



**National Laboratory
of the Rockies**

Modification of zeolite catalysts to boost bio-oil yield in biomass catalytic pyrolysis

Cody Wrasman (Cody.Wrasman@nlr.gov)

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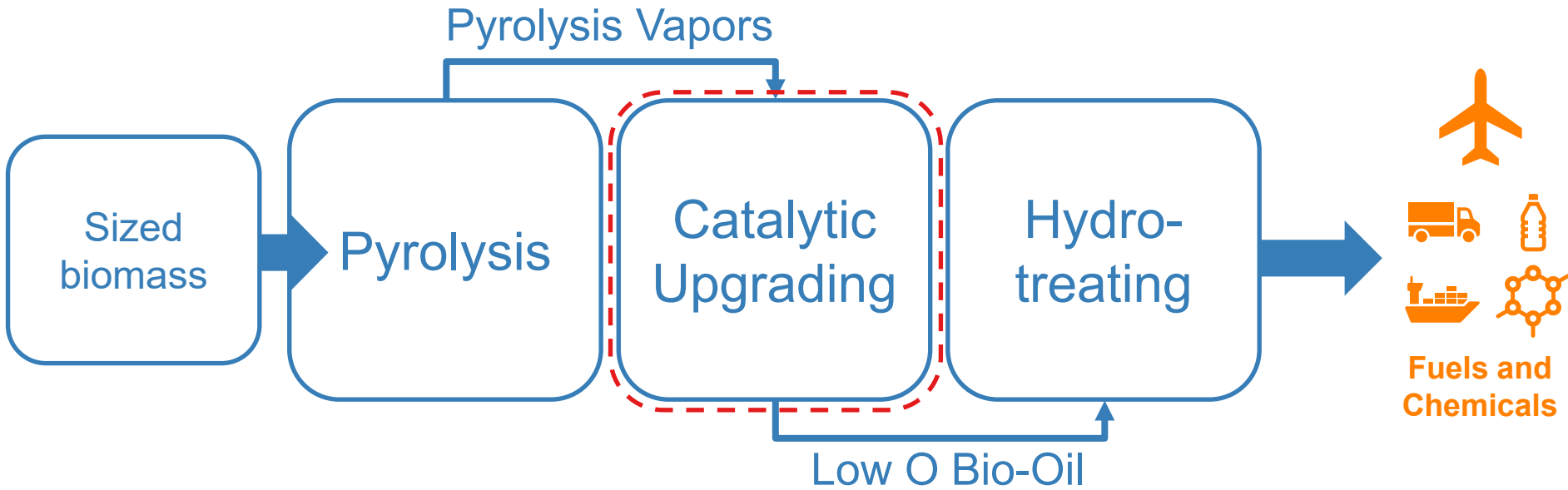
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Catalytic pyrolysis provides a pathway from biomass to hydrocarbon fuels and chemicals



Catalytic upgrading enables hydrotreating by stabilizing bio-oil



Catalytic Upgrading Goals

1. Stabilize Bio-oil by deoxygenation and cracking
2. Maintain high carbon yields to bio-oil

Catalytic upgrading goals are in tension with each other

1. Stabilize Bio-oil by deoxygenation and cracking

- Less Bio-oil O requires less H_2 during hydroprocessing
 - 5 wt.% less O reduced fuel selling price by over 10 %
- O groups in bio-oil can cause instability and processing challenges

2. Maintain high carbon yields to bio-oil

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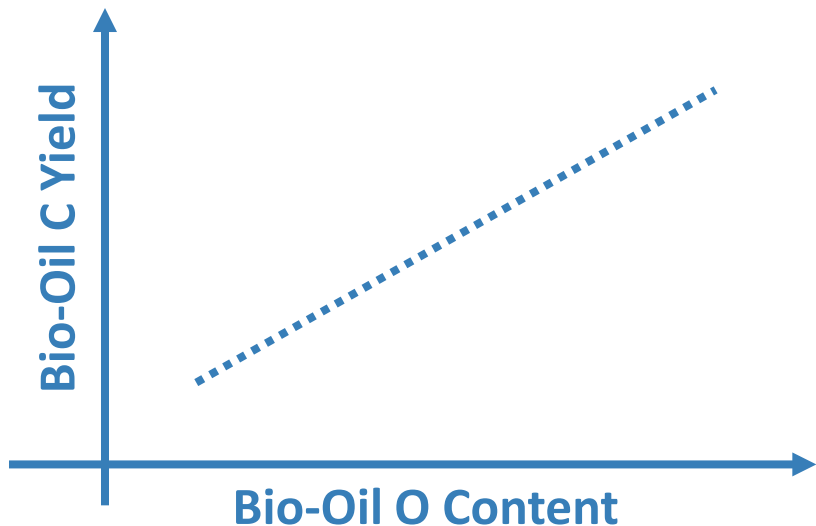
2. Maintain high carbon yields to bio-oil

- Feedstock cost is a major contributor to fuel selling price
 - 3 % higher carbon yield to bio-oil reduced fuel selling price by 8 %.

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deoxygenation and cracking

2. Maintain high carbon
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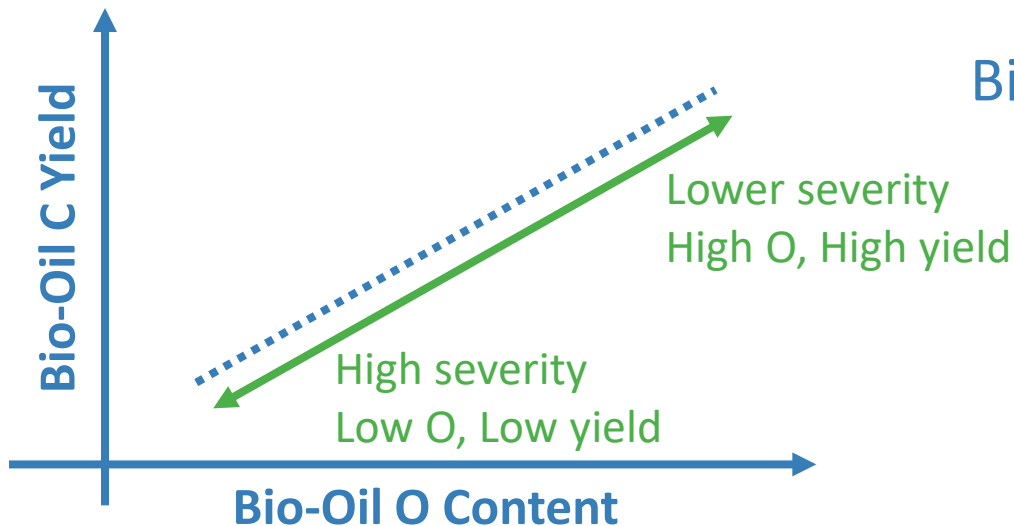


Bio-oil O content and C yield
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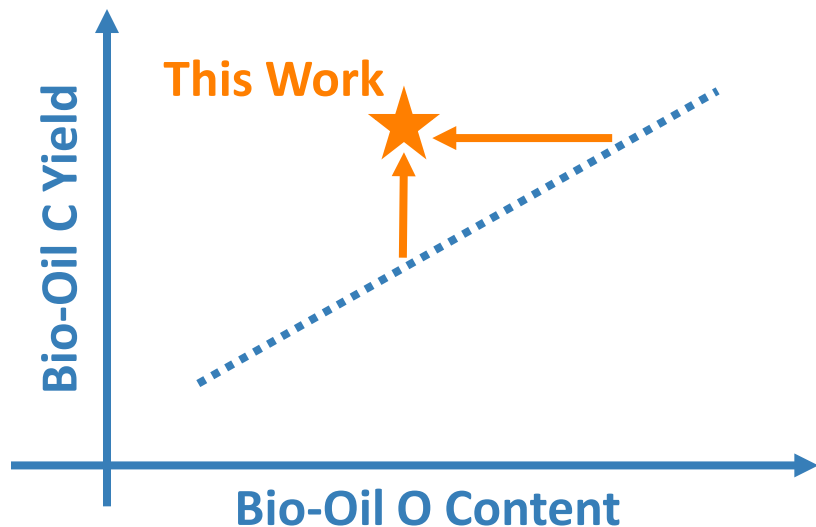
Bio-oil O content and C yield are often correlated

Increase severity by increasing temperature or increasing biomass to catalyst ratio

Catalytic upgrading goals are in tension with each other

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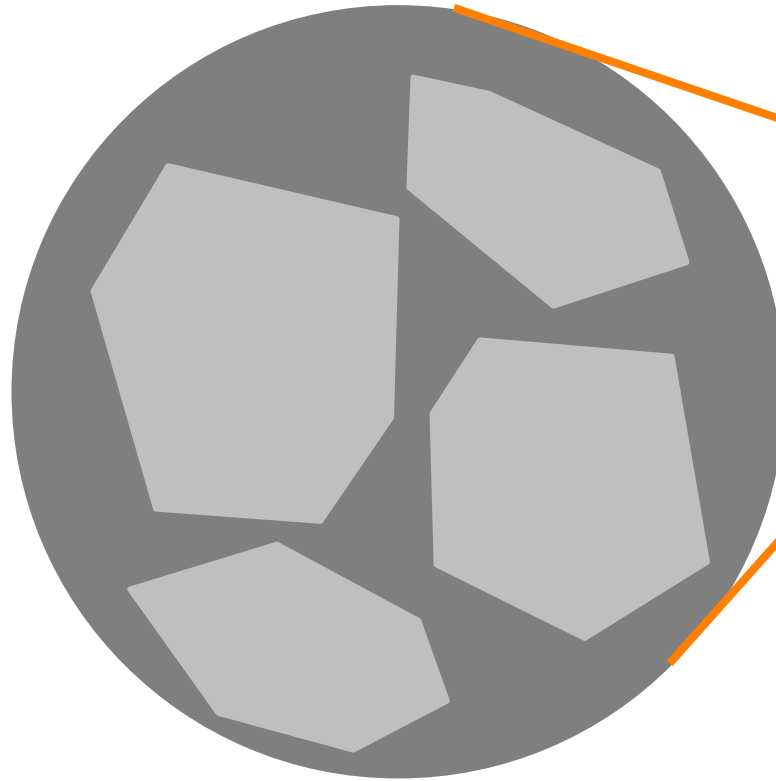


Bio-oil O content and C yield are often correlated

Zeolite modification can break scaling relationship, increasing yield while lowering O content

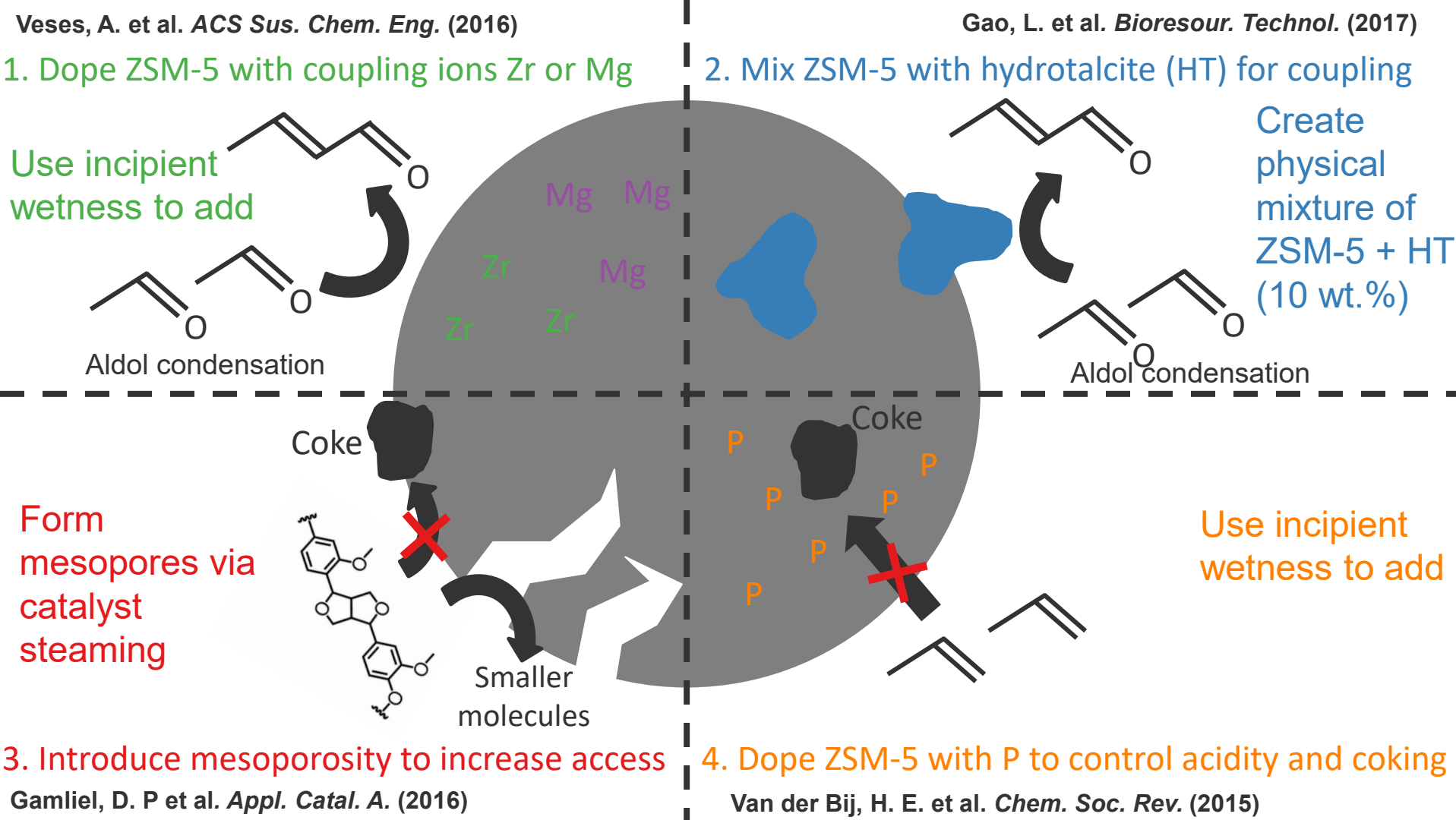
ZSM-5 uses acid sites to upgrade pyrolysis vapors

Modify formed
material to enable
use in semi-
integrated
fluidized bed
process



Formed ZSM-5
catalyst
 $d = 0.5 - 1 \text{ mm}$
Fluidizable

80 wt. % ZSM-5 SAR=30
20 wt. % Al_2O_3 Binder



Catalysts were screened at small scale to identify the most promising candidates

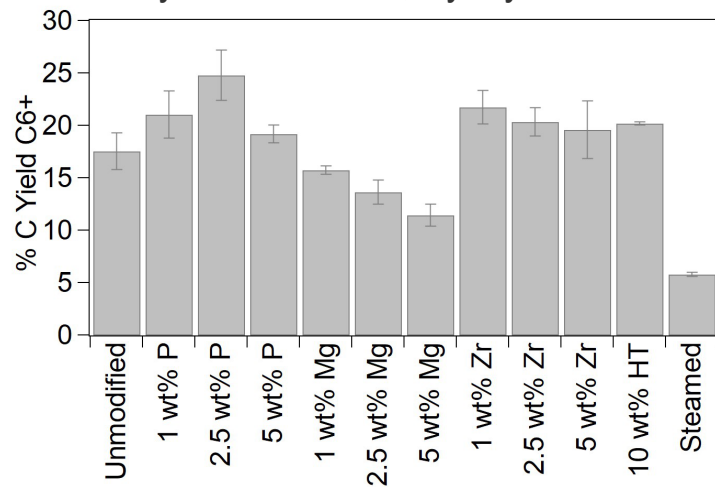
Test the ability of 12 catalysts to:

1. Maximize detectable molecules with 6+ carbon atoms that can be transformed into fuels (crack large molecules without overcracking)
2. Remove oxygen from the products (deoxygenation)

Utilize tandem micro-reactor from Frontier for these experiments with 0.5 mg pine biomass with 5 mg catalyst

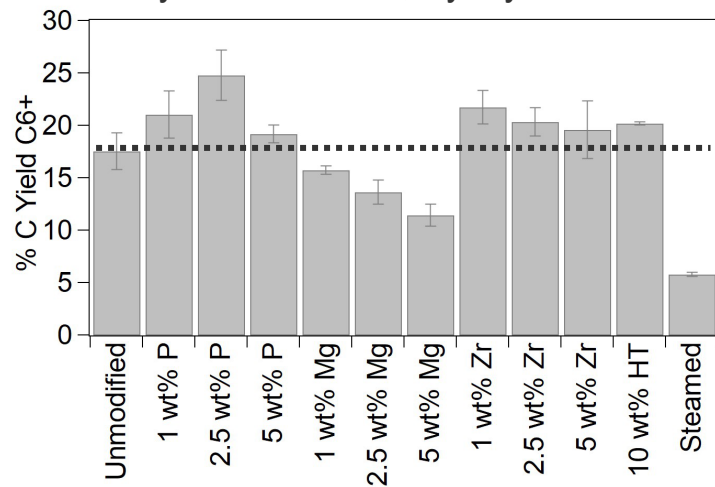
Catalysts were screened at small scale to identify the most promising candidates

Catalysis T = 500 °C, Pyrolysis T = 500 °C, Biomass/Catalyst = 0.2, Average of 3 measurements



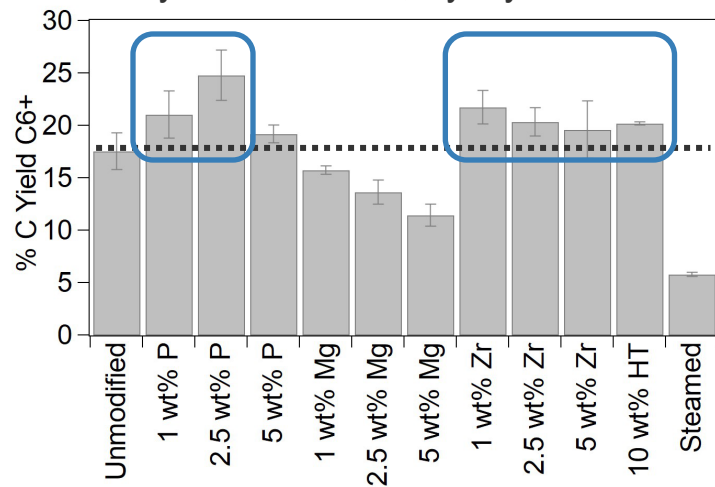
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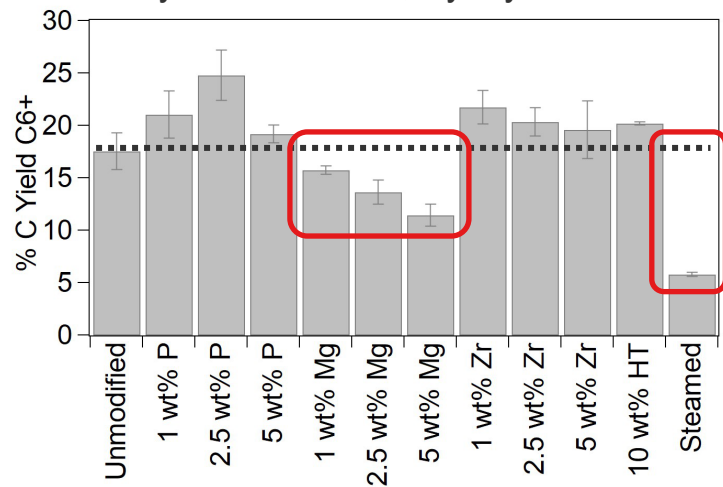
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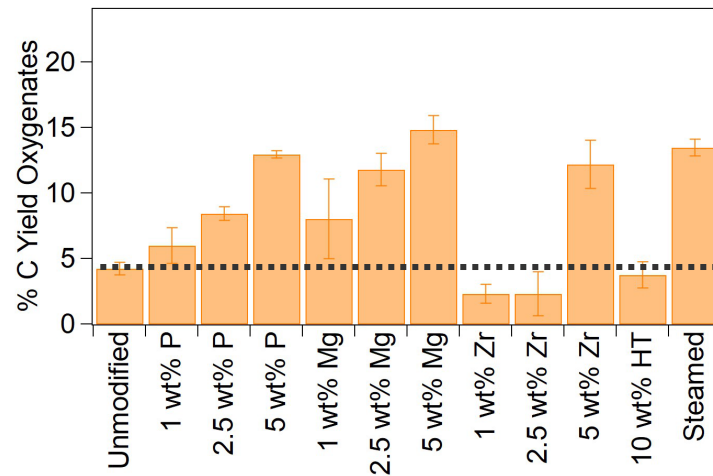
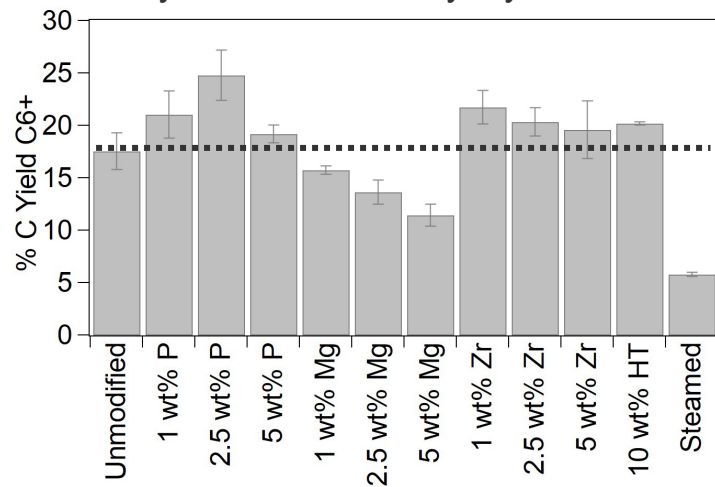
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- Low P and Zr loadings and HT increased C6+
- Mg and steaming lowered C6+ yield

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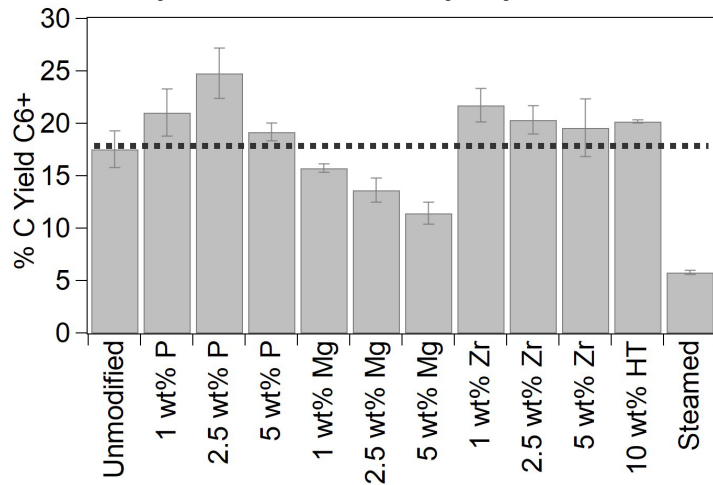
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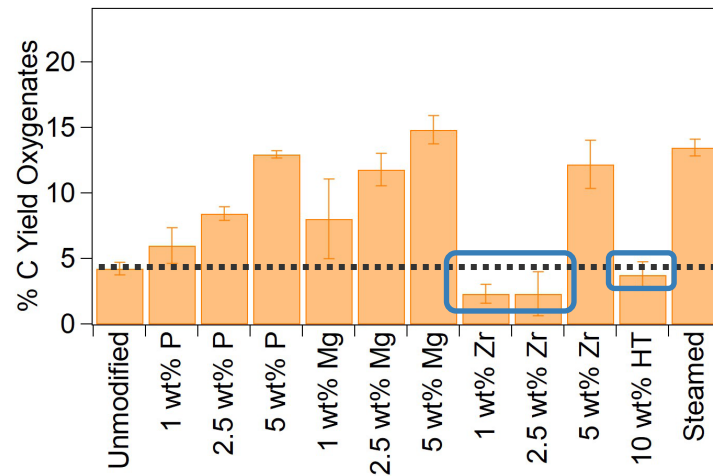
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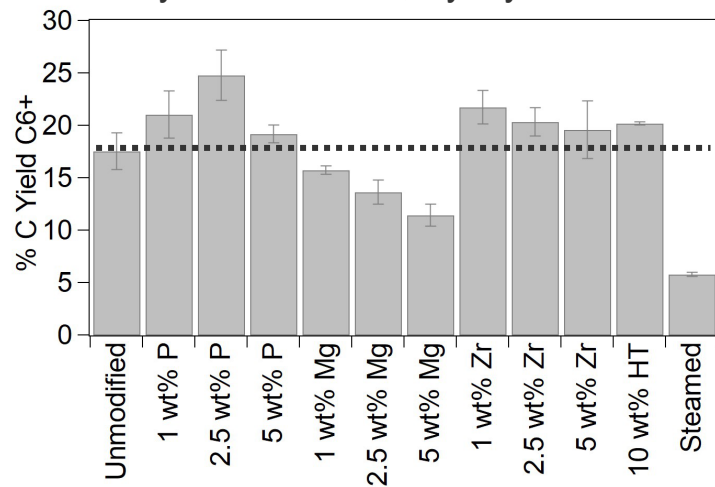
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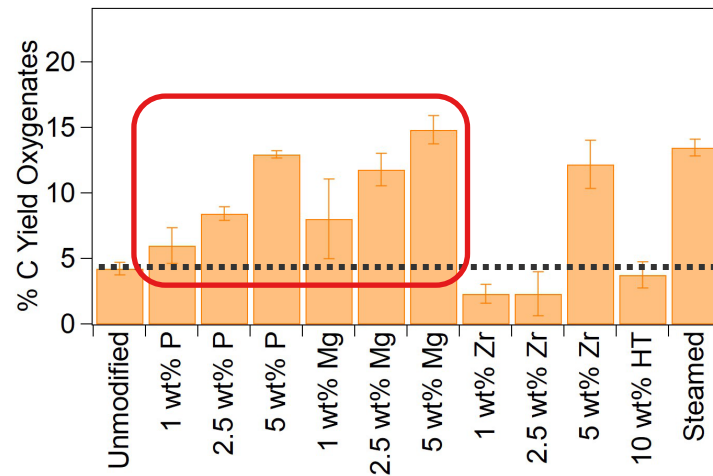
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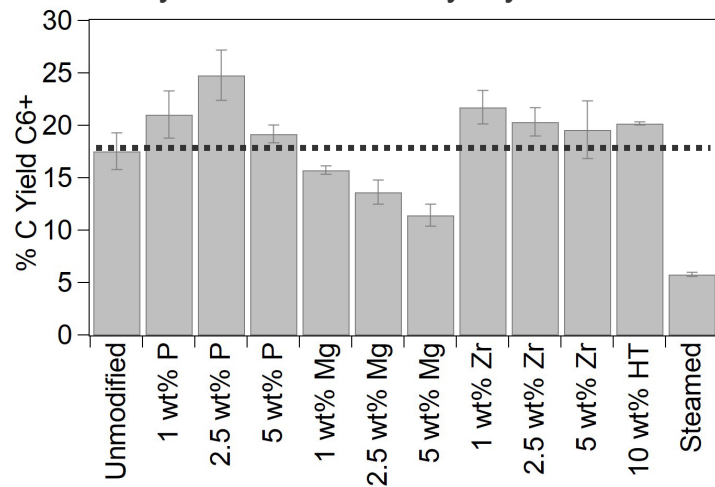
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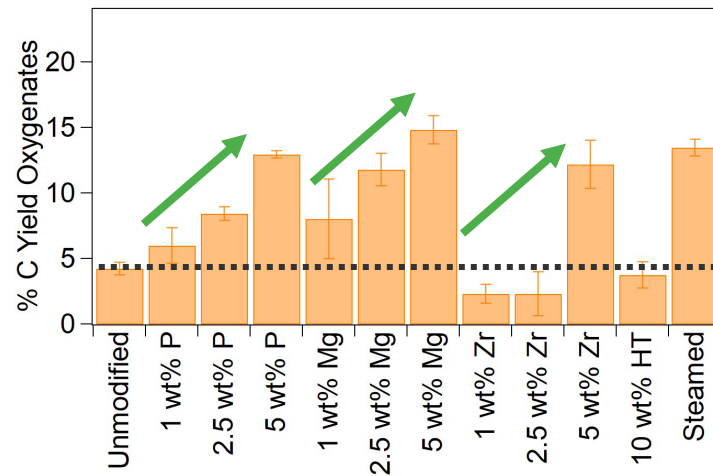
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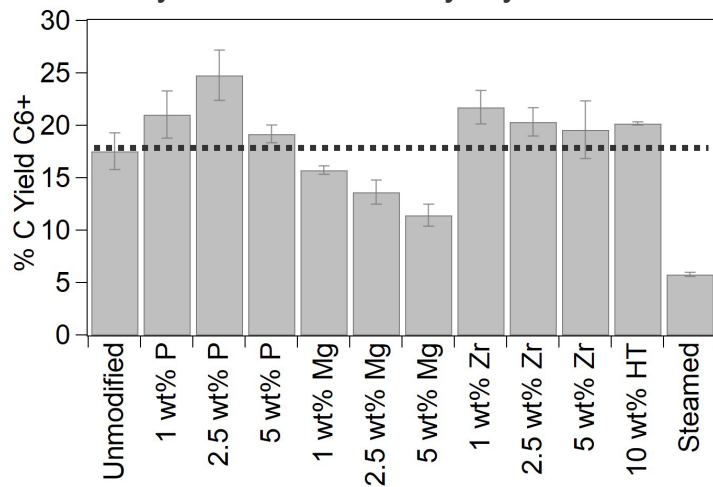
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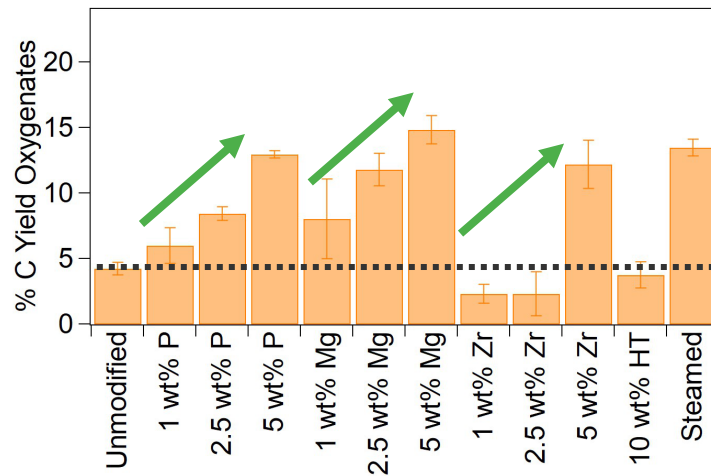
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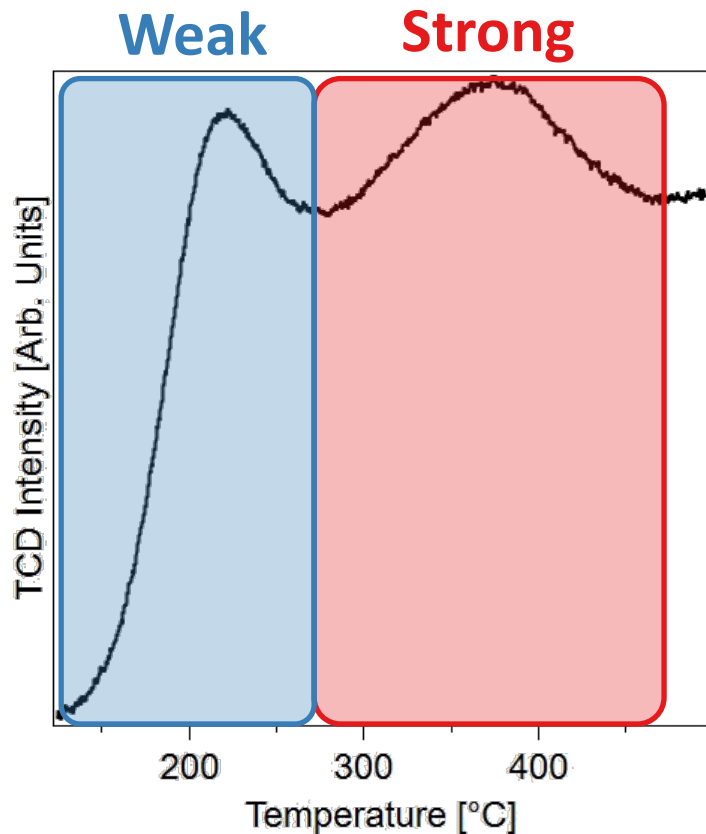
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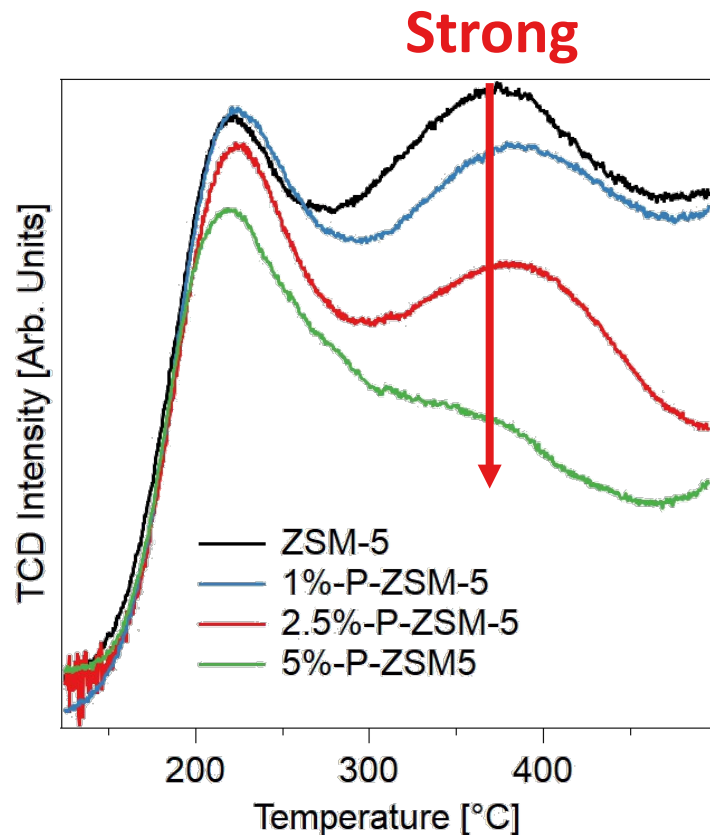
Target 2.5 wt. % P for large scale testing

Added P interacts with catalyst Al to moderate strong acidity



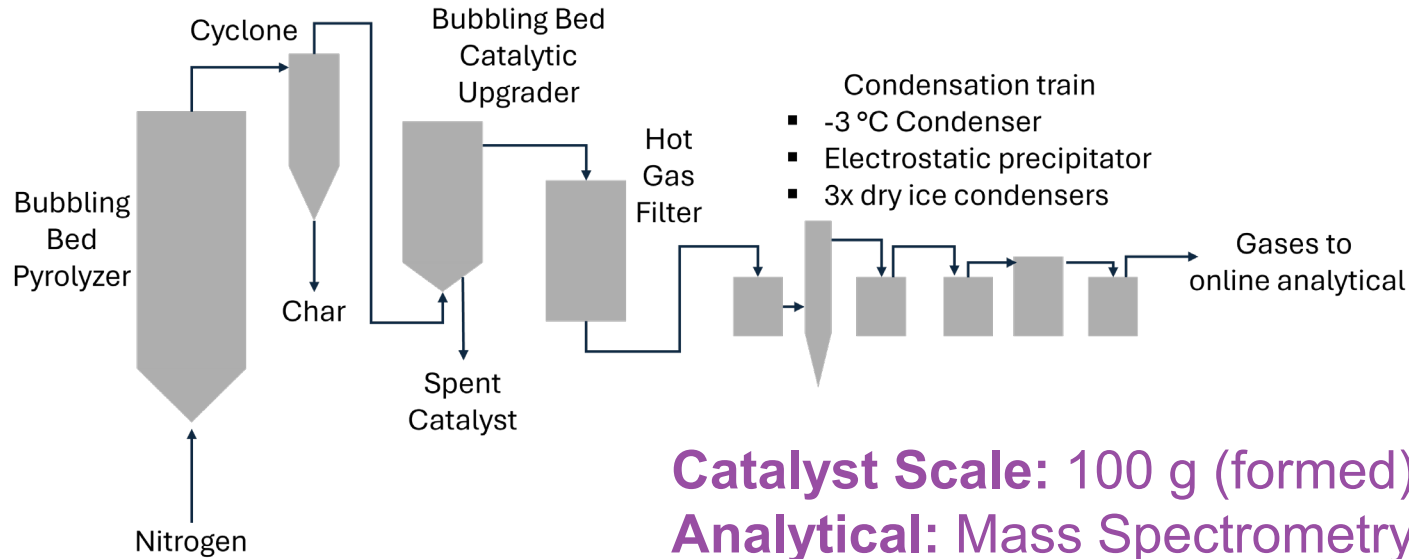
1. Use NH_3 TPD to quantify catalyst acid site density
2. Parent ZSM-5 contains both weak and strong acid sites

Added P interacts with catalyst Al to moderate strong acidity



1. Use NH₃ TPD to quantify catalyst acid site density
2. Parent ZSM-5 contains both weak and strong acid sites
3. Addition of P diminishes strong acidity

Utilize continuous reactor to evaluate catalyst performance and close mass balances



Catalyst Scale: 100 g (formed)

Analytical: Mass Spectrometry, microGC, moisture sensor, NDIR, post reaction catalyst and product fraction characterization

Oil recovery: 100's mL

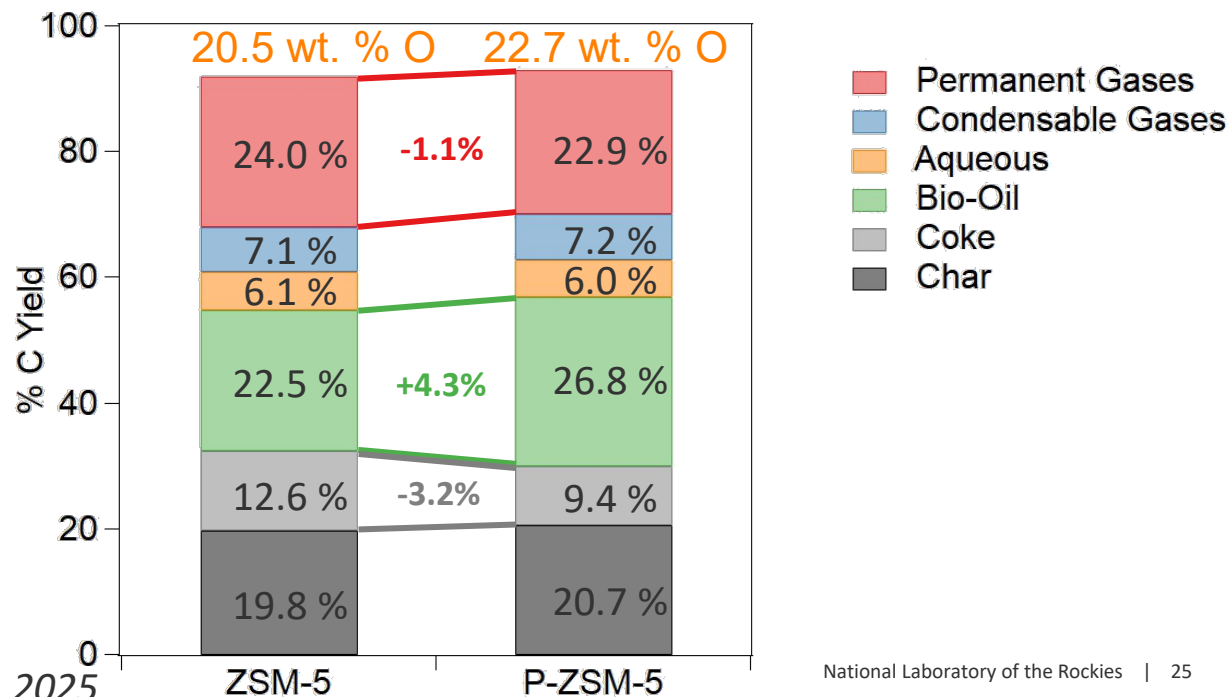
Mass balance closure: $\pm 5\%$

Compare 2.5 wt. % P-ZSM-5 to unmodified ZSM-5 in continuous process

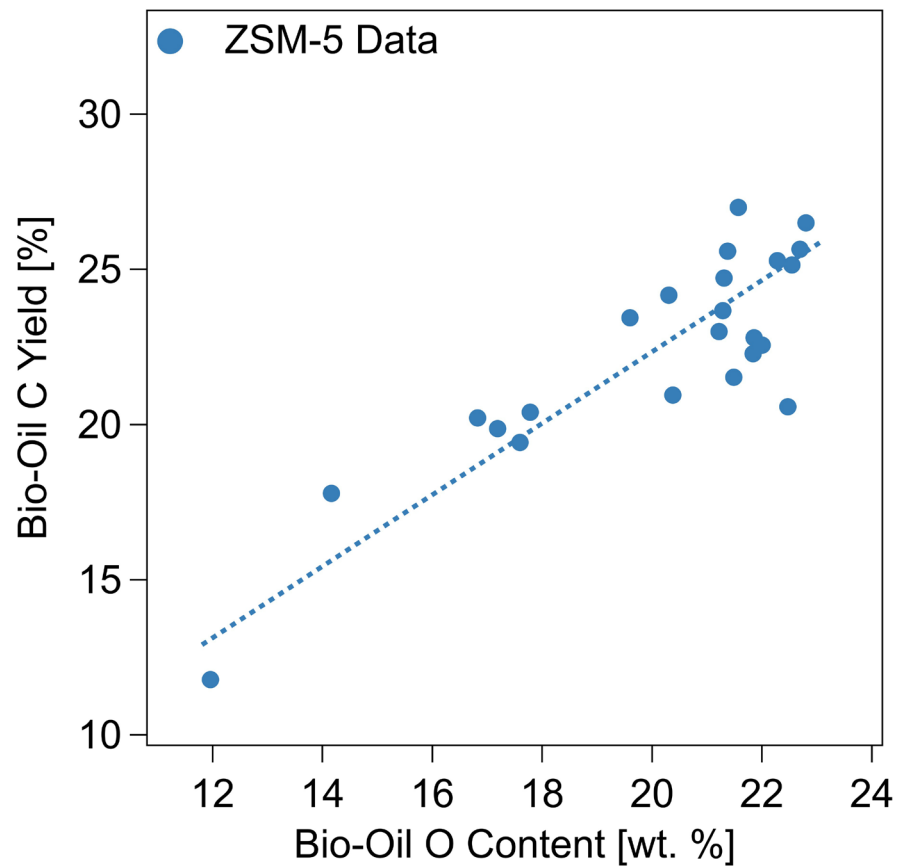
- 500 °C pyrolysis 300 g/hour of a 1 wt. % ash pine feedstock
- Upgrade vapors at 500 °C and a B/C of 2.7

Adding 2.5 wt. % P to ZSM-5 caused:

- A 19% relative improvement in bio-oil yield
- A 25% relative decrease in coke
- A 5% relative decrease in permanent gas production
- An increase in oil O content

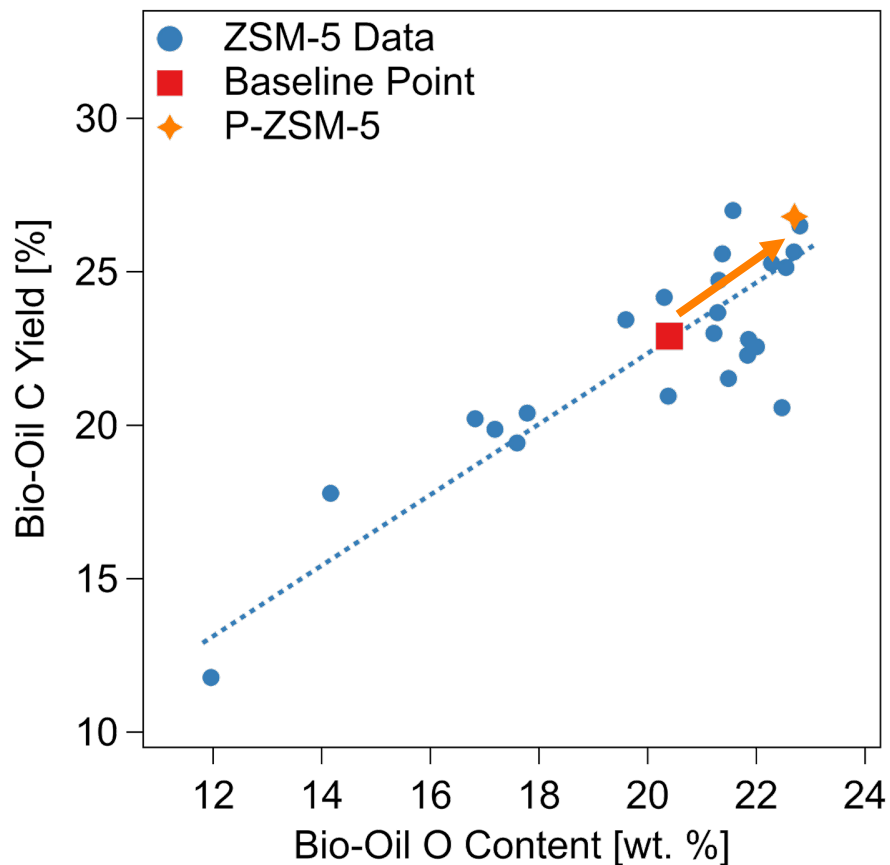


Compare modified catalyst to existing CFP data

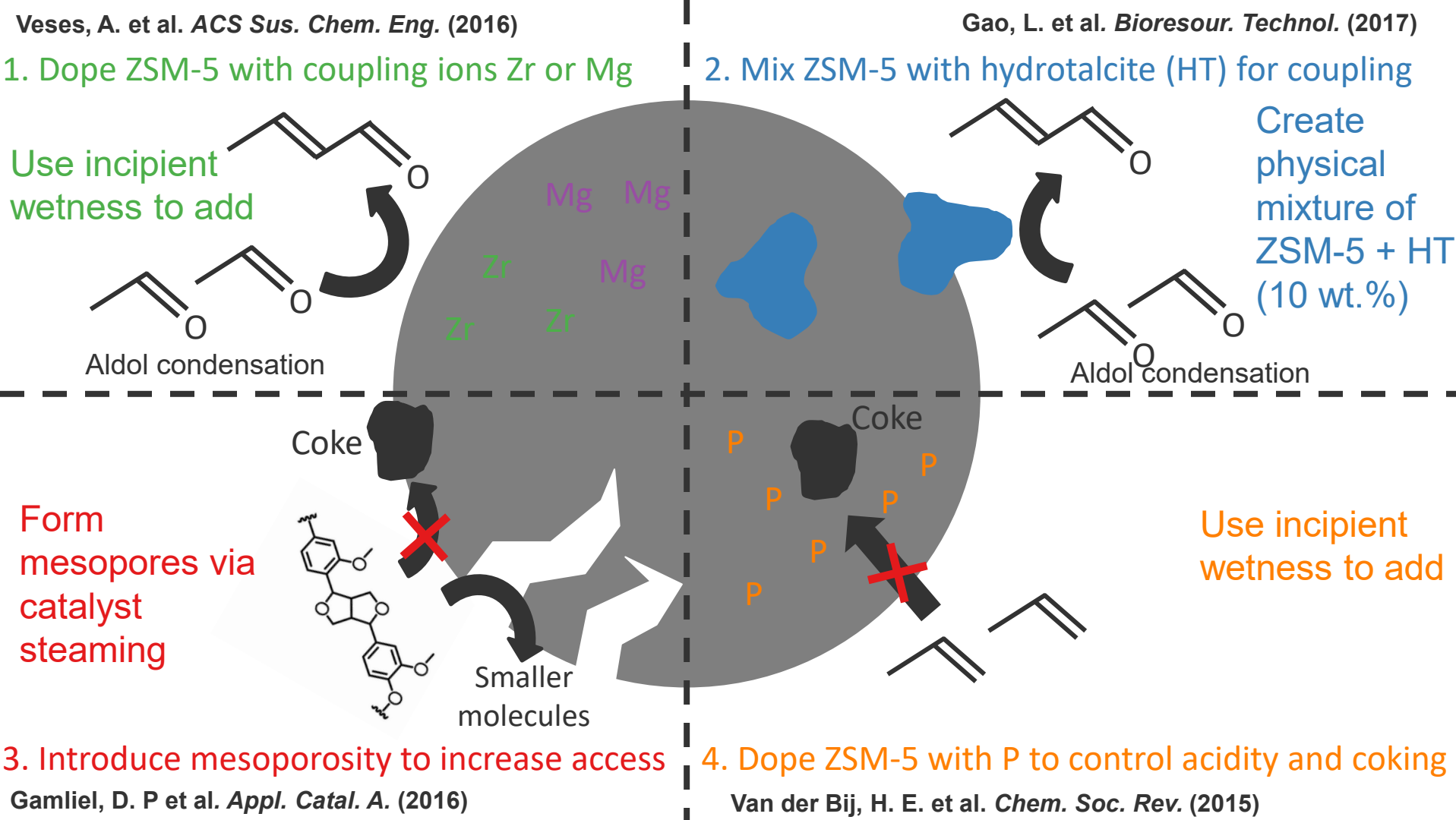


- CFP results of pine/forest residue blend (1 wt. % ash) over ZSM-5

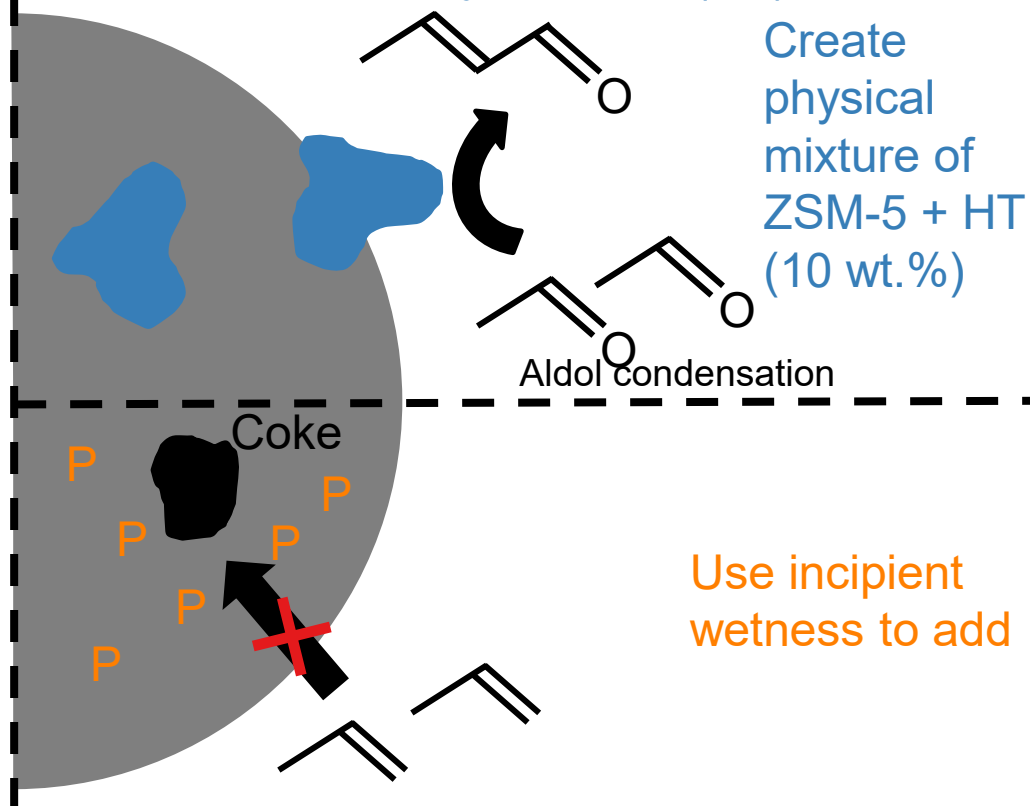
P-ZSM-5 Results with C vs O



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- Addition of P showed similar performance to lowering severity of CFP



2. Mix ZSM-5 with hydrotalcite (HT) for coupling



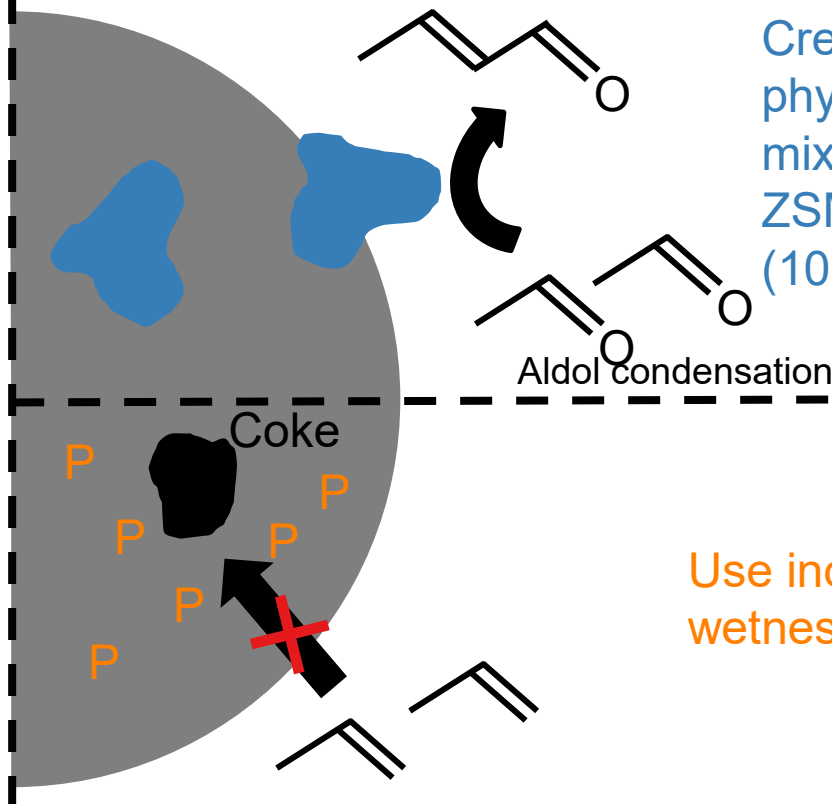
4. Dope ZSM-5 with P to control acidity and coke

Can benefits of HT and P be combined in a single catalyst

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Gao, L. et al. *Bioresour. Technol.* (2017)

Create physical mixture of ZSM-5 + HT (10 wt.%)

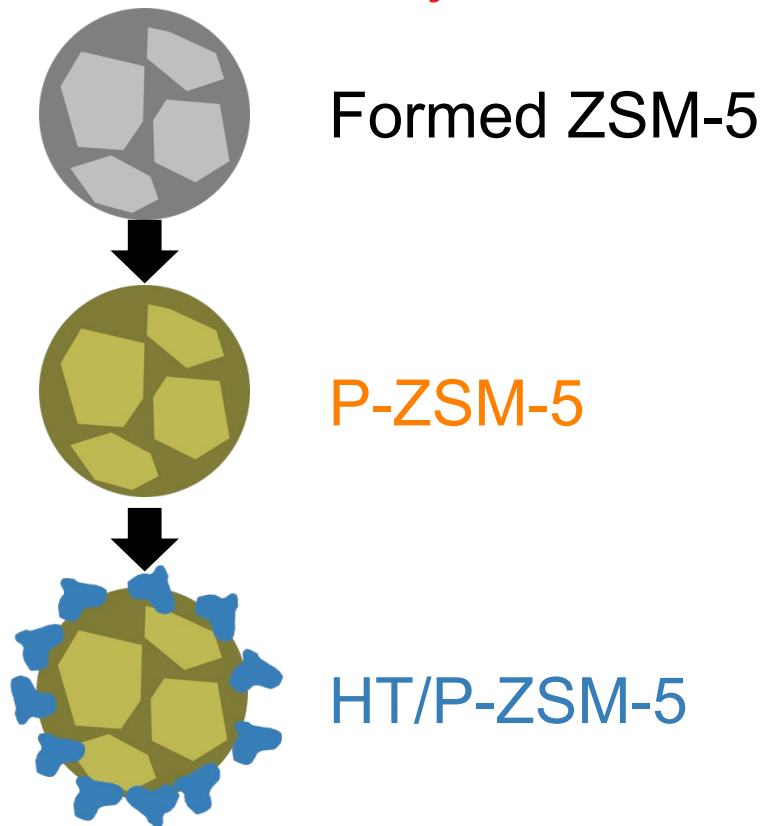


Use incipient wetness to add

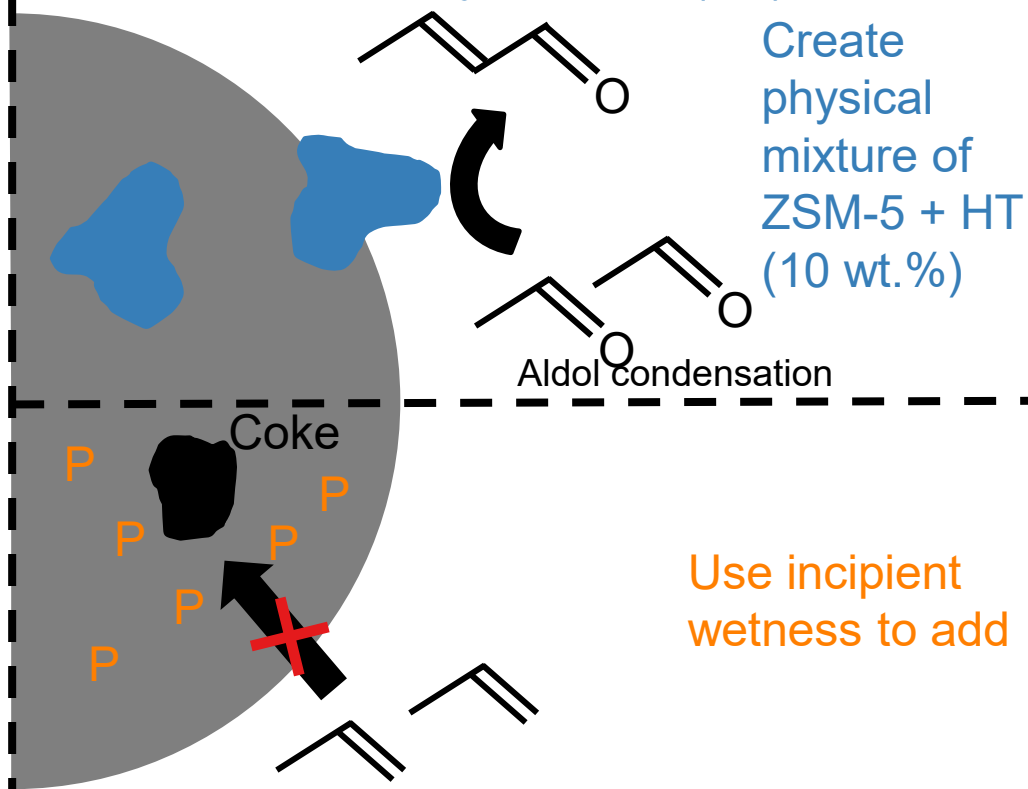
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Aldol Condensation

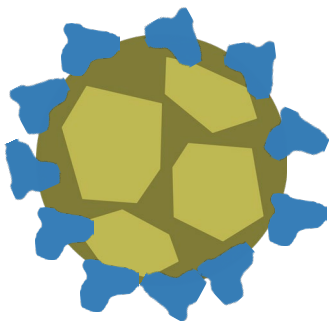
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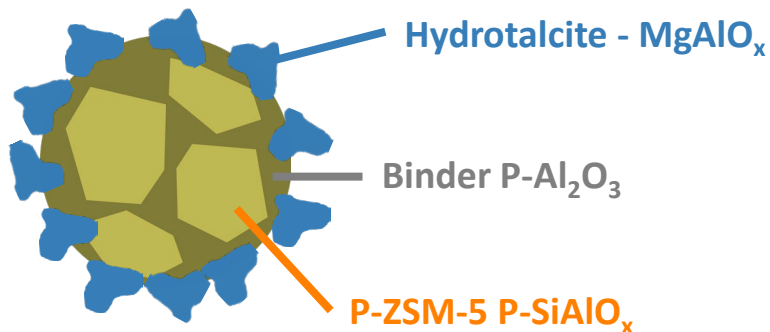
Verify hierarchical catalyst using elemental mapping

Use STEM-EDS mapping of a single catalyst particle to understand site distribution



Verify hierarchical catalyst using elemental mapping

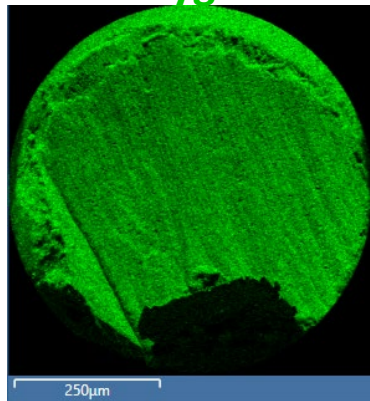
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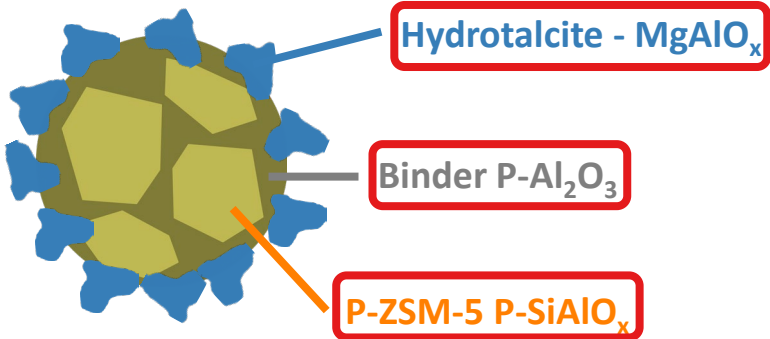
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Oxygen

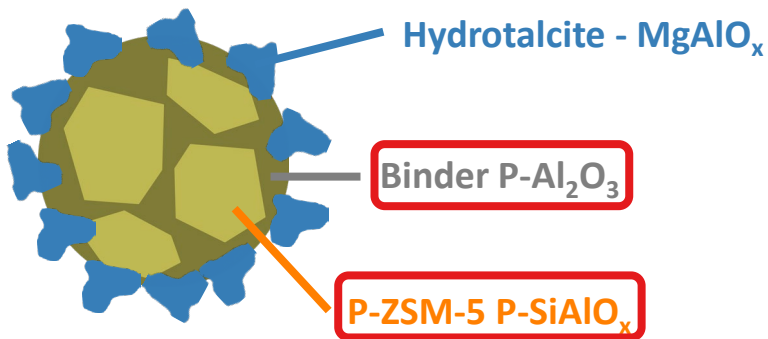
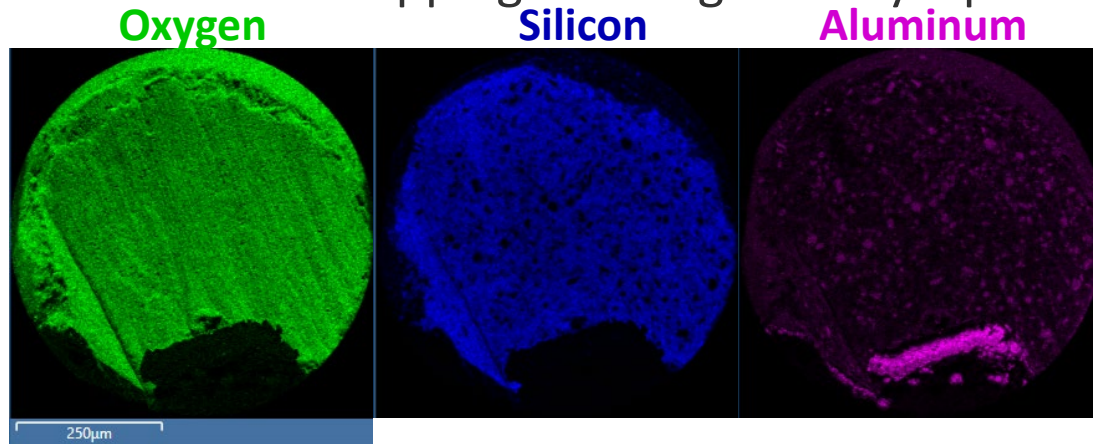


- Oxygen throughout particle



Verify hierarchical catalyst using elemental mapping

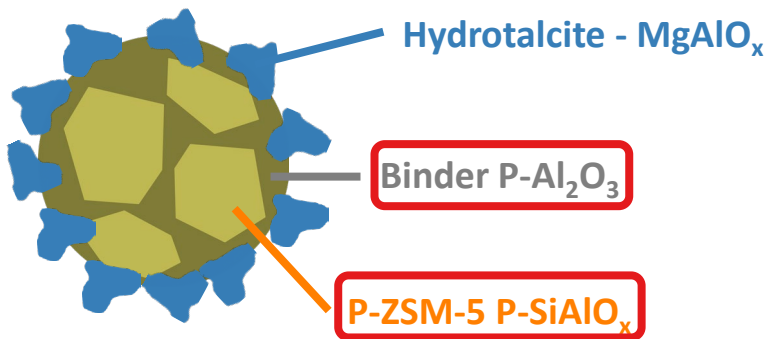
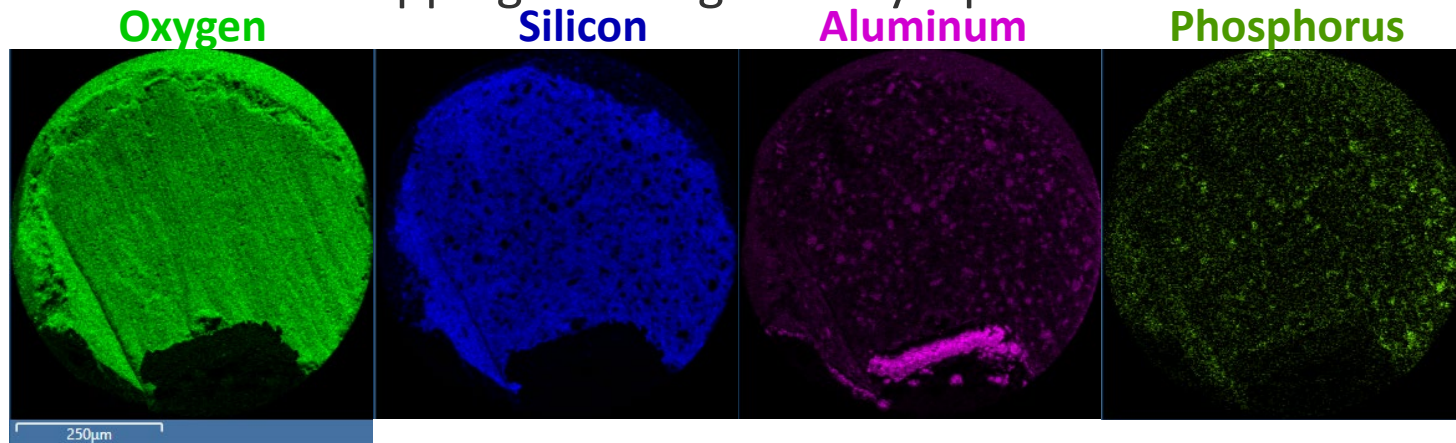
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- Oxygen throughout particle
- Si present in majority but not in Al voids

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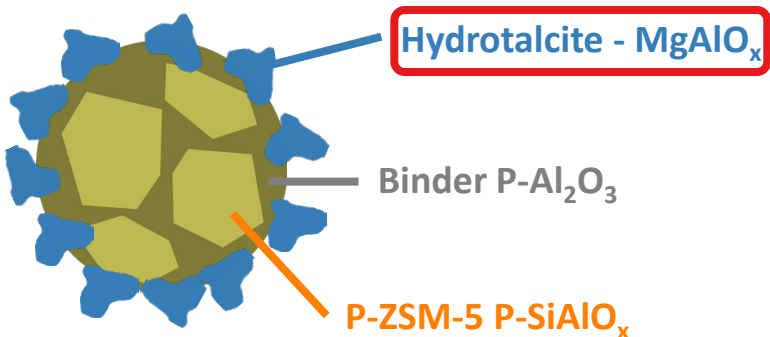
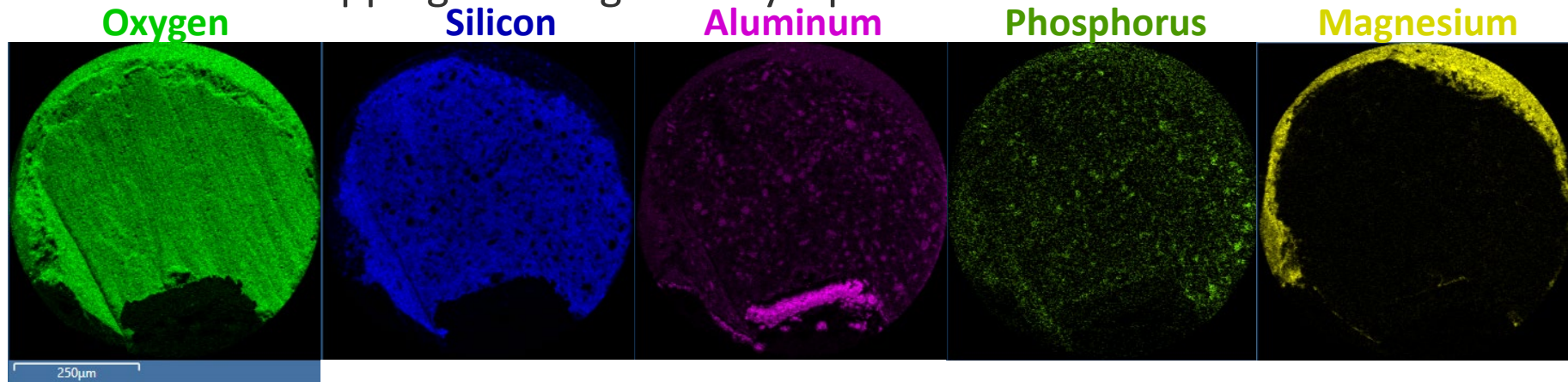
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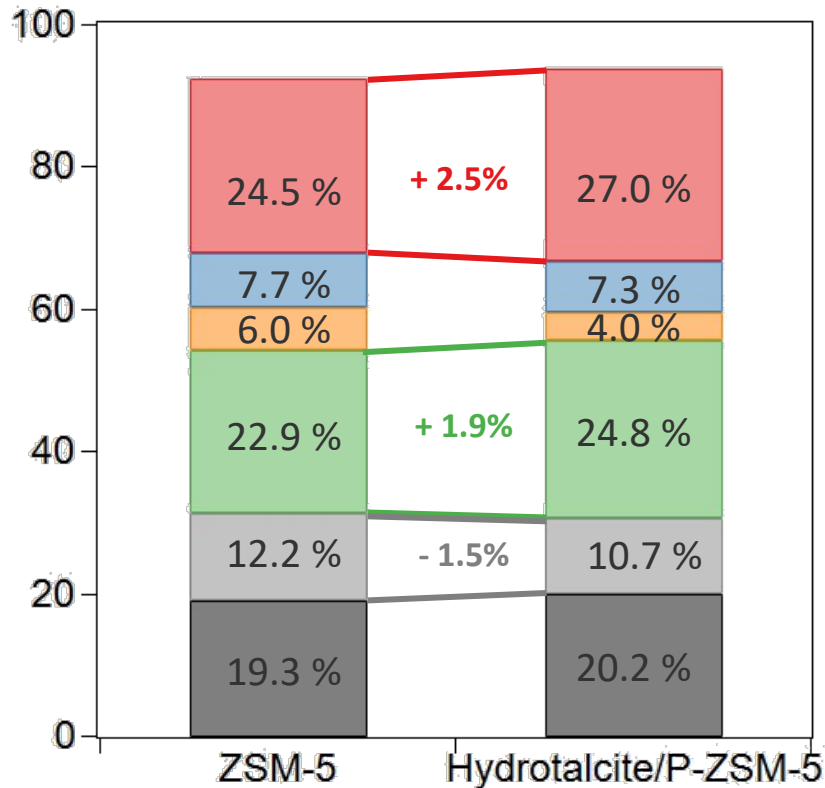
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- Oxygen throughout particle
- Si present in majority but not in Al voids
- P present throughout but preference for Al_2O_3
- Mg only located on particle exterior – hydrotalcite shell

Hydrotalcite/P-ZSM-5 outperforms baseline catalyst

Wrasman, C. et al. *Submitted*

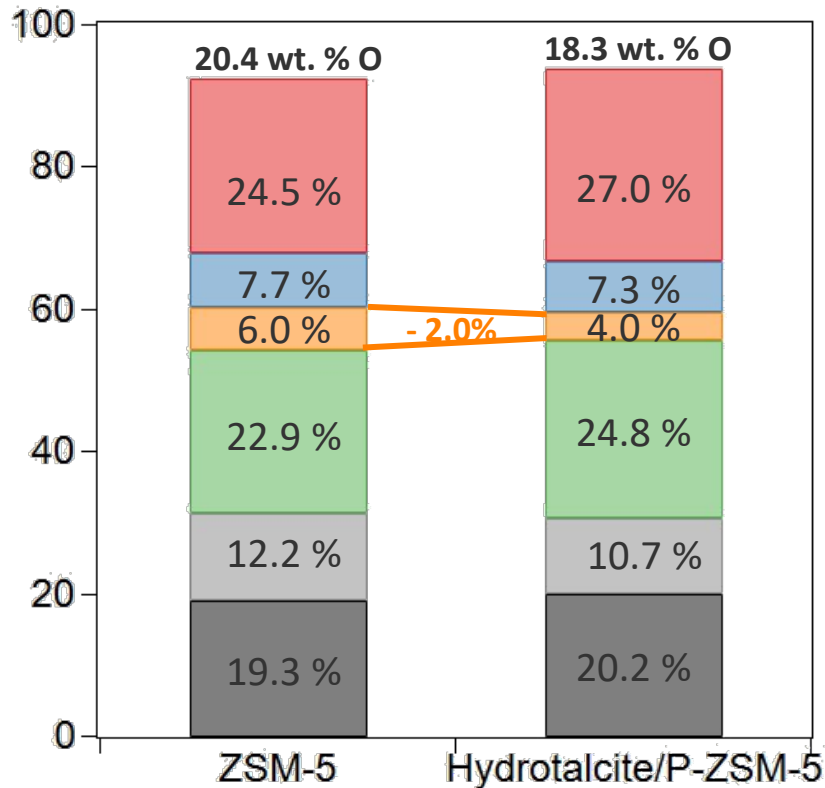


- Permanent Gases
- Condensable Gases
- Aqueous
- Bio-Oil
- Coke
- Char

Adding 2.5 wt. % P and 20 wt. % hydrotalcite to ZSM-5 caused:

- A 8% relative improvement in bio-oil yield
- A 12% relative decrease in coke
- A 10% relative increase in permanent gas production
 - CO₂ is a product of condensation

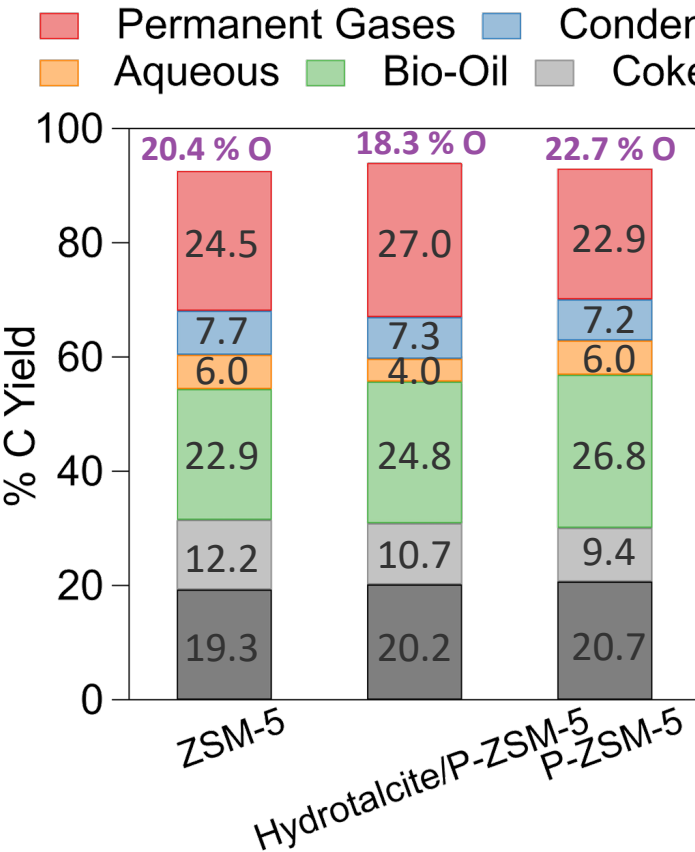
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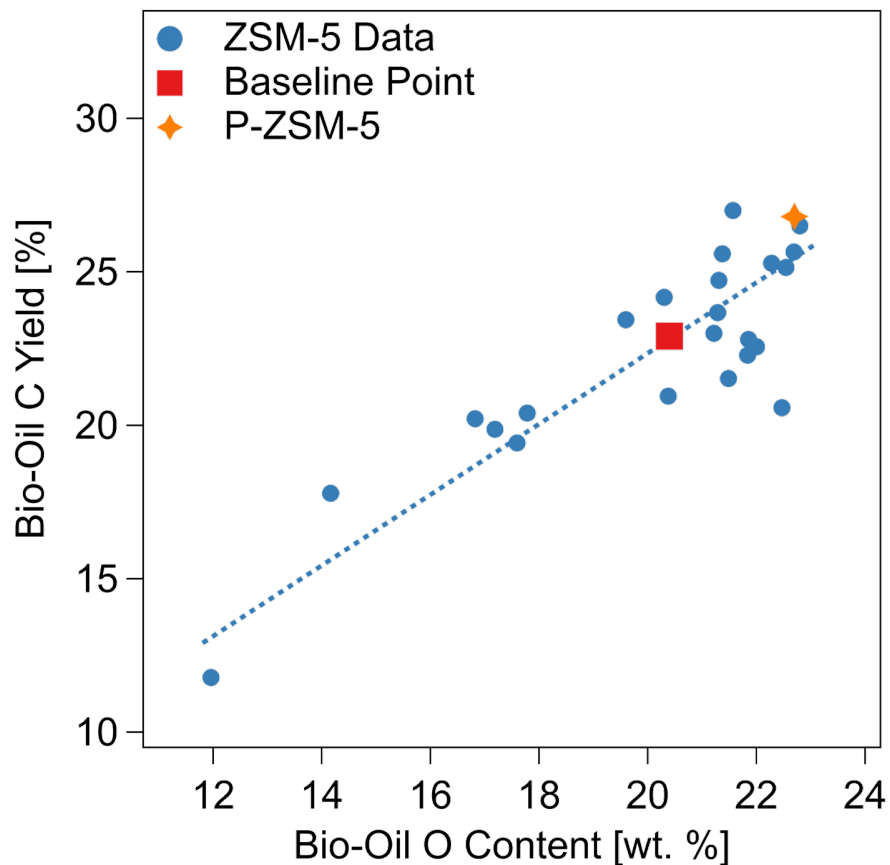
- Oil contains 2.1 wt. % less O than baseline
- Aqueous carbon decreased by 33% relative to ZSM-5
- GCMS analysis showed adding hydrotalcite eliminated <C5 aldehydes in bio-oil
 - These species have been implicated in oil instability

Hydrotalcite/P-ZSM-5 combines advantages of P and HT addition



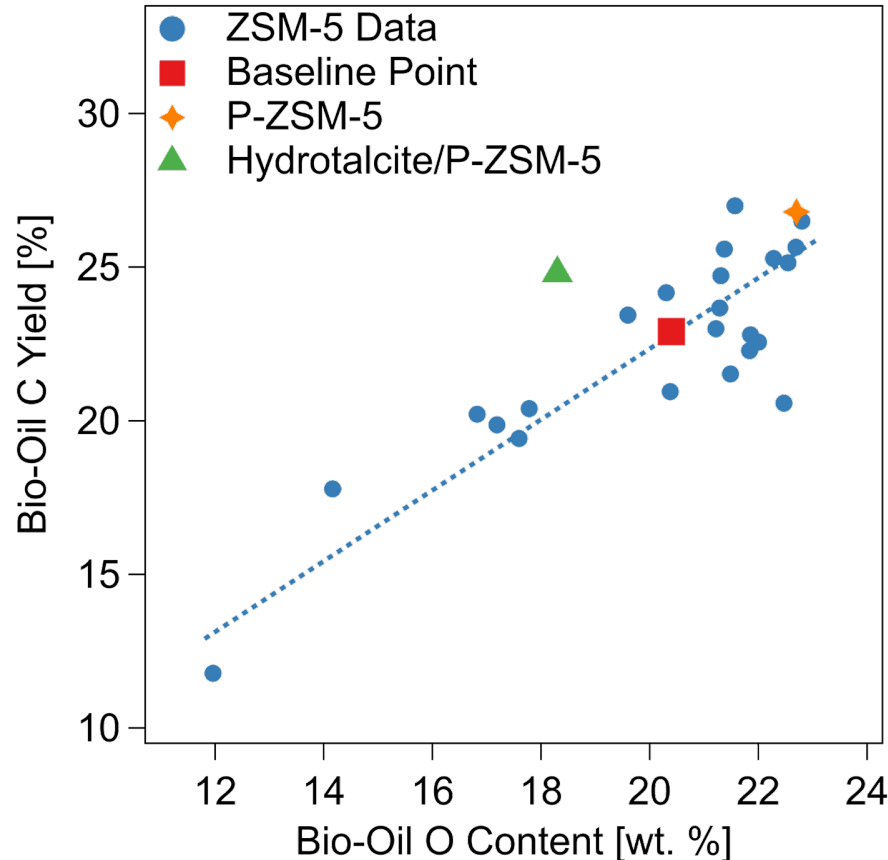
Combination of HT and P
maintains coke reduction of P
while also reducing oil O content

P-ZSM-5 Results with C vs O



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- Addition of P showed similar performance to lowering severity of CFP

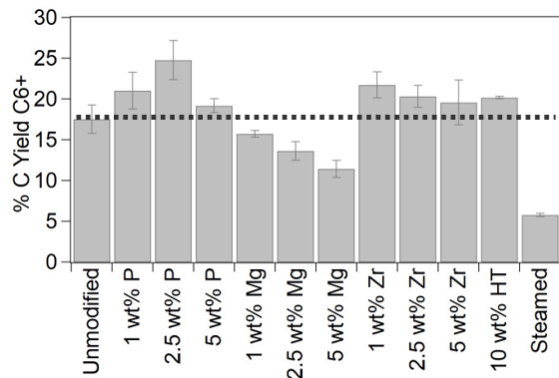
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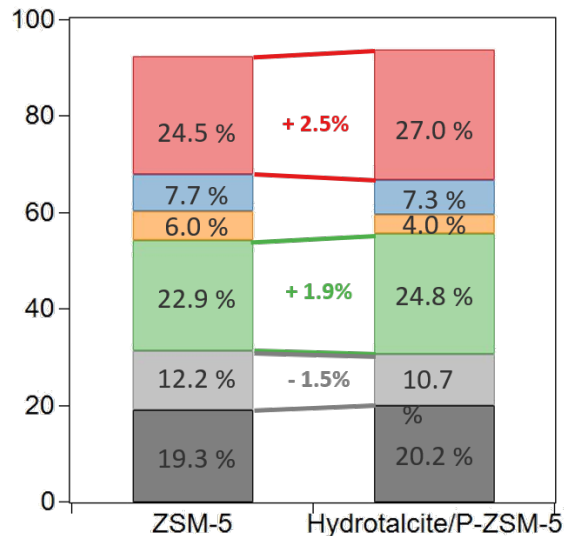
- CFP results of pine/forest residue blend (1 wt. % ash) over ZSM-5
- Addition of P showed similar performance to lowering severity of CFP
- Adding HT produced a higher yield (~5% C) than expected for the O content
- Would lower fuel costs by ~10 %

Catalytic pyrolysis offers many opportunities for utilization of biomass and waste feedstocks

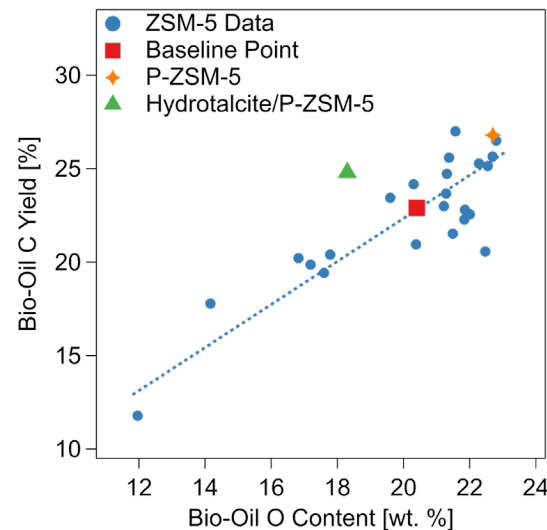
Screen series catalyst modifications for improved performance



Compare select catalysts in continuous process



Achieve higher yields of higher quality bio-oils with designed catalyst





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Cody Wrasman (Cody.Wrasman@nlr.gov)

TCBiomass 2026

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Thank you

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