Catalytic upgrade of bio-oil in vapor and liquid phase to improve biofuel properties

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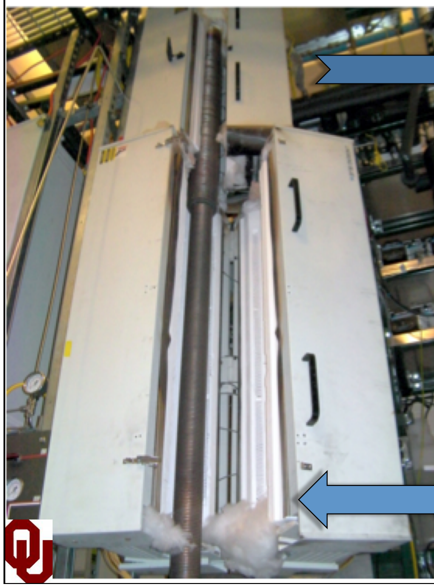
Center for Biomass Refining
(www.ou.edu/cbr)

Products from Fast Pyrolysis of Biomass



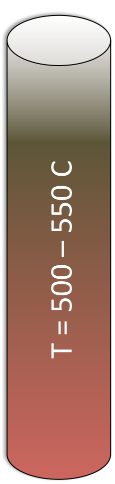
GAS: 15 - 20%

OIL: 50 - 70%

CHAR: 10 - 20%

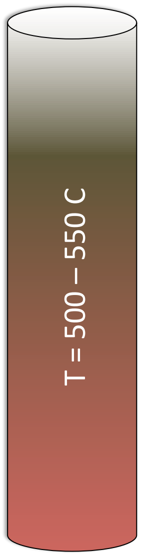
BIOMASS

Products from Fast Pyrolysis of Biomass



- **Small oxygenates**
  (aldehydes, alcohols, ketones, acids)
- **Sugar-derived compounds**
  (levoglucosan, furfurals)
- **Lignin-derived phenolics**
  (guaiacol, vanillin, anisole, etc.)

Two Problems:
- to eliminate excess oxygen
- to bring products to gasoline/ diesel ranges



- **Small oxygenates**
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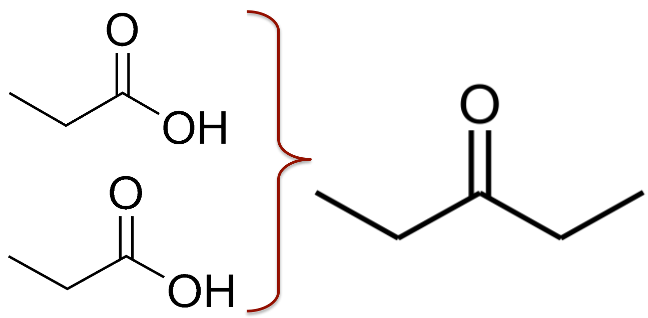

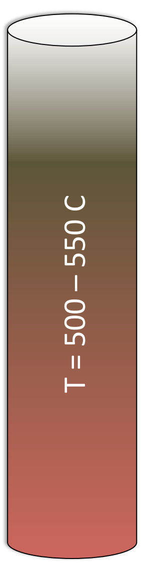

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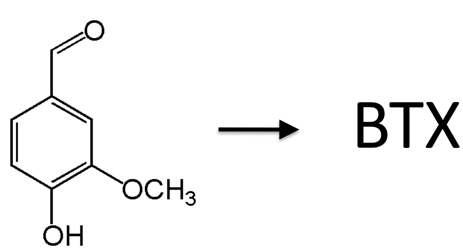
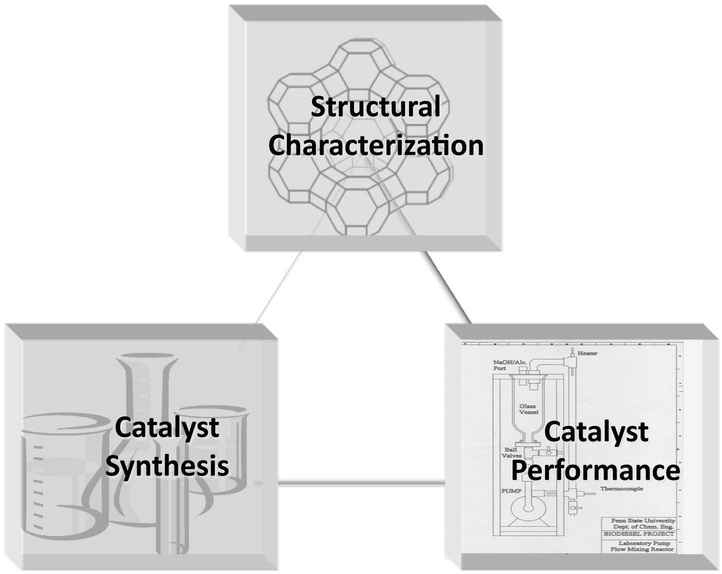


Research Approach in Heterogeneous Catalysis



A. CONDENSATION REACTIONS

<u>VAPOR PHASE REACTORS</u>

- Aldehydes to Alkyl-Aromatics
  (T. Hoang, X. Zhu, T. Sooknoi)

- Aldehydes and Alcohols to Longer Ethers
  (T. Pham, S. Crossley, T. Sooknoi)

- Aldehydes and Acids to Longer Ketones
  (A. Gangadharan, J. Bourgeois)

Aromatization of Propanal on Acidic Zeolites (H-ZSM5)

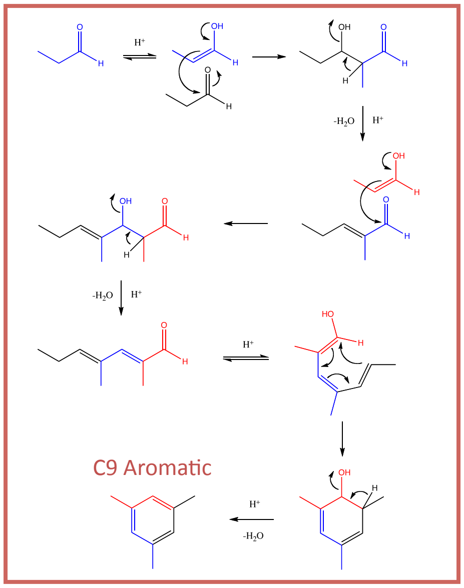
Feed	Propanal	Propylene	
Conditions	W/F =0.13 h HZSM-5 (45) 400 °C	W/F =4 h HZSM-5 (45) 400°C	W/F =4h HZSM-5 (25) 500°C
Conversion	76	42	66
Gas (C_1-C_3)	32	-	38
isoalkenes (C_4-C_9)	3	42	10
Aromatics	41	1	17

Product Yield Distribution after 60 min on stream in a fixed bed reactor

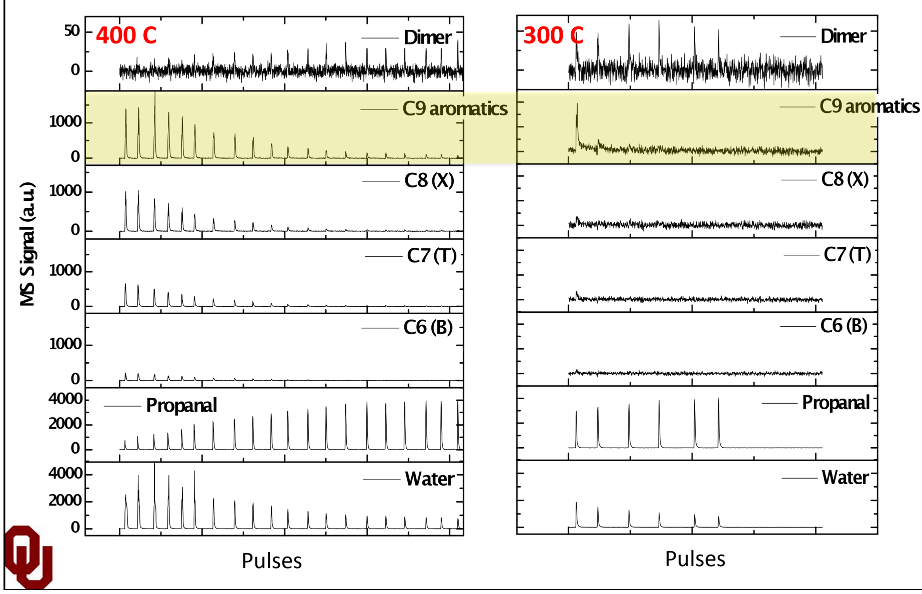
Aromatization of Propanal on Acidic Zeolites (H-ZSM5)

- Aldol Dimerization
- Dehydration
- Aldol Trimerization
- Dehydration
- Enol and Rearrangement
- Aromatization
- Dehydration

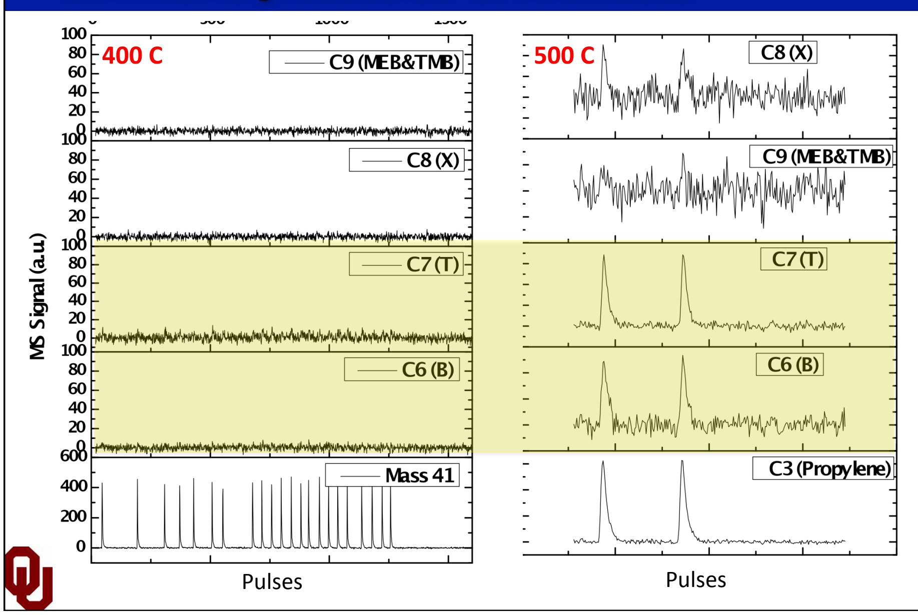
Hoang, Zhu, Sooknoi, Resasco and Mallinson, *J. Catalysis* 271, 201-208, **2010**



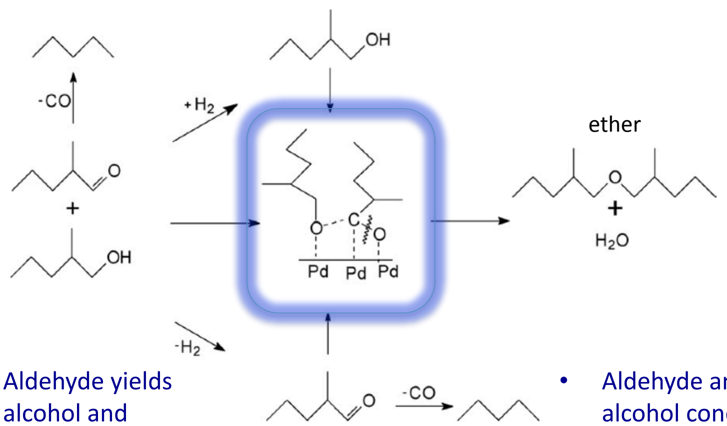
Pulses of Propanal on H-ZSM5 produce C9 Aromatics



Pulses of Propylene on H-ZSM5 produce C6-C7 Aromatics



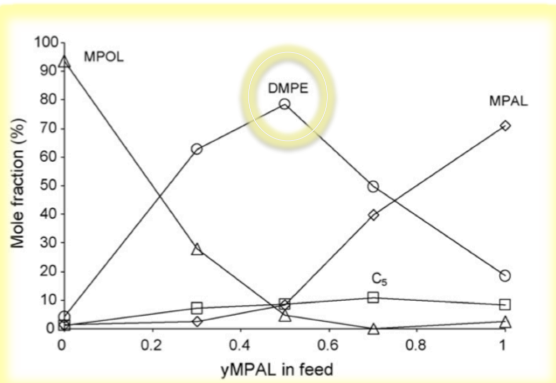
Etherification of methyl pentenal and alcohols on Pd catalysts



- Aldehyde yields alcohol and alkane
- Aldehyde and alcohol condense into long ether

T. T. Pham, S. P. Crossley, T. Sooknoi, L. L. Lobban,D. E. Resasco, R. G. Mallinson *Applied Catalysis A: General* 379 (2010) 135–140

Etherification of methyl pentenal and alcohols on Pd catalysts

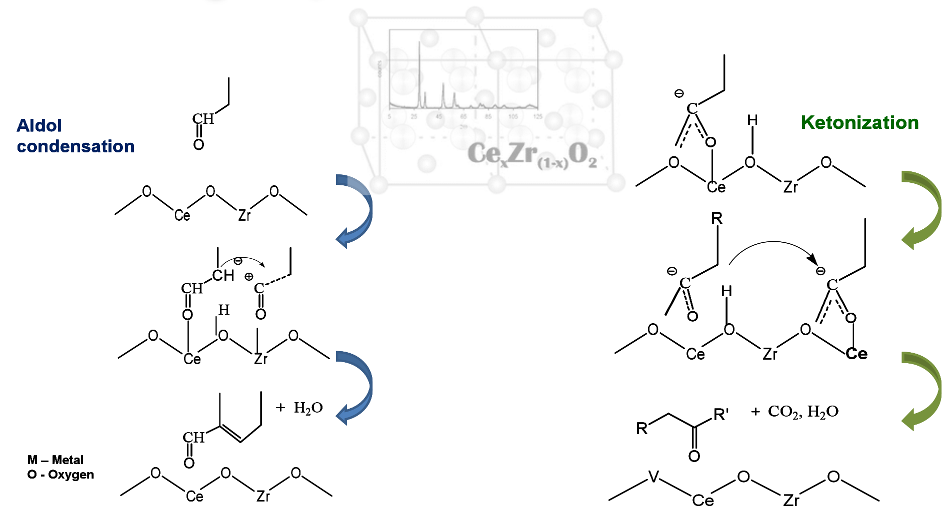


- Either pure Aldehyde or pure alcohol produce small amounts of ether
- Co-feeding Aldehyde and alcohol maximize ether yield

Mixed Feeds C(AL) ≠ C(OL) C4 (AL) + C6 (OL) ➔ ether
* C8 (LOW)
* C10 (HIGH)
* C12 (NONE)

T. T. Pham, S. P. Crossley, T. Sooknoi, L. L. Lobban,D. E. Resasco, R. G. Mallinson *Applied Catalysis A: General* 379 (2010) 135–140

Aldol Condensation and Ketonization of Propanal on $CeZrO_2$ catalysts

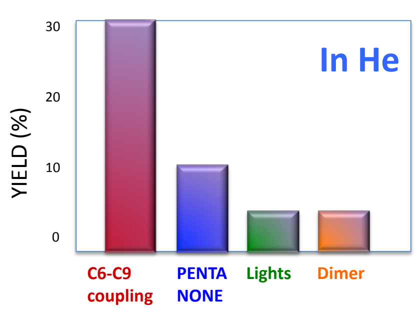


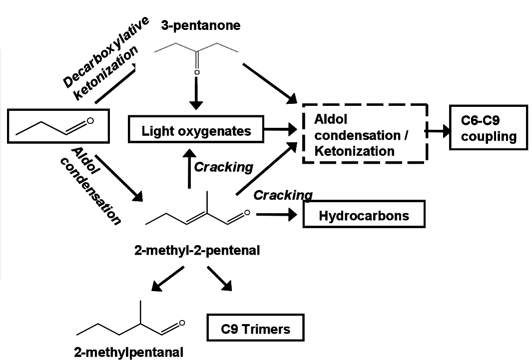
Metal center (Lewis acid site) and oxygen anion (Lewis base), catalyze aldol condensation

Lewis acid sites (metal centers) promote ketonization by forming a surface coordinated species

Aldol Condensation and Ketonization of Propanal on $CeZrO_2$

Reaction conditions: W/F = 0.6 h
Catalyst, $Ce_{0.5}Zr_{0.5}O_2$ Temp, 400ºC

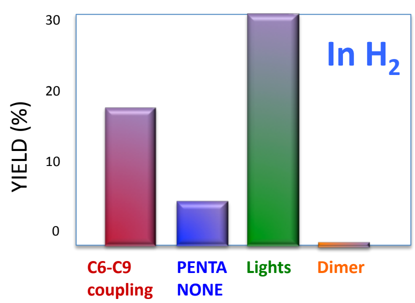


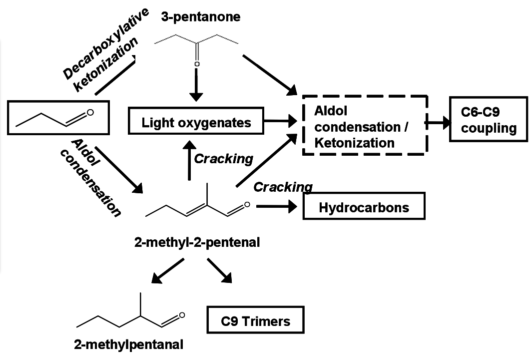


- Lights refer to light hydrocarbons and oxygenates
- C6 – C9 coupling are higher ketones and aldehydes
- Propionic acid or 3-hydroxy-2-methylpentanal is not seen in products

Aldol Condensation and Ketonization of Propanal on $CeZrO_2$

Reaction conditions: W/F = 0.5 h
Catalyst, $Ce_{0.5}Zr_{0.5}O_2$ Temp, 400°C





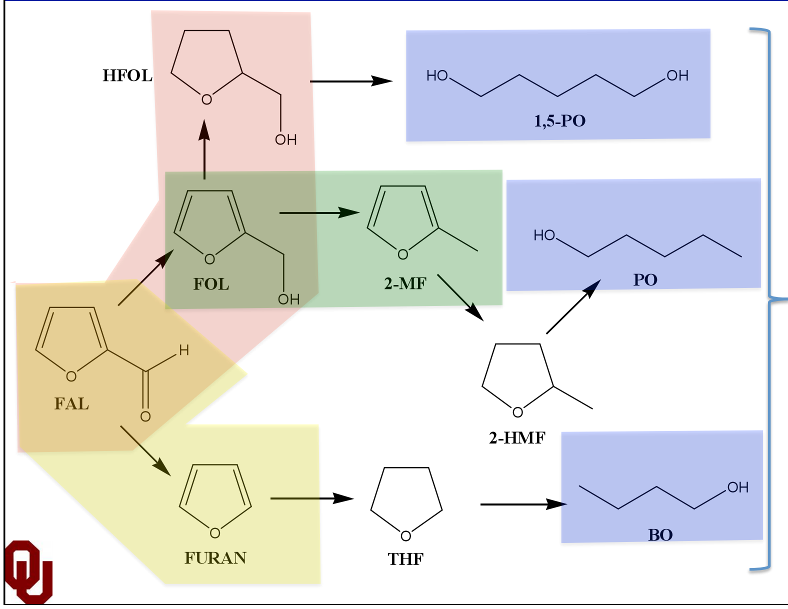
- In hydrogen, higher tendency to produce lighter compounds
- Yield of coupling products reduced in H_2

B. DEOXYGENATION REACTIONS

VAPOR PHASE REACTORS

- Decarbonylation, hydrogenation, and hydrogenolysis of furfurals
  (S. Sitthisa, T. Pham, T. Sooknoi)
- Decarbonylation and hydrogenolysis of phenolics, benzaldehyde, anisole, guaicol
  (A. Peralta, A. Ausavasukhi, T. Sooknoi)

Deoxygenation of Furfurals on Metal Catalysts



MOLECULAR ENGINEERING

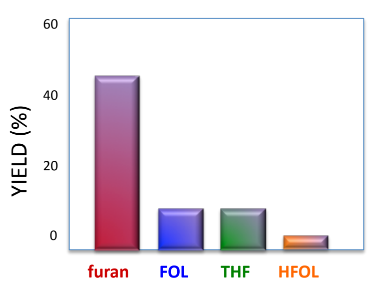
Different Catalysts And Reaction Conditions

Different Products

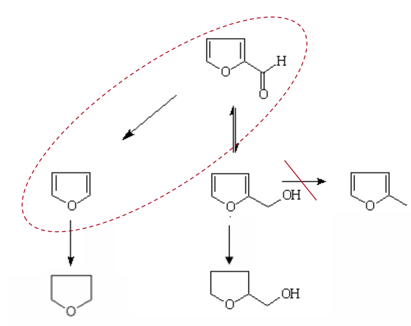
Different Fuel Properties

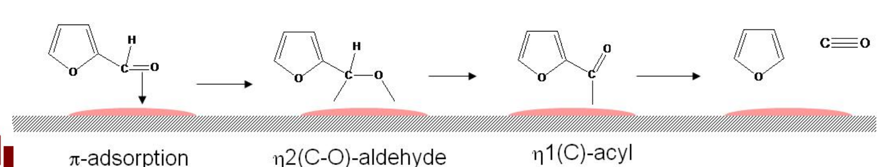
Deoxygenation of Furfurals on Pd catalyst

Reaction conditions: Feed, FAL 0.5 ml/min,
Catalyst, 0.5% Pd/SiO_2 Temp, 230^{o}C



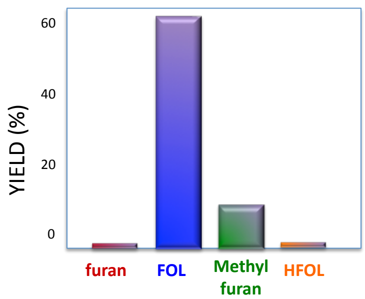
Decarbonylation

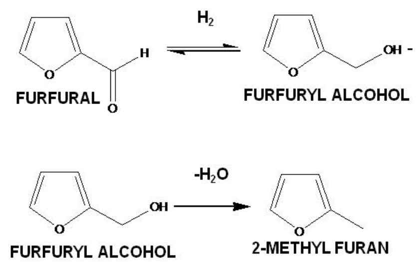


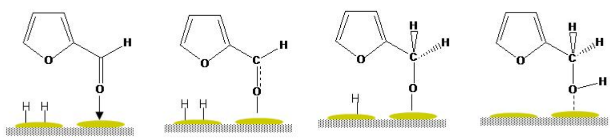


Deoxygenation of Furfurals on Cu catalyst

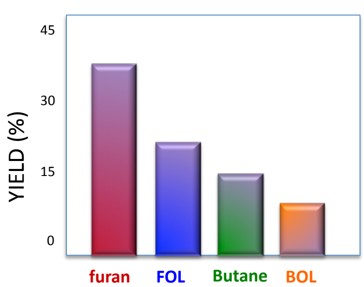
Reaction conditions: Feed, FAL 0.5 ml/min, W/F = 50 g cat hr /mol
Catalyst, 0.5% Cu/SiO_2 Temp, 290°C, H_2/feed ratio = 25



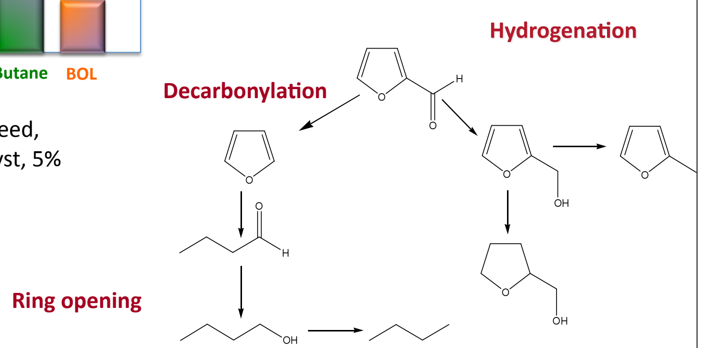




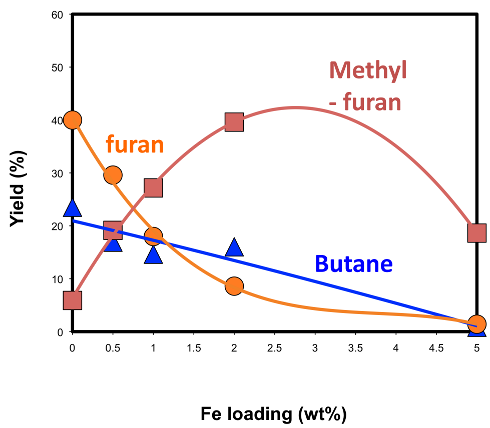
Deoxygenation of Furfurals on Ni catalyst



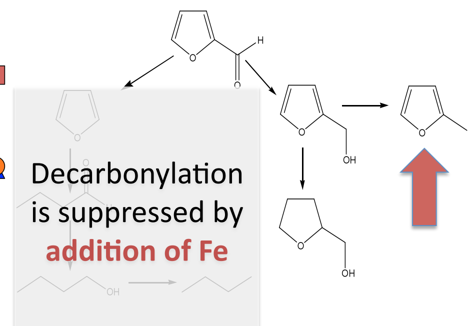
Reaction condition: Feed, FAL 0.5 ml/min Catalyst, 5% Ni/SiO_2 Temp, 230°C



Deoxygenation of Furfurals on Ni-Fe catalysts



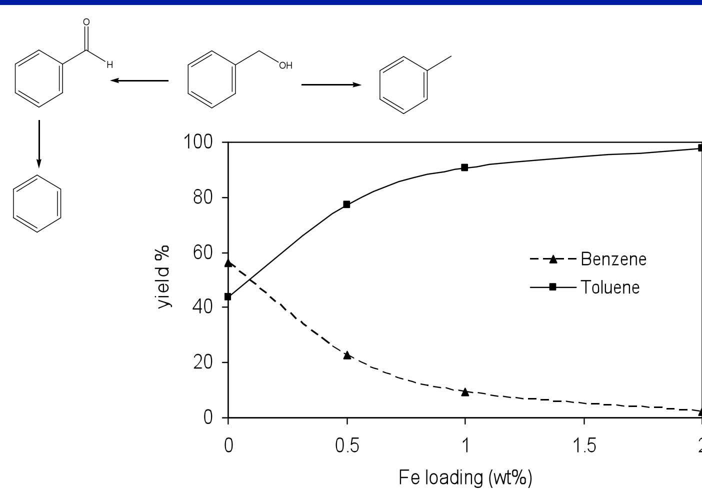
HYDROGENOLYSIS or HYDROGENATION / DEHYDRATION Is enhanced by **addition of Fe**



Reaction conditions

Feed, FAL 0.5 ml/min Catalyst, 0.5-5Fe on 5% Ni/SiO_2 Temp, 250°C, W/F = 0.1 h^{-1}

Reactions of Benzyl alcohol over Ni-Fe Catalysts



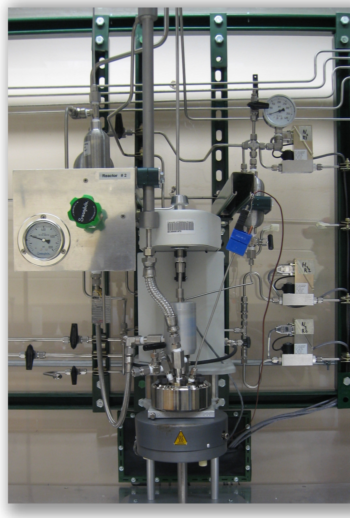
Reaction condition: Feed = Benzyl alcohol 0.5 ml/min, Catalyst = 0.5-2Fe on 5% Ni/SiO_2 Temp= 250°C, W/F = 0.1 h^{-1}

C. BIO-OIL UPGRADE IN BI-PHASIC SYSTEMS

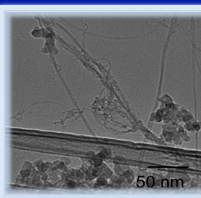
LIQUID PHASE REACTORS

(J. Faria, P. Zapata, Tu Pham)

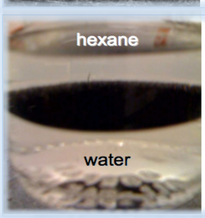
- Condensation reactions (aldol)
- Decarbonylation, hydrogenation, and hydrogenolysis of furfurals
- Decarbonylation and hydrogenolysis of phenolics, benzaldehyde, anisole, guaicol



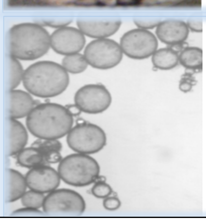
Catalyst-Emulsifier Nanohybrids for Reactions at the Liquid / Liquid Interface



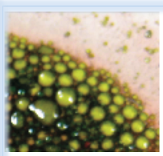
TEM of the Nanohybrids SWNTs/SiO_2



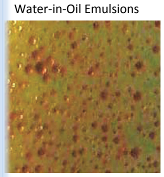
Nanohybrids at the interface of hexane/ water



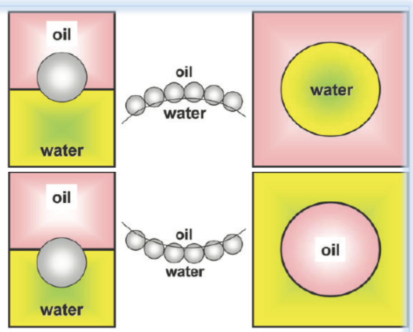
Water/oil emulsion stabilized by Nanohybrids.



Water-in-Oil Emulsions



Oil-in-Water Emulsions

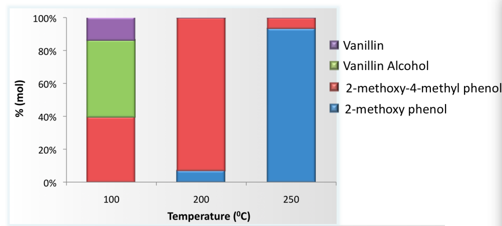


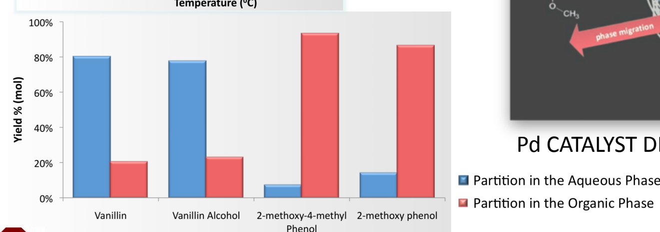
The Hydrophilic-Hydrophobic Balance (HHB) can be tailored by Functionalization

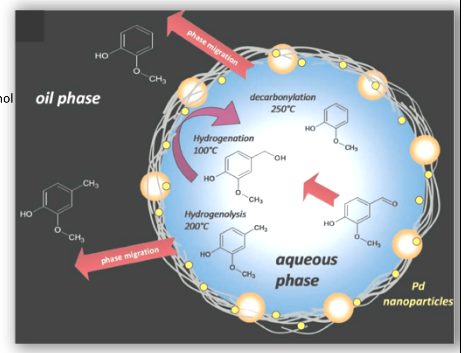
M. Shen, D. E. Resasco, *Langmuir,* 2009, **25**, 10843.

Catalyst-Emulsifier Nanohybrids for Reactions at the Liquid / Liquid Interface

Hydrodeoxygenation of Vanillin (lignin Fraction) over 5% wt. Pd/SWNTs/SiO_2 at the Water/Oil Interface.







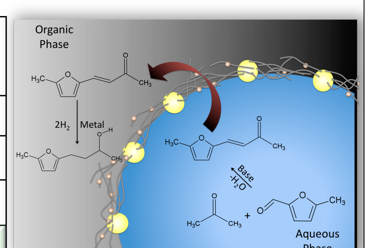
Pd CATALYST DEPOSITED ON NANOHYBRIDS

S. Crossley, J. Faria, and M. Shen, D. E. Resasco, *Science* 327, 68, **2010**

Catalyst-Emulsifier Nanohybrids for Reactions at the Liquid / Liquid Interface

Aldol-Condensation coupled with hydrogenation at the liquid-liquid interface over 5% wt. Pd/SWNTs/MgO

Compound	Before Reaction		After Condensation		After Hydrogenation	
	Water	Oil	Water	Oil	Water	Oil
Acetone	92	61	92	56	86	57
5-Methylfurfural	8	39	6	32	4	24
4-(5-Methylfuran-2 yl-butan-2-ol	0	0	0	0	2	16
4-(2-Furyl)-3-buten-2-one	0	0	2	12	0	0



After aldol-condensation solubility in water decreases and the product migrates to the oil phase

S. Crossley, J. Faria, and M. Shen, D. E. Resasco, *Science* 327, 68, **2010**

Conclusions

✪ Upgrading of bio-oil has two main objectives:
- to eliminate excess oxygen
- to bring products to gasoline/diesel ranges

✪ Studies with model feeds have allowed us to identify potential catalysts and conditions for specific reactions that will be crucial in the upgrading of bio-oil:

A. Condensation of small oxygenates
   - Acidic zeolites
   - Metals and Oxides

B. Deoxygenation
   - Metals (bimetallics)

} Vapor, Liquid, and Bi-phasic Systems

• Research Group

Faculty:

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Researcher Associates:
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– Oklahoma Bioenergy Center
– National Science Foundation (EPSCoR)
– Department of Energy (DoE)

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Anh To The, Paula Zapata,

Miguel Gonzalez Borja, Amalia Botero, Hernando Delgado, Santiago Drexel, Kyle Elam, Anirudh Gangadharan, Sunya Boonyasuwat, Kassie Ngo,

Matt Wulfers, Andrew D'Amico,

Tu Pham, Lei Nie, Xiaohan Zhong, Rattiya Saetang, Christian Scherer, Michael Lang, Julien Bourgeois

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