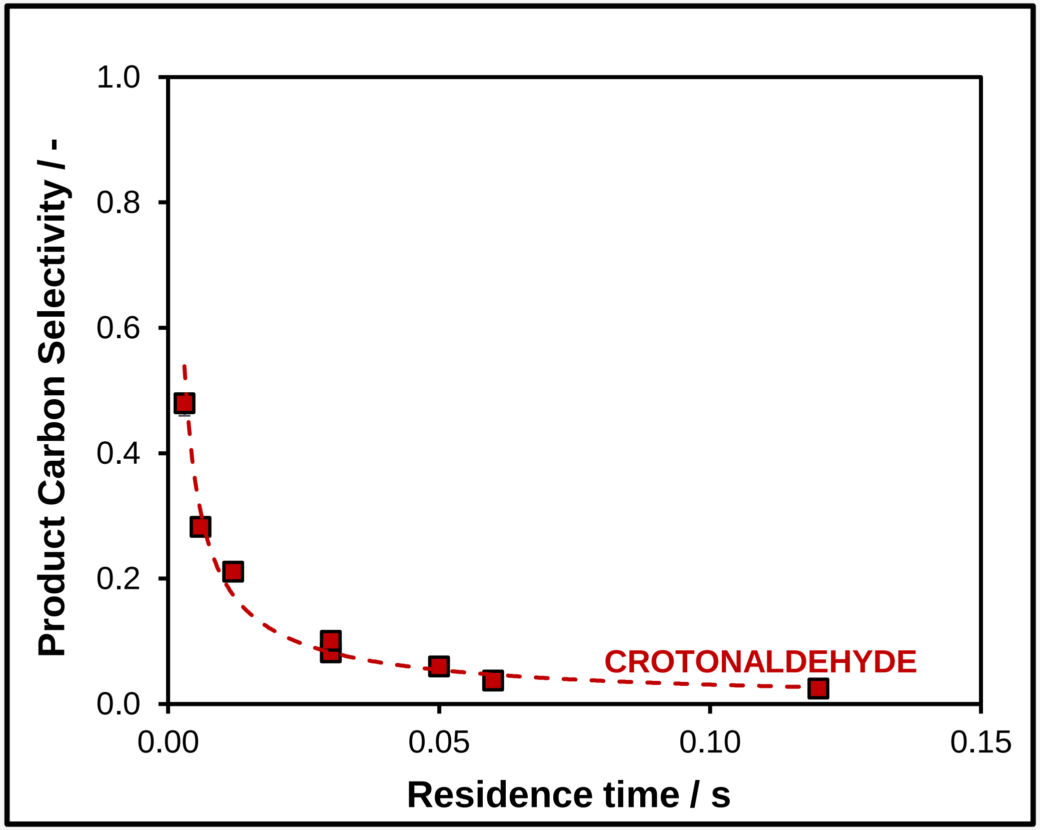


Is crotonaldehyde actually an intermediate en route to butadiene?

Zhang, Wegener, Samad et al., *ACS Catal.,* 11 (2021) 9885-9897

Probing reaction pathway by varying residence time





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Catalyst: Pure ~0.1 g $Y_{0.5}$/deAlBeta, diluted **~**0.01 g $Y_{0.5}$/Beta in ~0.09 g SiC

Borate, Samad, Harris et al., *in prep*

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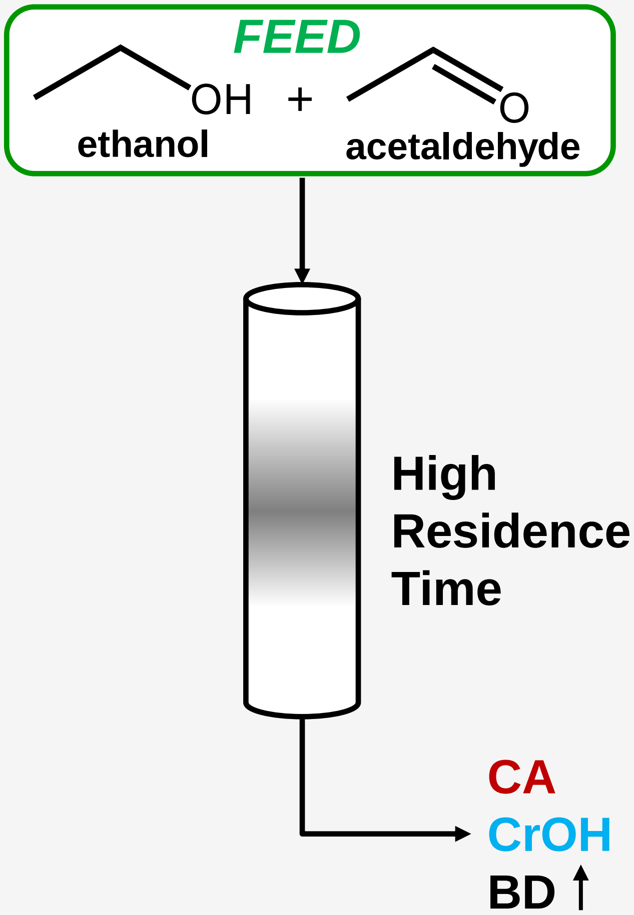

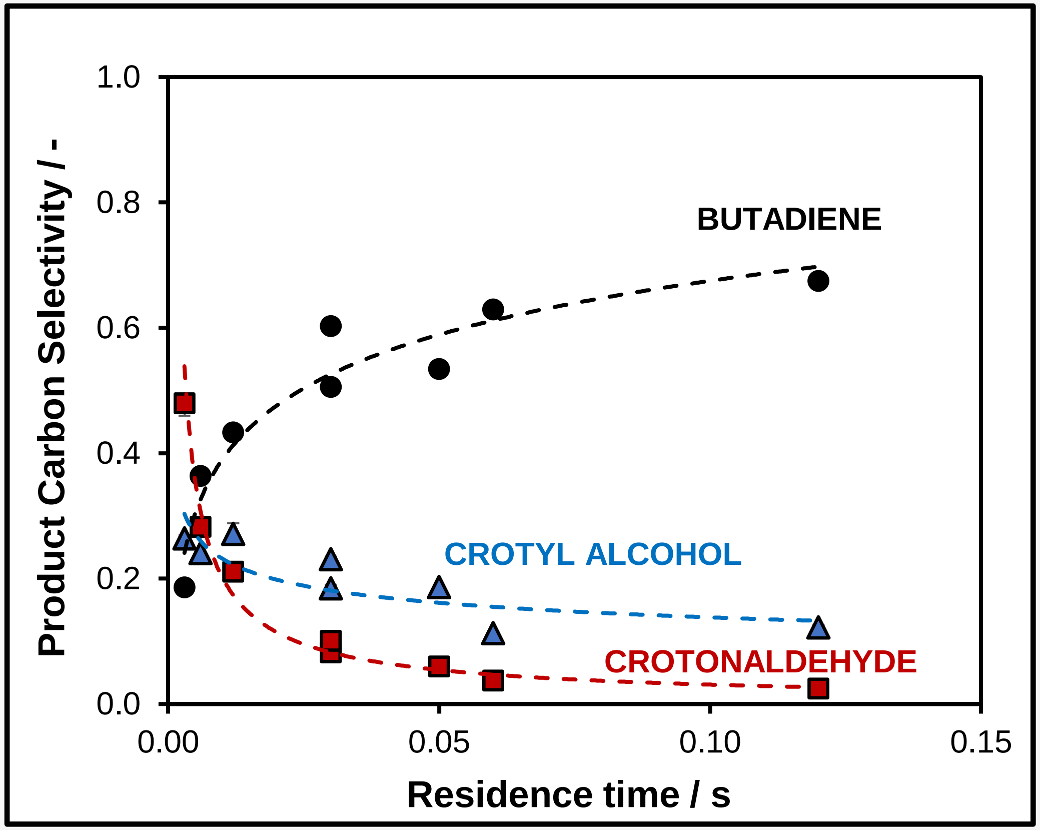

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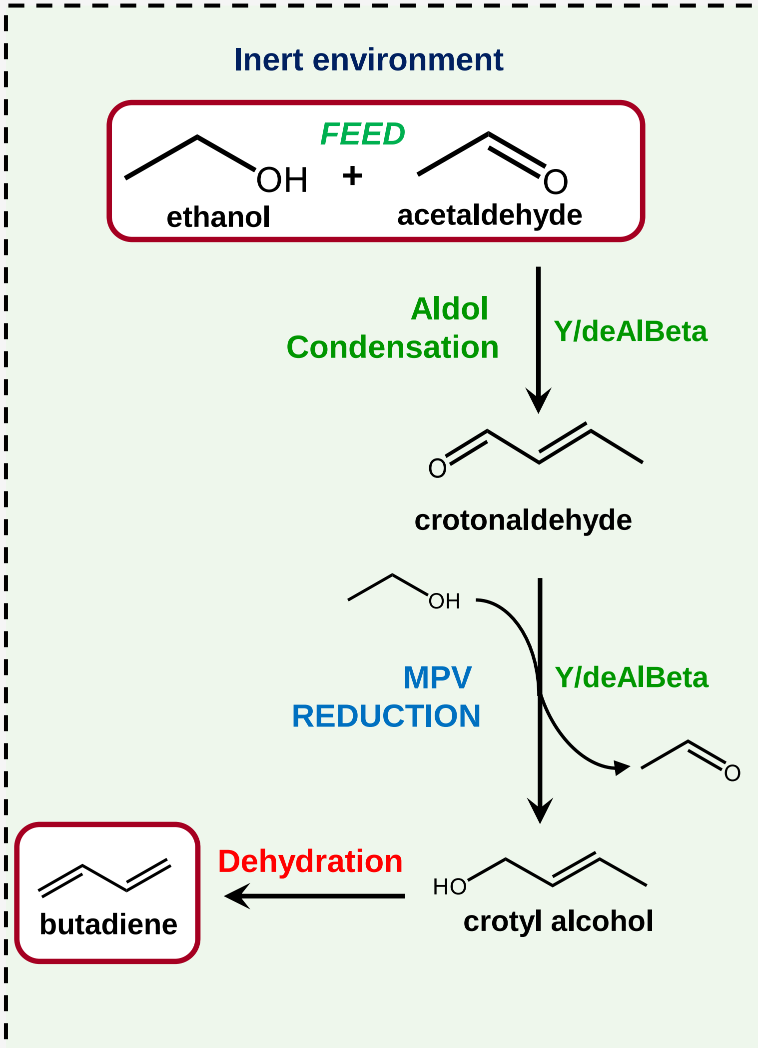

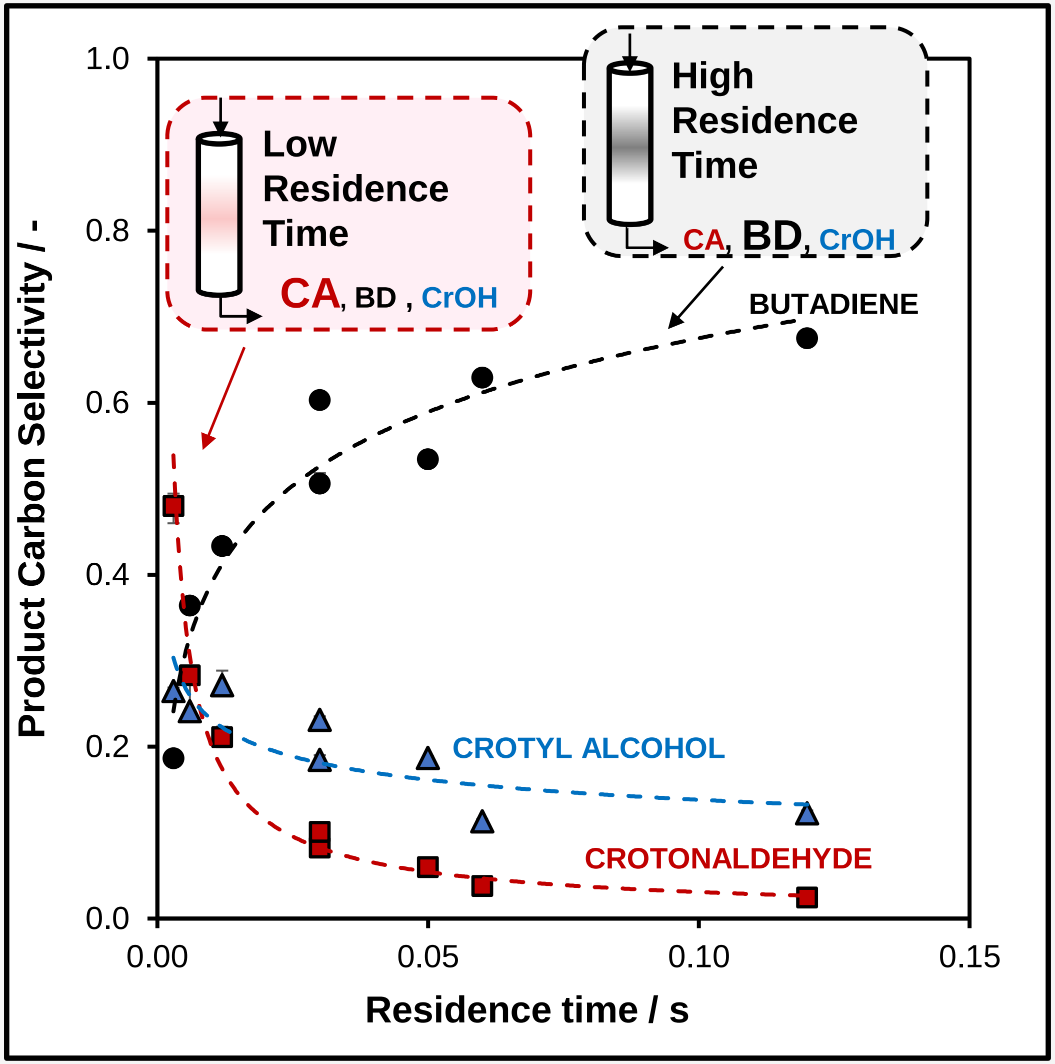

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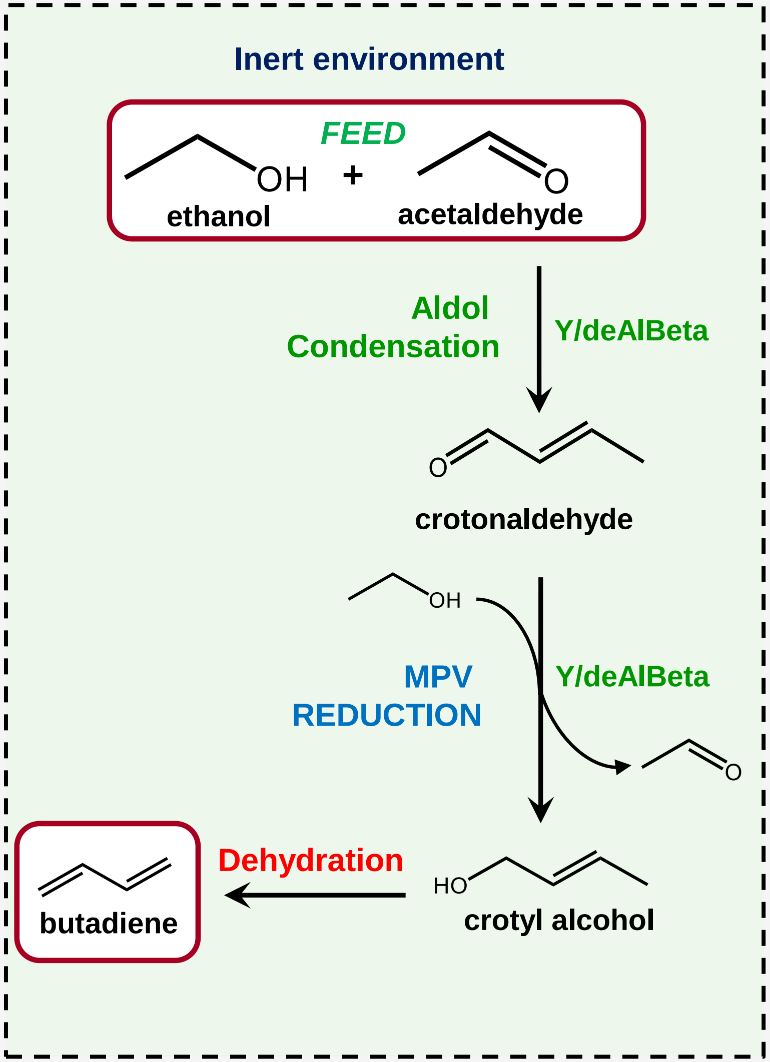
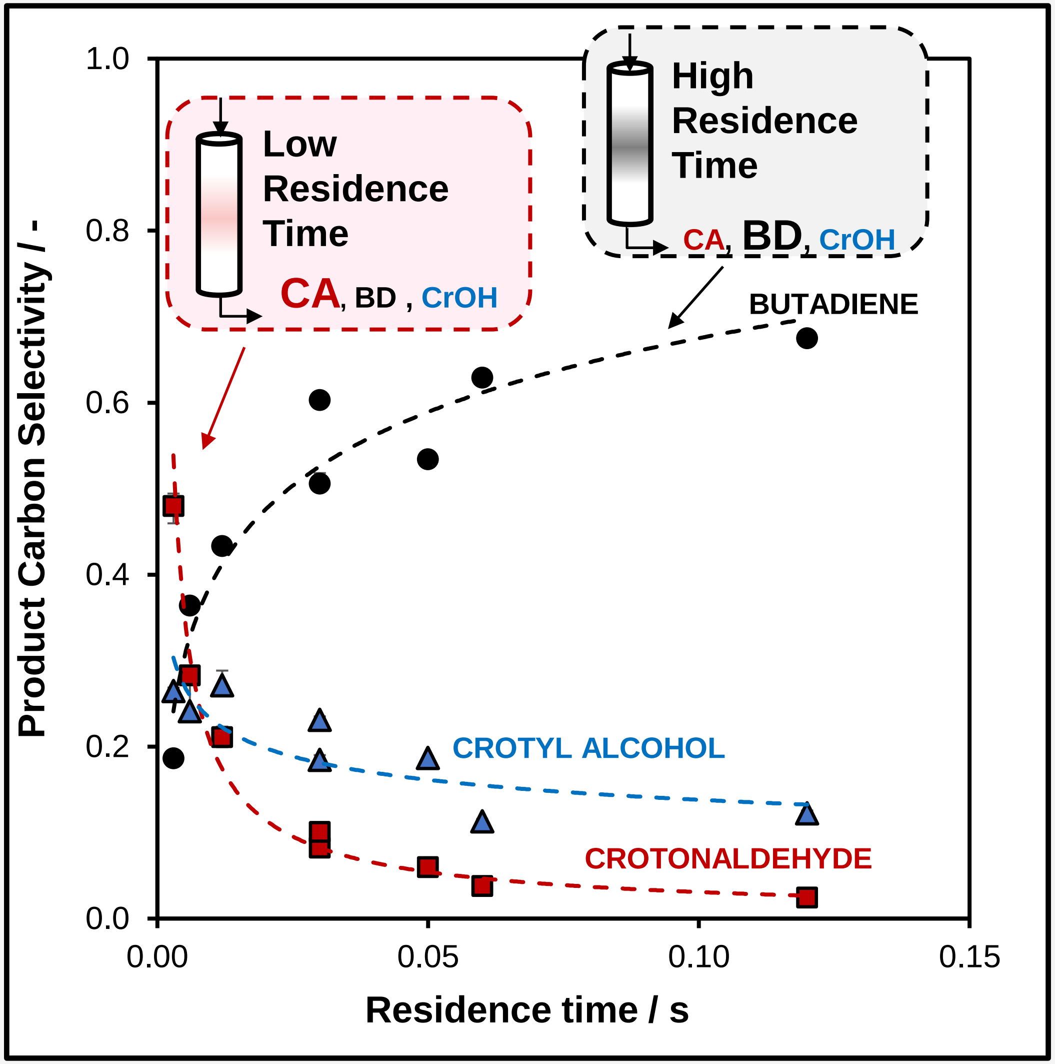
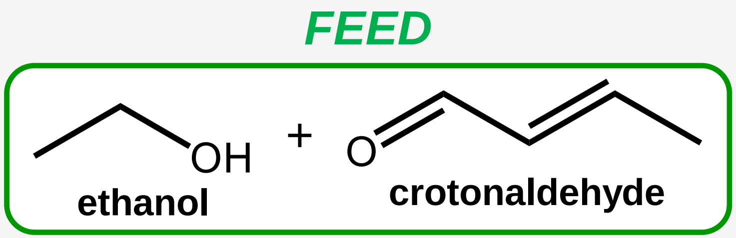
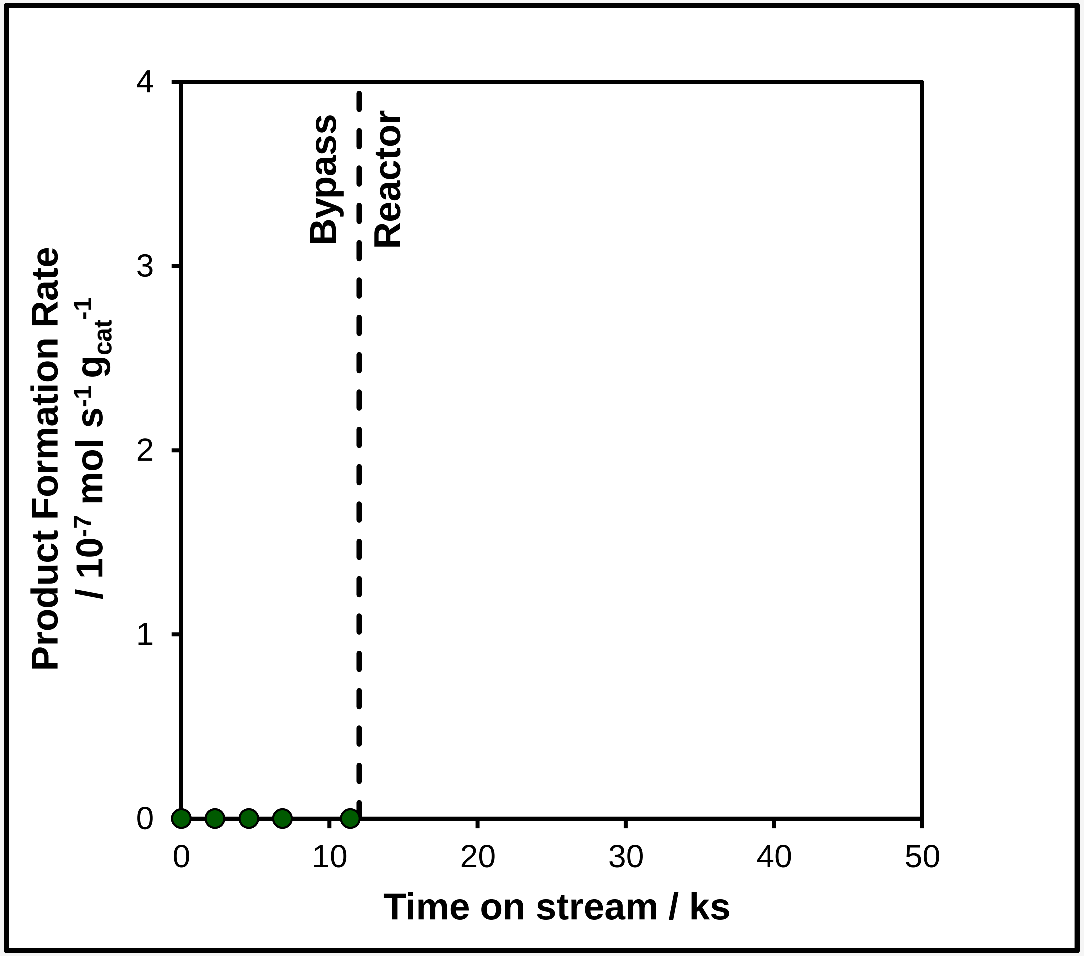




Crotonaldehyde is a primary product, butadiene is a terminal product

How is crotonaldehyde consumed? MPV reduction?





Reaction conditions: T= 483 K; P=124 kPa
Gas Flows: 0.014 kPa CA, 1 kPa EtOH, 0.98 kPa CH_4, bal He; Total flowrate 100 cm^3 min^{-1}
Catalyst: diluted ~0.01 g Y_3/deAlBeta in ~0.09 g SiC

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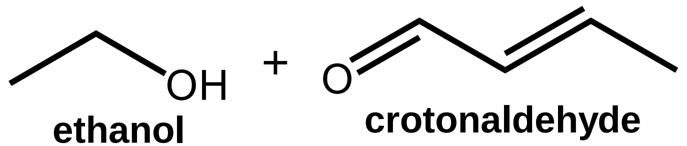
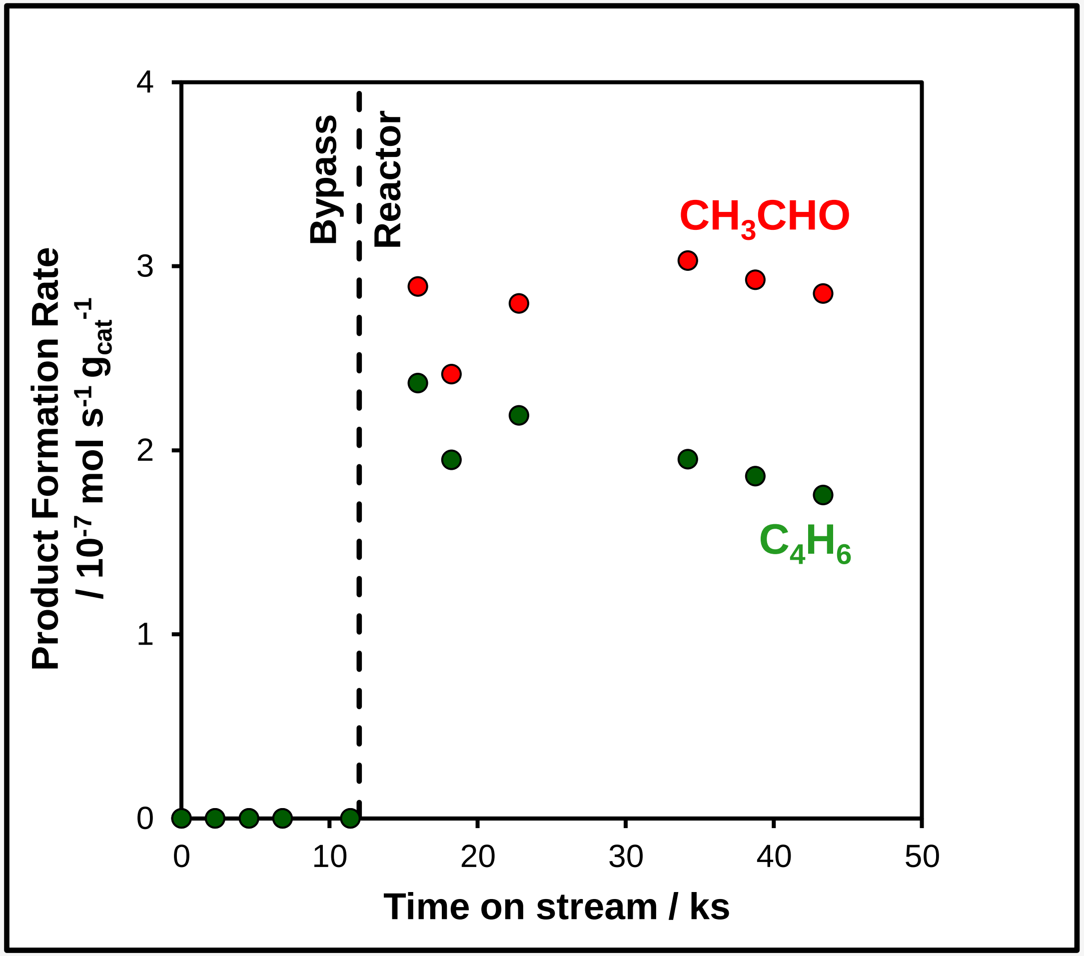
How is crotonaldehyde consumed? MPV reduction?

FEED





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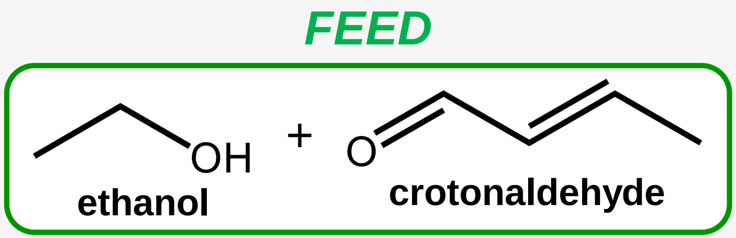
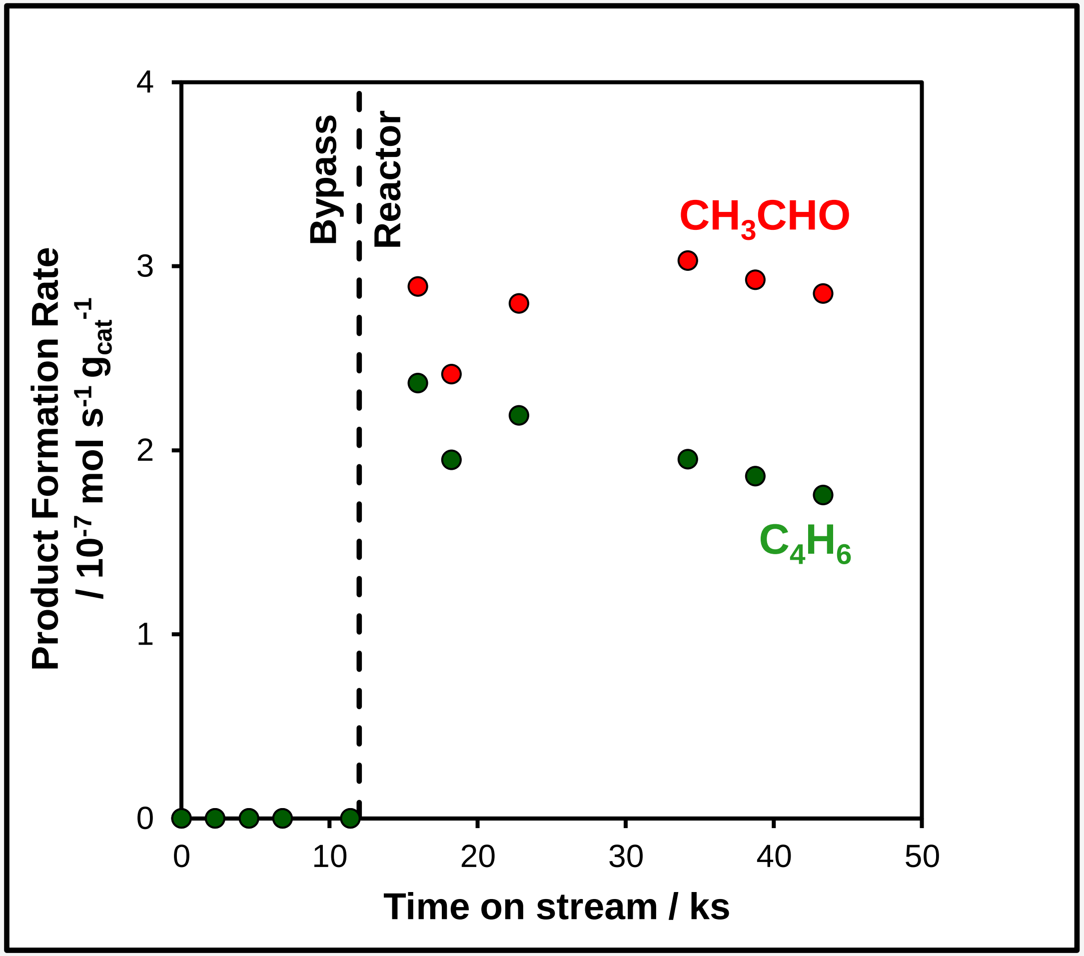




Crotonaldehyde reacts with ethanol to form acetaldehyde and BD

Reaction conditions: T= 483 K; P=124 kPa

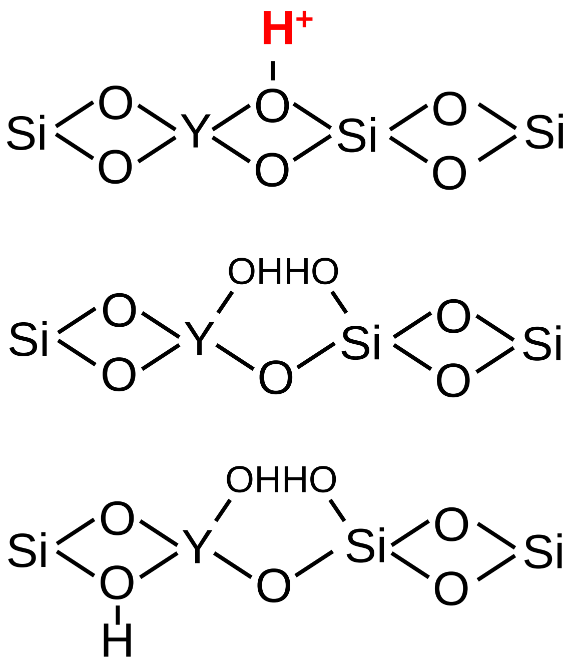
Gas Flows: 0.014 kPa CA, 1 kPa EtOH, 0.98 kPa CH_4, bal He; Total flowrate 100 $cm^3\ min^{-1}$

Catalyst: diluted ~0.01 g Y_3/deAlBeta in ~0.09 g SiC

Borate, Samad, Harris et al., *in prep*

How do we get from acetaldehyde and ethanol to butadiene?

What are the active sites and how many are there?



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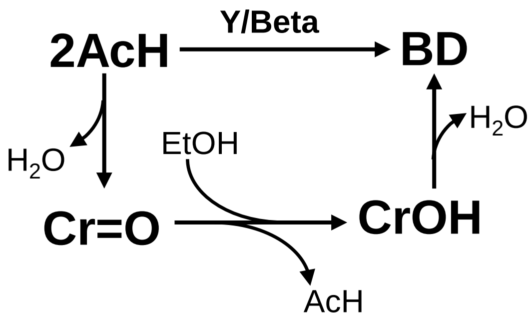
- *BD forming sites ≠ sites titrated in IR*
- *Crotonal forming sites unaffected by pyridine*

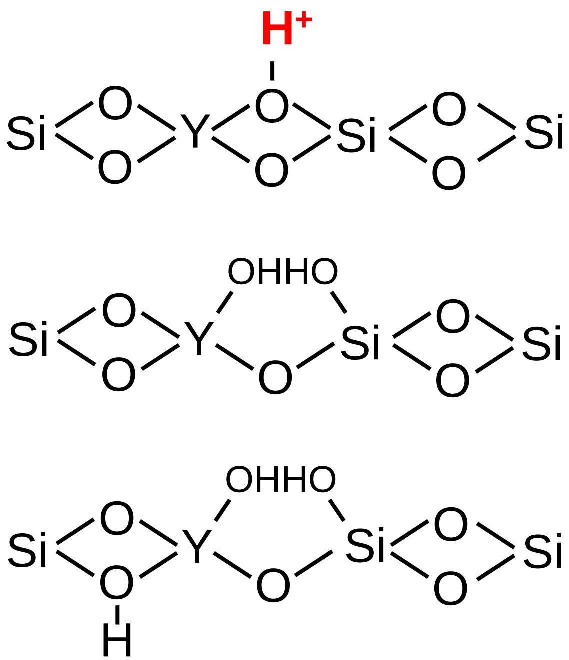
What is the reaction pathway?



- *Crotonal is an intermediate that can undergo MPV reduction with ethanol, which leads to BD formation*

Can we measure kinetics?

What are the active sites and how many are there?



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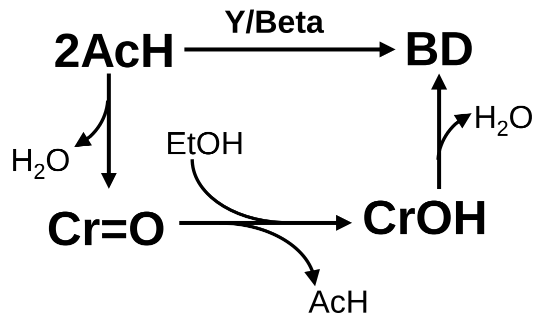
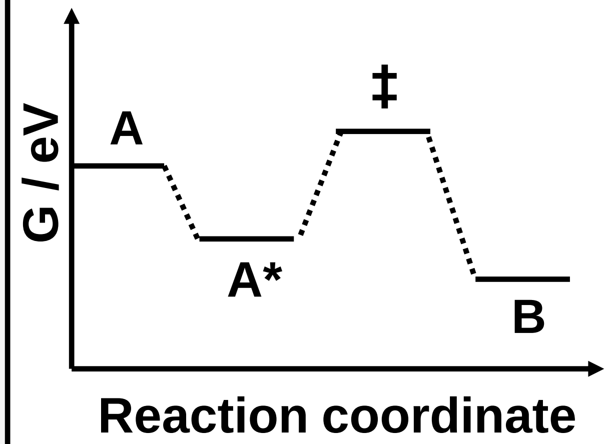


- ***Crotonal is an intermediate that can undergo MPV reduction with ethanol, which leads to BD formation***

What are the reaction mechanisms?

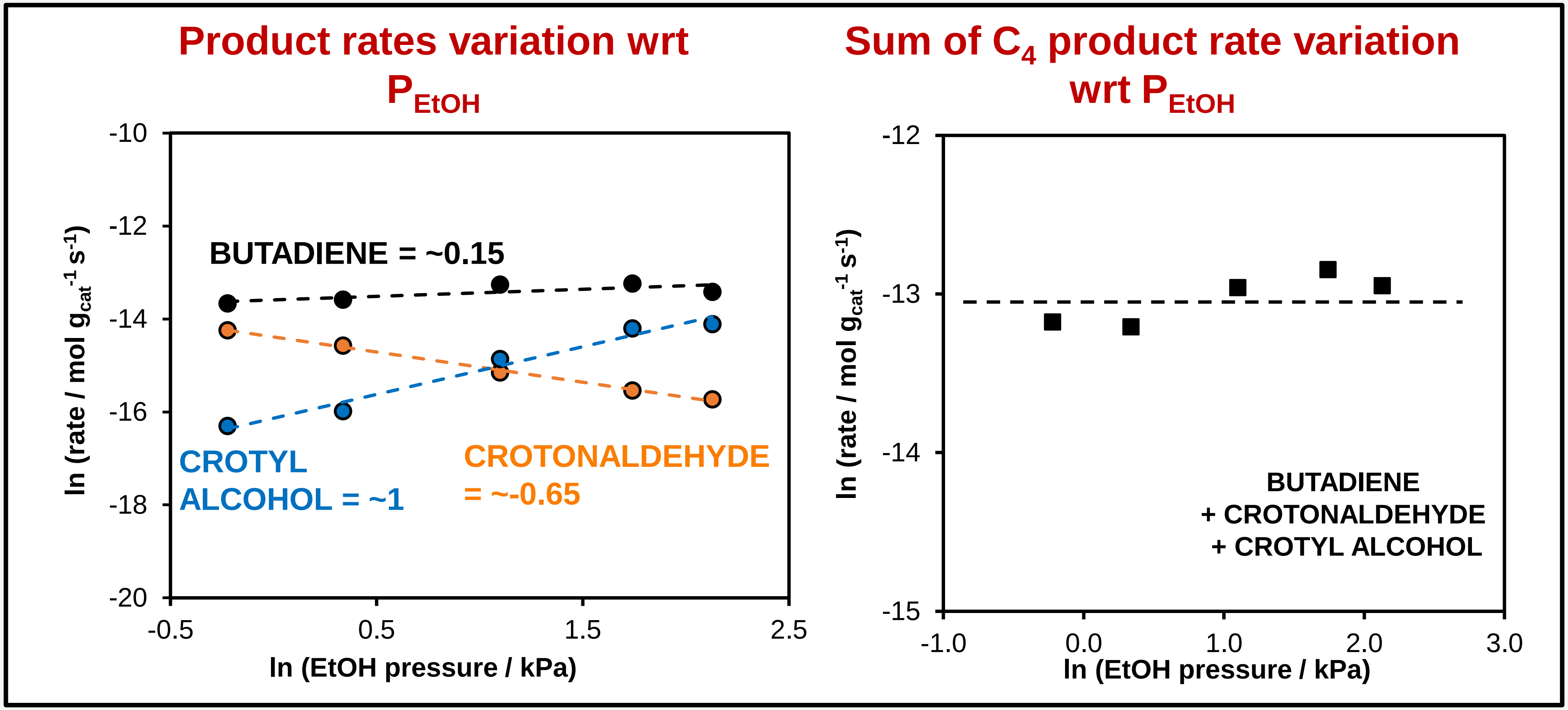


Reaction order test on Y_{10}/deAlBeta (IWI)

Product rates variation wrt P_{EtOH}

Sum of C_4 product rate variation wrt P_{EtOH}

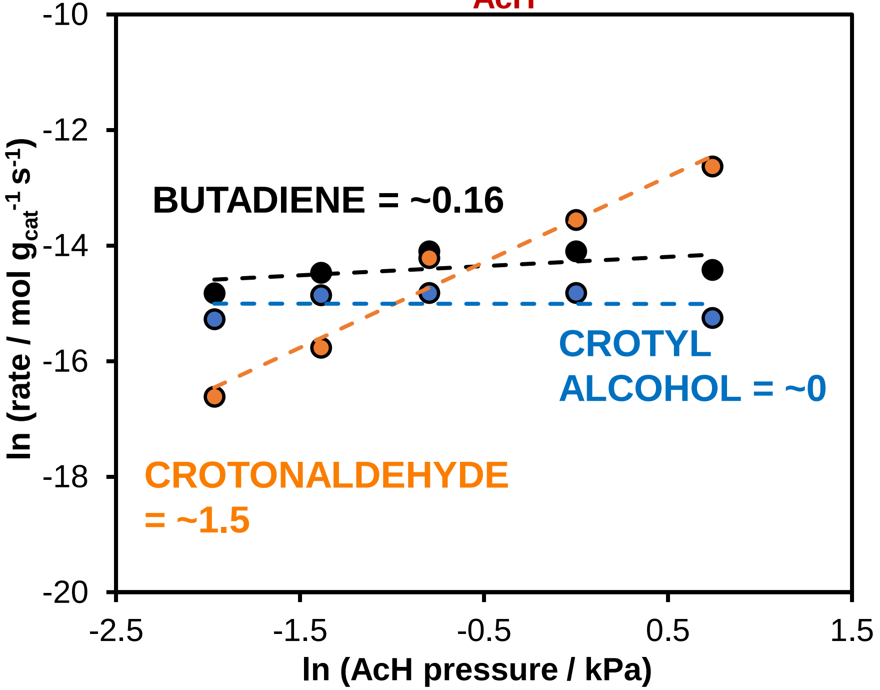
Ethanol Reaction Order over Y_{10}/deAlBeta (IWI)



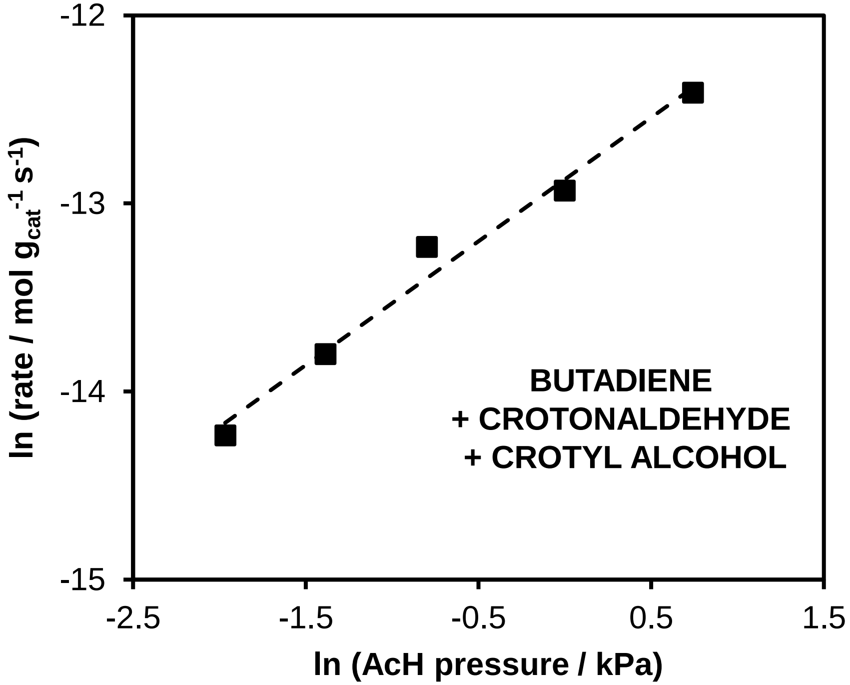
Reaction conditions: T= 503 K; P=124 kPa
Gas Flows: Partial pressure of EtOH and AcH varied, 0.098 kPa CH_4, bal He; Total flowrate 100 cm^3 min^{-1}
Catalyst: diluted ~0.01 g Y_{10}/deAlBeta in ~0.09 g SiC

Acetaldehyde Reaction Order over Y_{10}/deAlBeta (IWI)

Product rates variation wrt P_{AcH}



Sum C_4 variation with P_{AcH}



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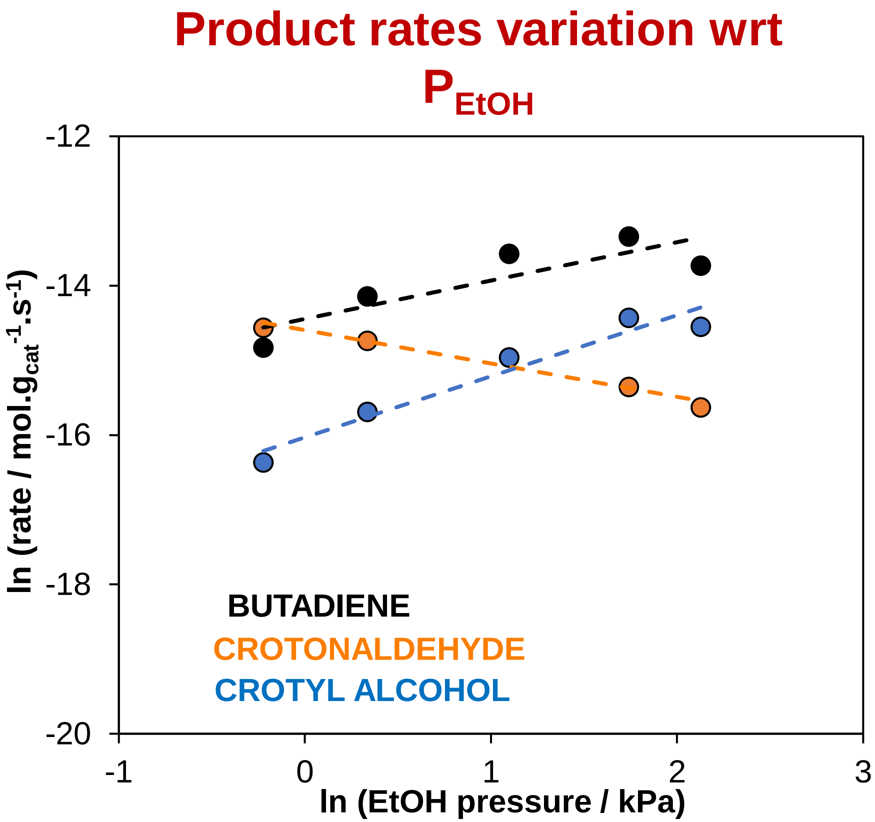
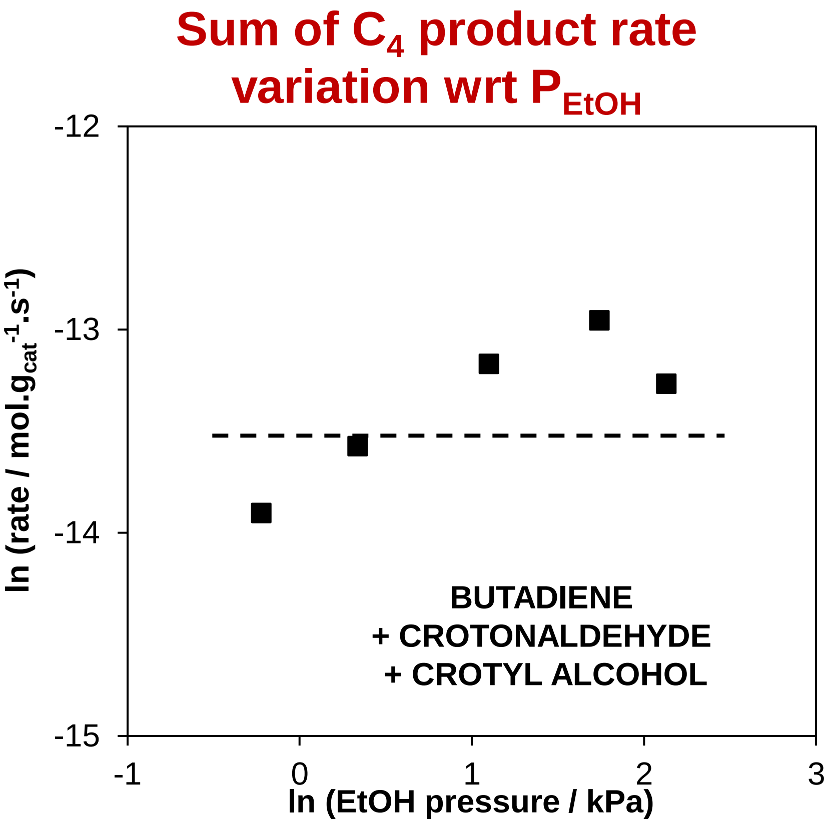
Reaction order test on La$_4$/deAlBeta (IWI)





Kinetic dependencies likely vary with identity of the rare earth metal

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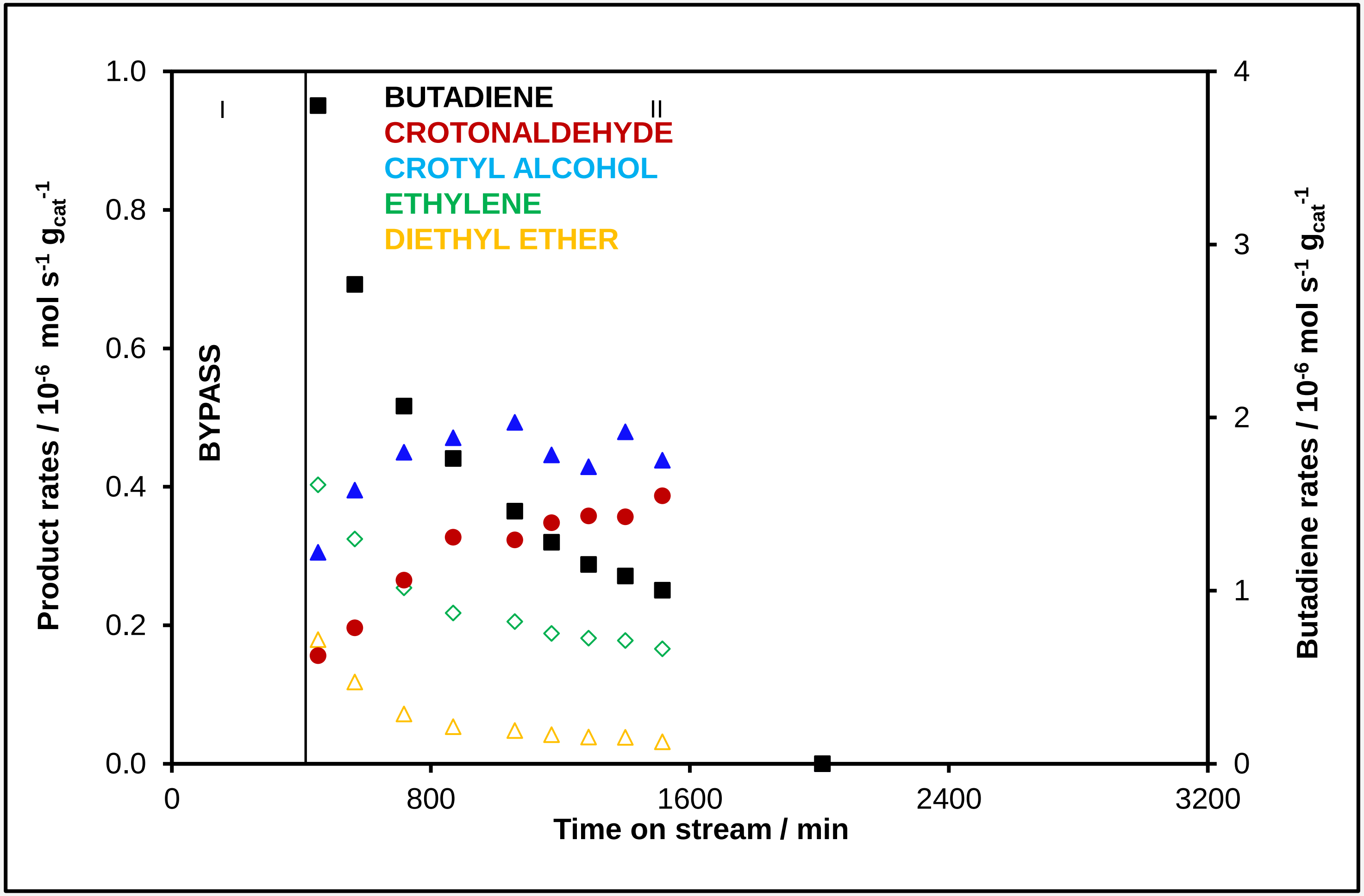
Kinetic isotope effect experiments on Y_5/deAlBeta



I-II. C_2H_5OH+CH_3CHO

Reaction conditions: T= 503 K, P= 124 kPa
Gas flows: 1.5 kPa EtOH, 0.2 kPa AcH (H form reagents: panels II and VIII, D-form EtOH and H-form AcH panel IV, D-form EtOH and AcH: panel VI, Bypass conditions: panels I,III, V and VII), 0.98 kPa CH_4, Balance He. Total flow 50 cm^3 min^{-1}
Catalyst: 0.01 g Y_5/deAlBeta(19) diluted with 0.09 g SiC

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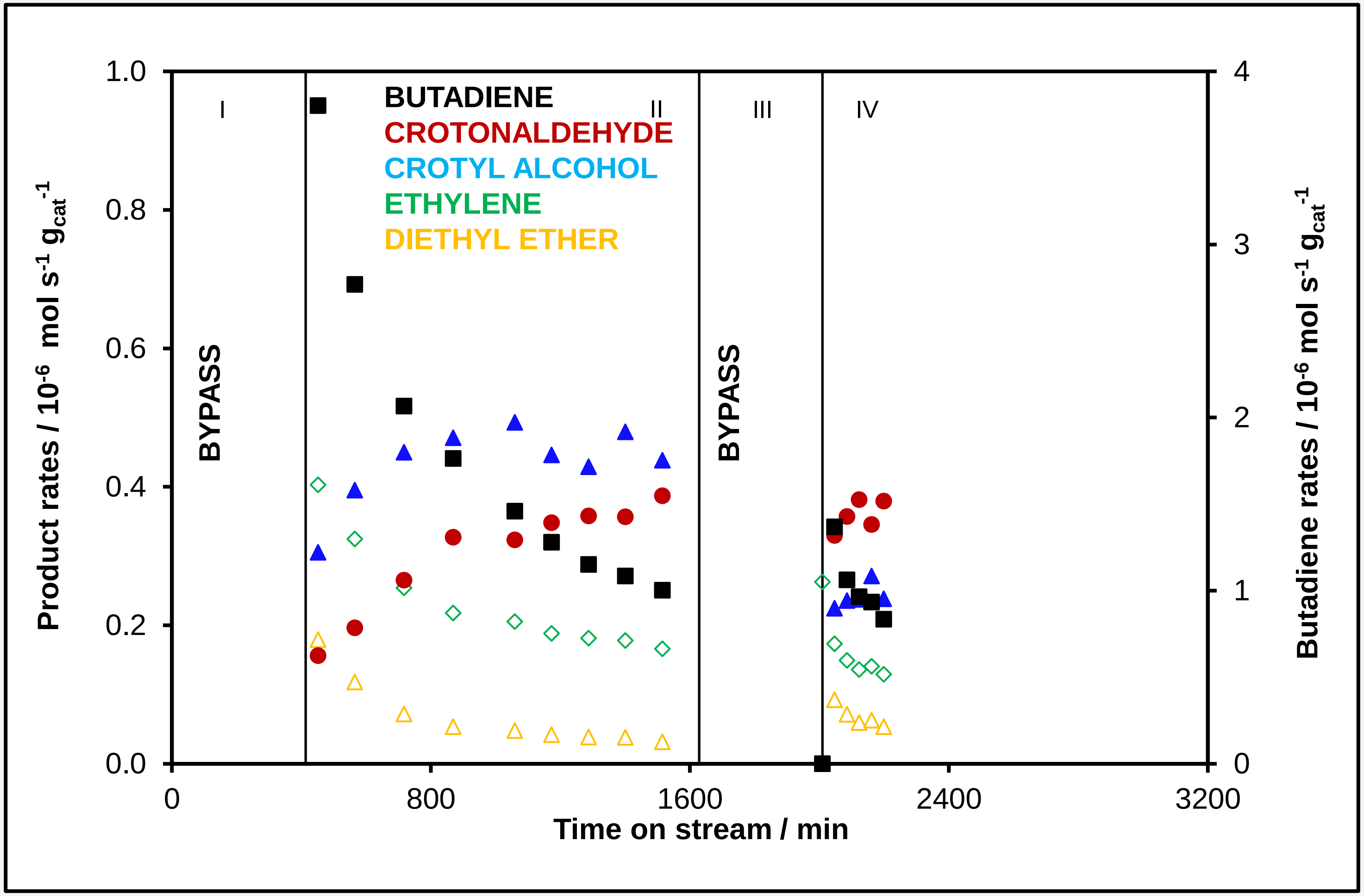

I-II. $C_2H_5OH+CH_3CHO$

III-IV. $C_2D_5OD+CH_3CHO$

Reaction conditions: T= 503 K, P= 124 kPa
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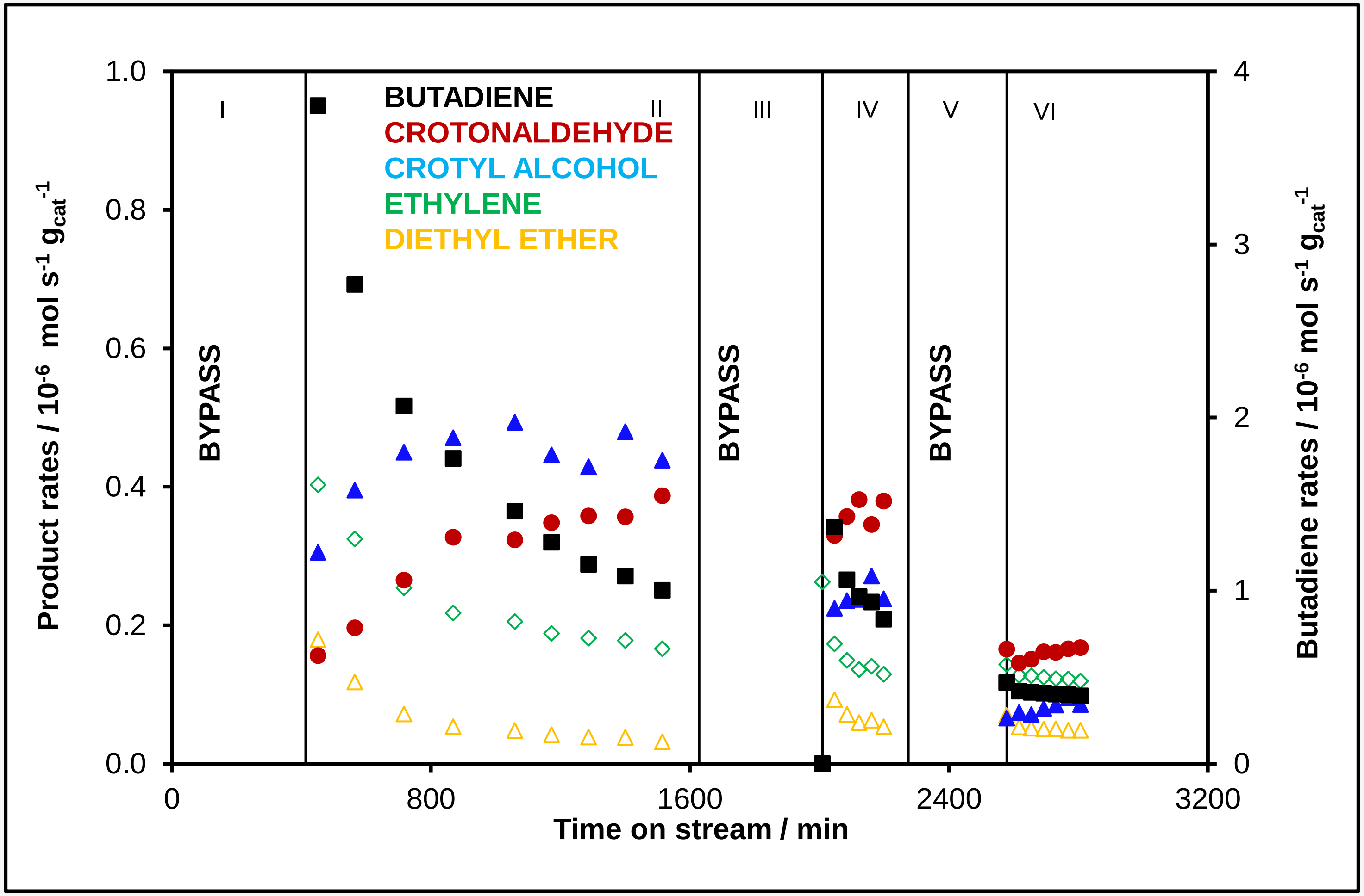

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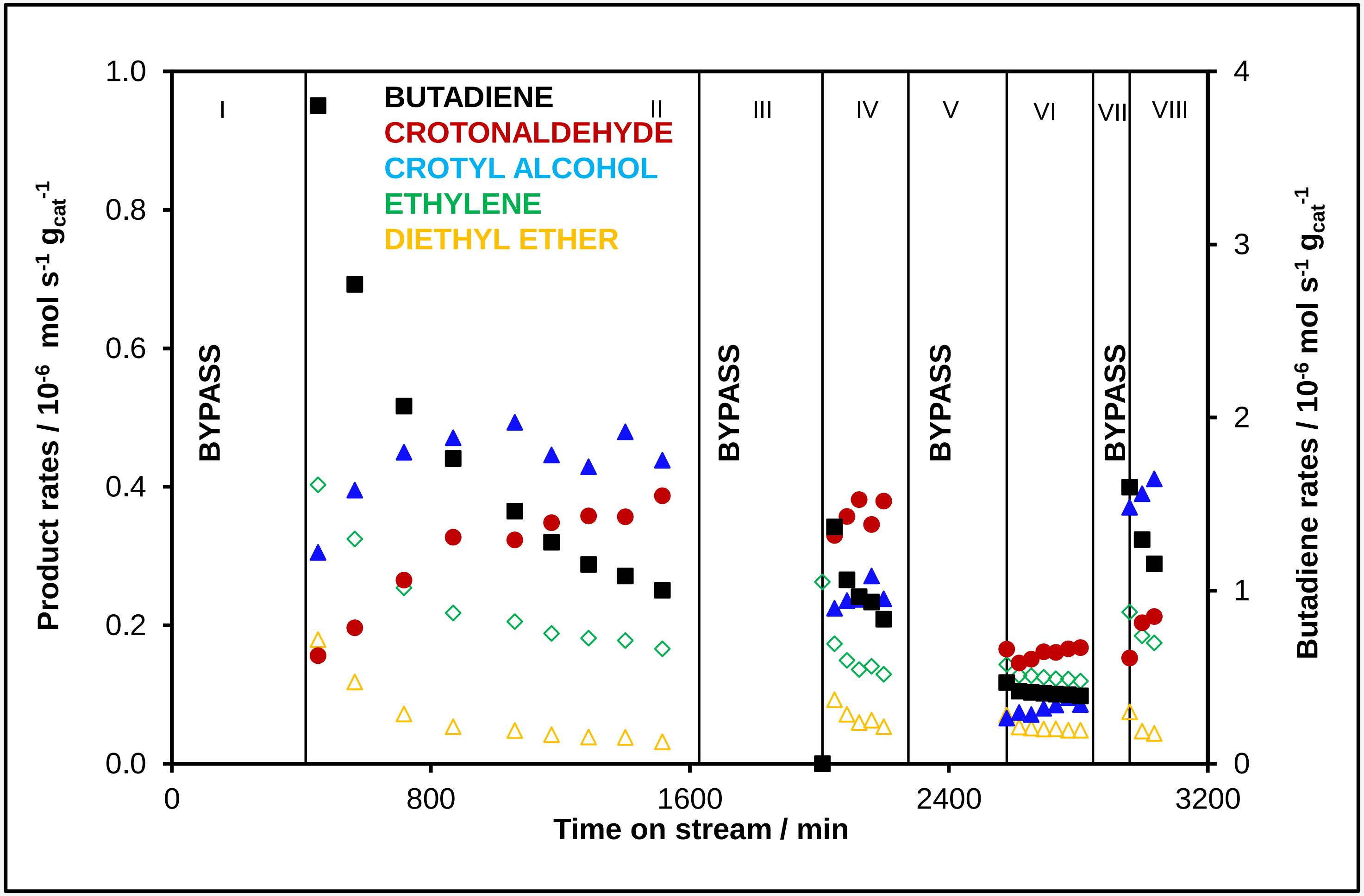

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III-IV. $C_2D_5OD+CH_3CHO$

V-VI. $C_2D_5OD+CD_3CDO$

VII-VIII. $C_2H_5OH+CH_3CHO$

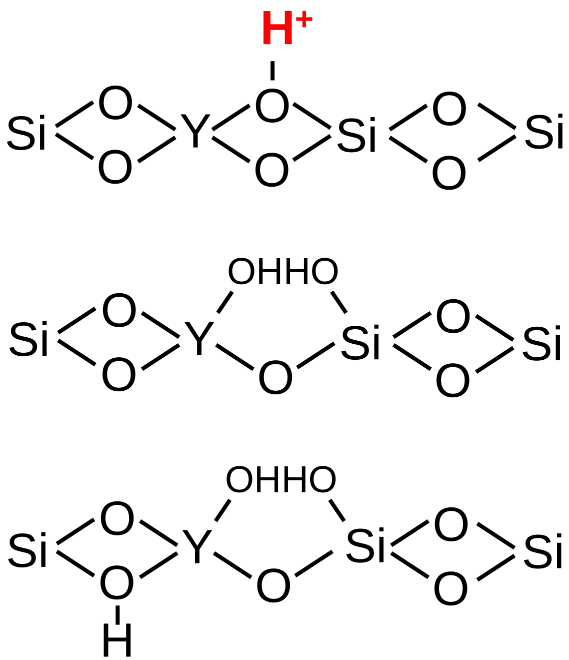
Reaction conditions: T= 503 K, P= 124 kPa
Gas flows: 1.5 kPa EtOH, 0.2 kPa AcH (H form reagents: panels II and VIII, D-form EtOH and H-form AcH panel IV, D-form EtOH and AcH: panel VI, Bypass conditions: panels I,III, V and VII), 0.98 kPa CH_4, Balance He. Total flow 50 cm^3 min^{-1}
Catalyst: 0.01 g Y_5/deAlBeta(19) diluted with 0.09 g SiC

Isotopic labeling experiments on Y_5/deAlBeta

Products	Measured rates averaged / 10^{-6} mol s^{-1} g_{cat}^{-1}				KIE values	
	R_{H}_initial	R_{H}_final	R_{D}_EtOH D_6	R_{D}_EtOH D_6+AcH-D_4	R_H/R_D only ethanol labeled	R_H/R_D both labeled
Butadiene	1.08	1.23	0.91	0.40	1.2	3.1
Crotonaldehyde	0.37	0.21	0.37	0.16	1.0	1.3
Crotyl alcohol	0.45	0.40	0.25	0.09	1.8	4.6
Total C_4	**1.90**	**1.83**	**1.53**	**0.65**	**1.2**	**2.8**
Ethylene	0.18	0.18	0.14	0.12	1.3	1.5
DEE	0.04	0.05	0.06	0.05	0.6	0.9

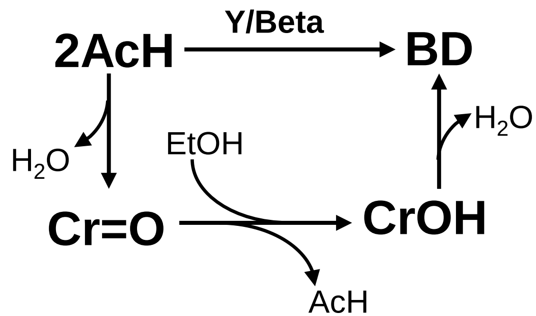
Can we measure kinetics?

What are the active sites and how many are there?



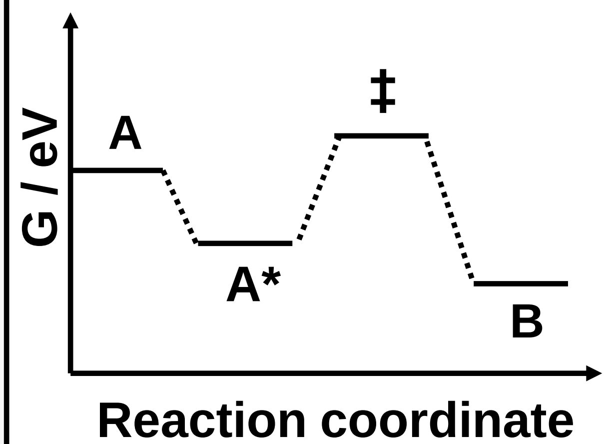
- ***Minimal H^+ in Y/deAlBeta***
- ***BD forming sites ≠ sites titrated in IR***
- ***Crotonal forming sites unaffected by pyridine***

What is the reaction pathway?



- ***Crotonal is an intermediate that can undergo MPV reduction with ethanol, which leads to BD formation***

What are the reaction mechanisms?



- ***C_{4+} product formation is:***
  - ***~0 order in C_2H_5OH***
  - ***>1st order in CH_3CHO***

Acknowledgements

U. Alabama

- Nohor "River" Samad (M.S. 2022, Westrock)
- Sumin Lee (B.S. 2020; Ga. Tech)
- Ryan Kitchen (B.S. 2022)
- Chase McGee (REU 2022, U. Conn.)
- Zahra Almohamedhusain (B.S. 2024)

Johns Hopkins U.

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- Prof. Michael Tsapatsis

Oak Ridge National Laboratory

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- Dr. Michael Cordon
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- Dr. Andrew Sutton
- Dr. Zhenglong Li (Now: Zhejiang University, China)

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Questions?

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