

2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Catalytic Upgrading of Pyrolysis Bio-oils

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Thermochemical Conversion Platform

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Project Goal



*To develop the **fundamental catalyst and process knowledge** required to design upgrading strategies of pyrolysis bio-oil (vapor and liquid) **to achieve a stable product**. Specific project objectives are to **maximize carbon retention and minimize H₂ consumption**. Direct hydrotreating is not optimal to achieve these objectives. A balanced **cascade of catalytic steps** is a preferred alternative strategy. The project combines studies with **model compounds** (single and mixtures) **and real bio-oils**, with catalyst design, characterization, density functional theory (DFT) calculations, and kinetic models.*

This project addresses barriers Tt-E (bio-oil stabilization) and Tt-G (fuels catalyst development).

Quad Chart Overview

Timeline

- Project start date: 1/1/2009
- Project end date: 7/29/2013
- Percent complete: 90%

Budget

- Total project funding
 - DOE share: \$1,951,625
 - Contractor share: \$487,906
- Funding received in FY11: none
- Funding in FY 2012 (DOE & cost share) none
- Funding for FY 2013 (DOE & cost share) none
- ARRA Funding none
- Years the project has been funded & average annual funding 4.75 years ~\$411,000 per year.
- ARRA Funding: 0

Barriers

- Barriers addressed
 - Tt-E: Pyrolysis of biomass and bio-oil stabilization
 - Tt-G: Fuels catalyst development

Partners

Research collaborations include:

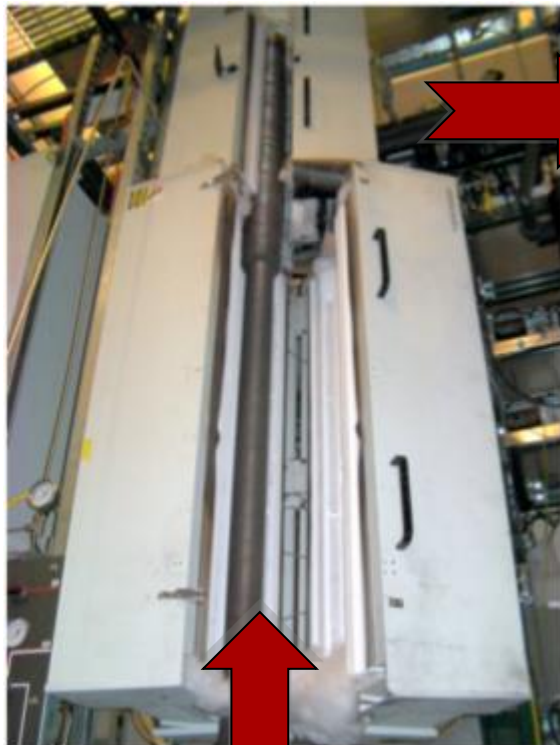
- Oklahoma State University
- Noble Foundation
- USDA ARS
- Texas A&M
- Drexel
- Oklahoma Botany & Microbiology
- Iowa State University

NOTE: research collaborations not funded through this project, but made possible through this funding. 3

Project Overview

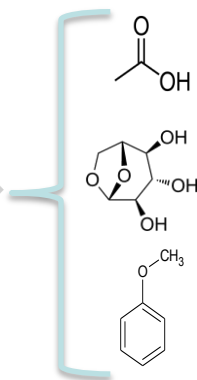
- History and Context:
 - University of Oklahoma (OU) strengths in catalysis, reaction engineering, hydrocarbon processing, natural gas conversion, combustion
 - Oklahoma Bioenergy Center – \$14 million State initiative covering the entire biomass value chain (emphasis on switchgrass), involving OU, Oklahoma State University, Noble Foundation
 - NSF EPSCoR Research Infrastructure Improvement program in cellulosic bioenergy
- DoE project focused on catalyst development for bio-oil upgrading and conversion of oxygenated compounds to fuel components:
 - Vapor phase catalytic conversion to retain carbon and deoxygenate with minimum hydrogen consumption
 - Liquid phase (mild conditions) catalytic conversion

Concept: catalytic cascade to stabilize and upgrade pyrolysis oil liquids



Biomass

- Cellulose
- Hemicellulose
- Lignin



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

- Challenges to catalysts:
- Remove O
- Maximize C capture
- Minimize H₂ consumption
- Minimize catalyst deactivation
- Tolerate hot liquid water

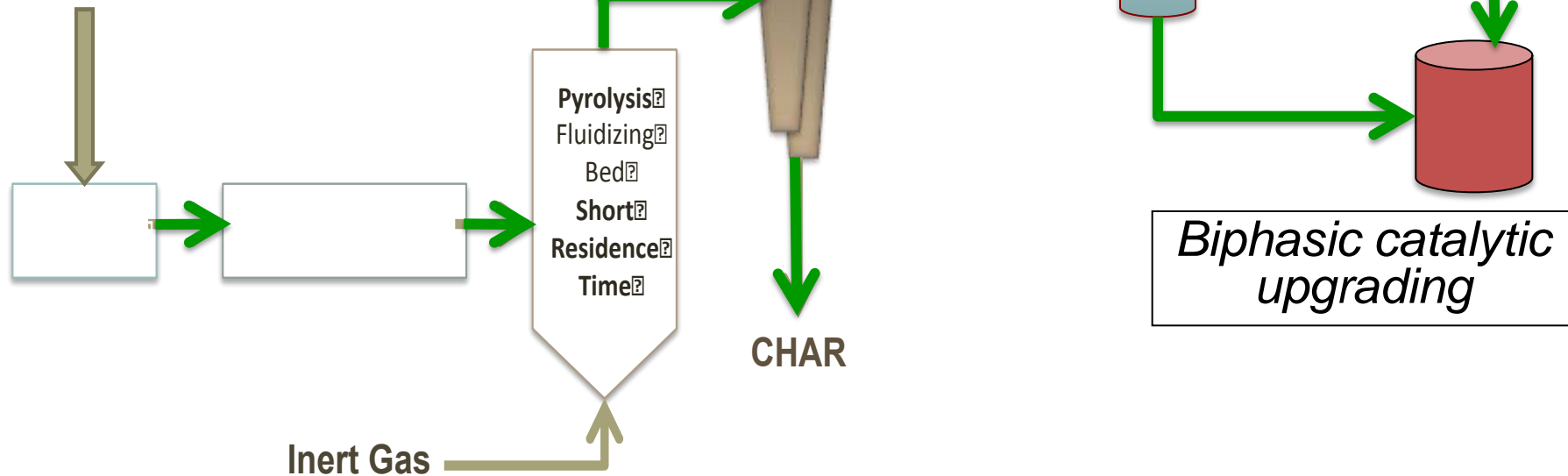
Concept: catalytic cascade



BIOMASS

Switch grass
Sawdust, Pine
Torrefied-biomass

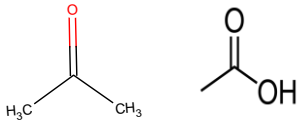
OBJECTIVES
Increase Liquid Yield
Remove Oxygen
Minimize Deactivation



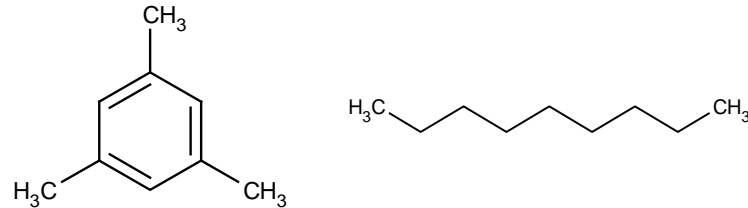
Concept: catalytic cascade- utilize reactions that maximize C retention in liquid

Objective

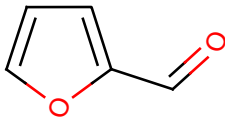
Light oxygenates:
Acetic acid,
Acetol,
Acetaldehyde,
Water



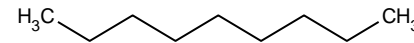
- Grow C-C chain to liquid fuel range



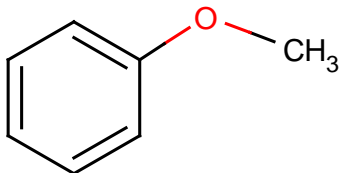
Sugar derived
compounds:
Furfurals



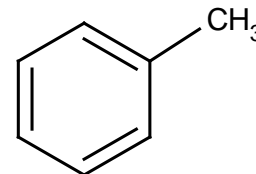
- Condense with light oxygenates
- Minimize C-C cleavage



Lignin derived
compounds:
Phenolics



- Remove oxygen without losing methoxy C to gas





1- Approach

- Catalytic processes:
 - Vapor phase condensation of small oxygenates to **build carbon chains**
 - **Controlled C-O cleavage vs. C-C cleavage** of furanics to preserve carbon in the liquid fuel range.
 - Balance transalkylation with hydrogenolysis to **preserve carbon in the liquid fuel range** when converting lignin derived phenolics.
 - **Conversion of bio-oil vapors prior to condensation**
- Technical approach:
 - Model compound and bio-oil studies and physicochemical characterization to identify active and selective catalysts, reaction pathways, and deactivation mechanisms
 - Theoretical (DFT) studies to understand reaction mechanisms and guide catalyst development
 - Development of quantitative structure-property relationships to help identify desired products (fuel properties, oxygen content, yield) and aid in analytical chemistry.



Strategy No. 1

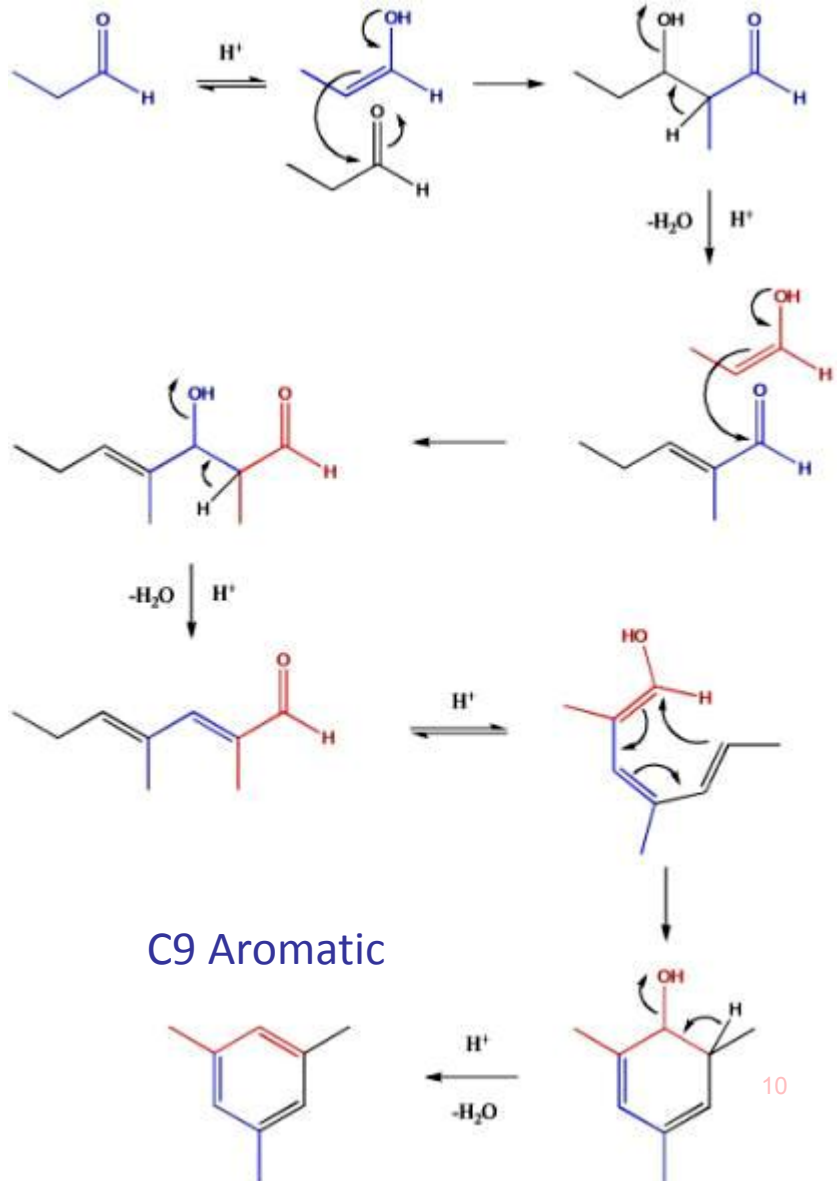
“Building up C-C chains”



Aromatization of Propanal on H-ZSM5

Aromatization through aldol condensation

Aldol Dimerization
Dehydration
Aldol Trimerization
Dehydration
Enol and
Rearrangement
Aromatization
Dehydration



Aromatization of Propanal on H-ZSM5

aldol condensation enhances aromatics yield



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



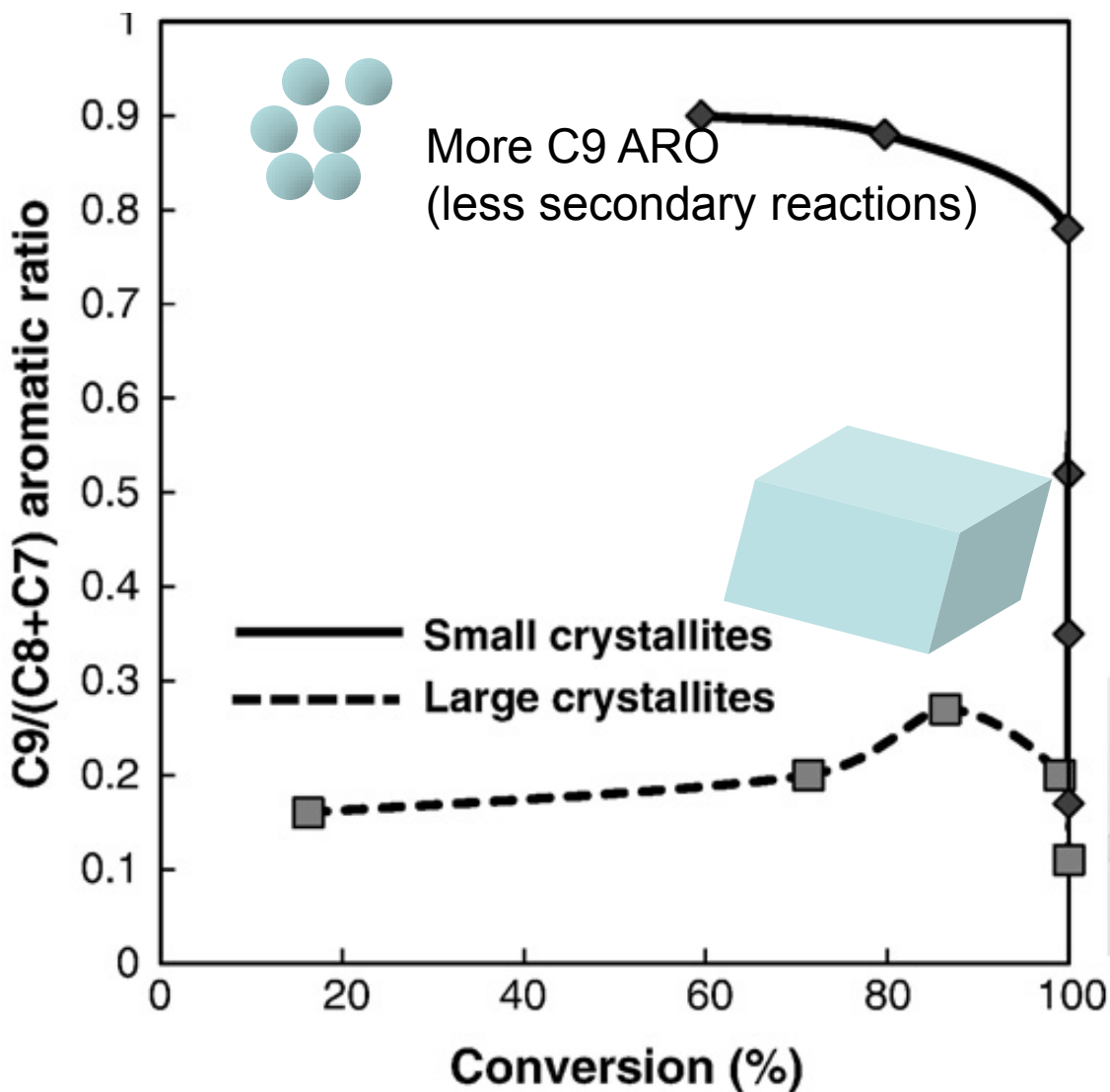
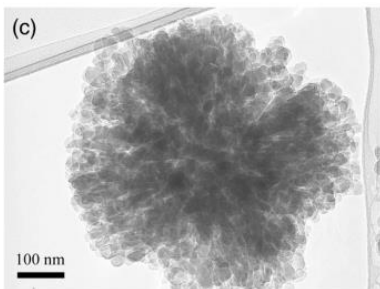
Smaller crystal size decreases secondary reactions

H-ZSM-5

Si/Al = 45

Crystallite
Size < 100 nm

From
Sud
Chemie

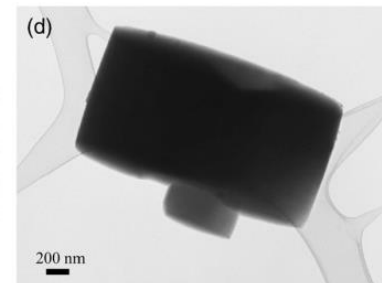


H-ZSM-5

Si/Al = 45

Crystallite
Size >1,000 nm

Synthesized
In-House





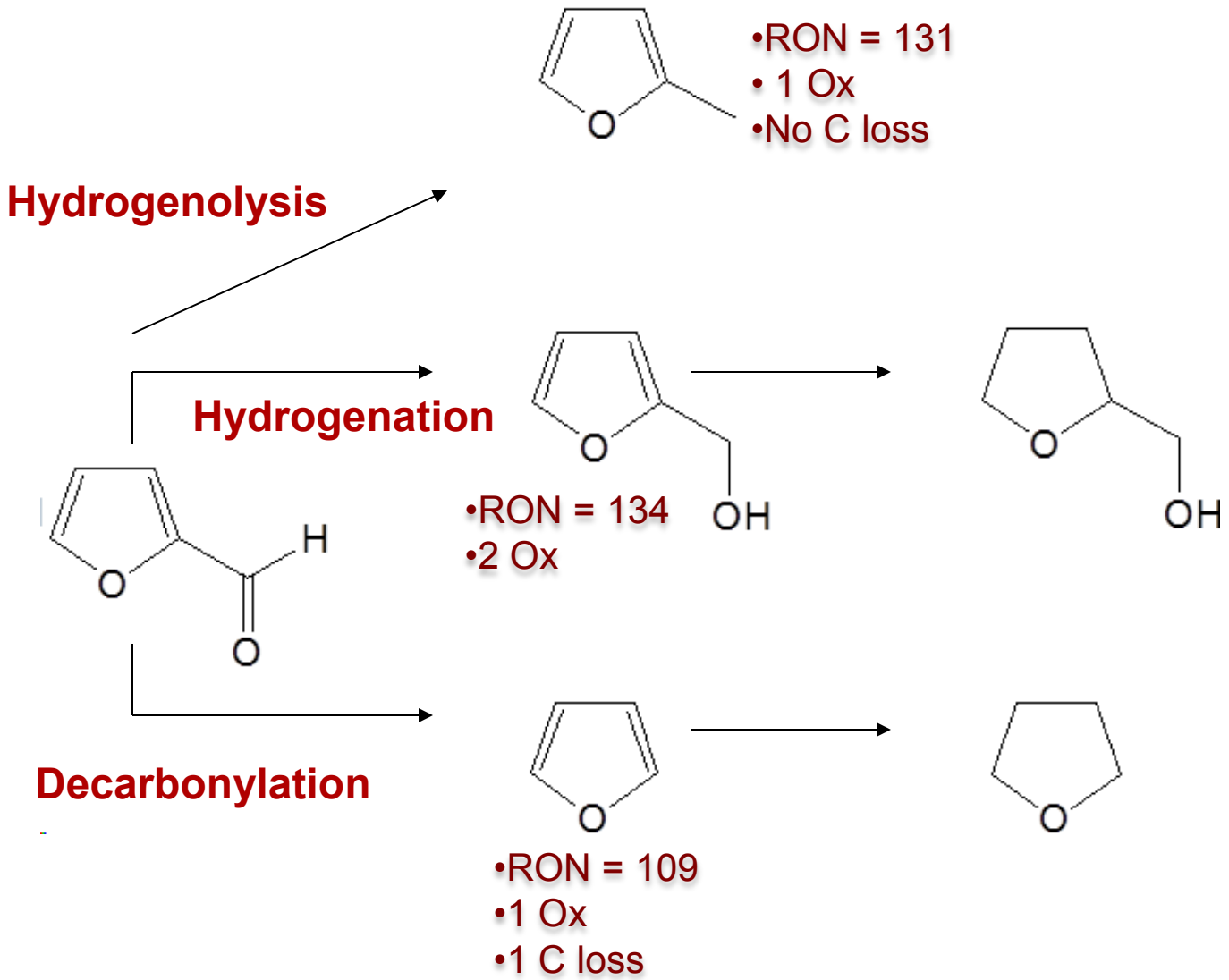
Strategy No. 2

“Breaking C-O bonds instead of C-C bonds”

Hydro-deoxygenation
of Furfural



Furfural conversion routes on metal catalysts



Furfural conversion selectivity over Cu, Pd, and Ni/SiO₂

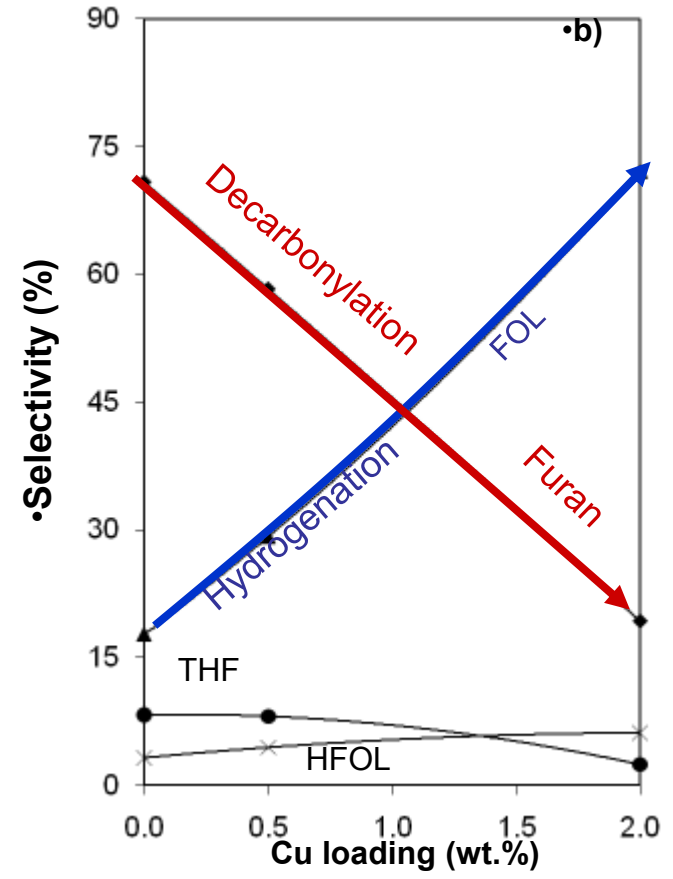
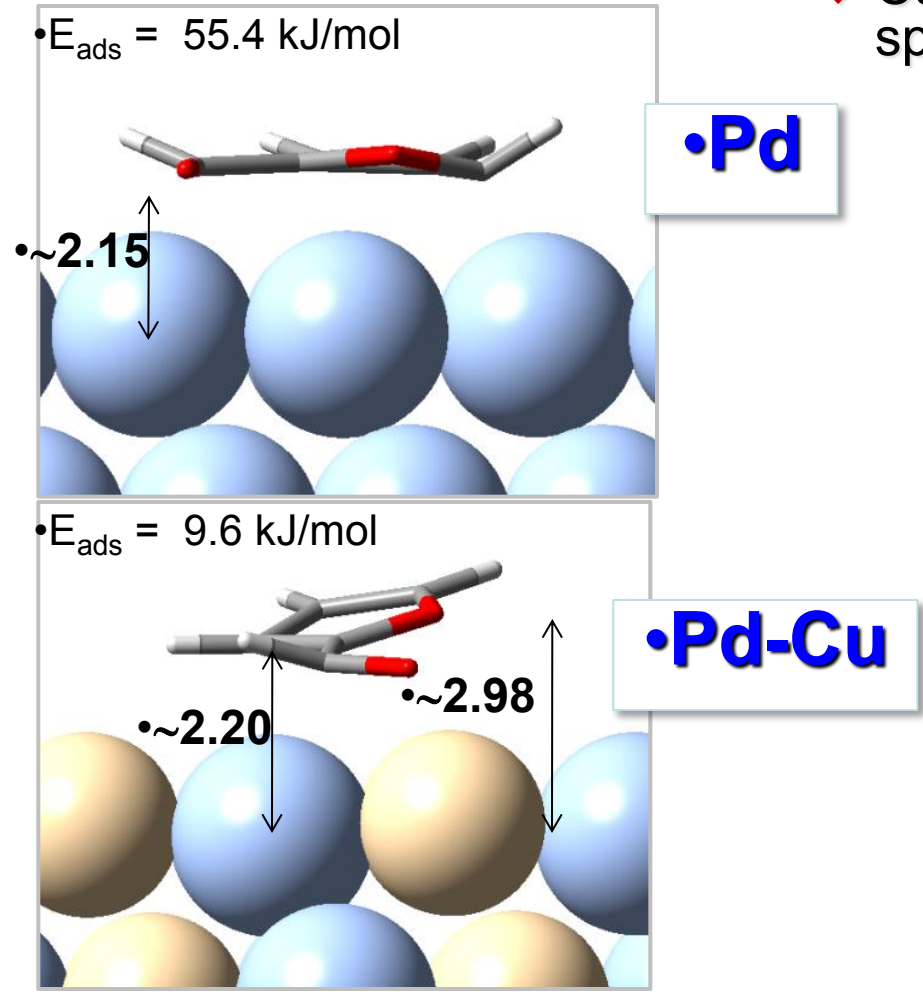


Catalysts	Cu	Pd	Ni
TOF (s ⁻¹) (x ~ 0)	1.3	266	77
Conversion (%)	69.2	69	72.1
Temperature	230 C	230 C	230 C
Hydrogenation (%)			
Furfuryl alcohol (FOL)	98	14	25
Methylfuran	2	0	2
Tetra hydro FOL	0	5	4
Decarbonylation (%)			
Furan	0	60	43
THF	0	20	-
Ring opening (%)			
C4 compounds	0	0	25



Pd-Cu/SiO₂ : alloy modifies decarbonylation selectivity

❖ Cu inhibits the formation of the acyl species (C-H bond activation)

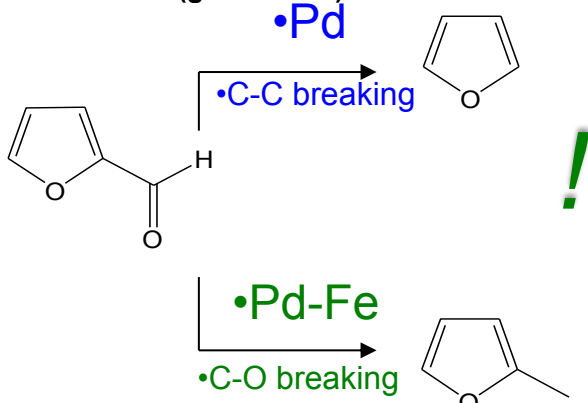
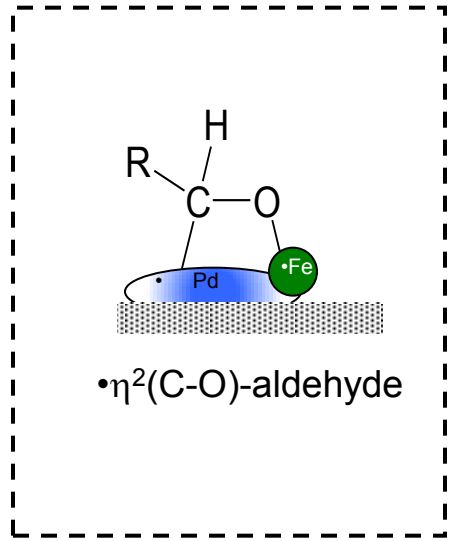
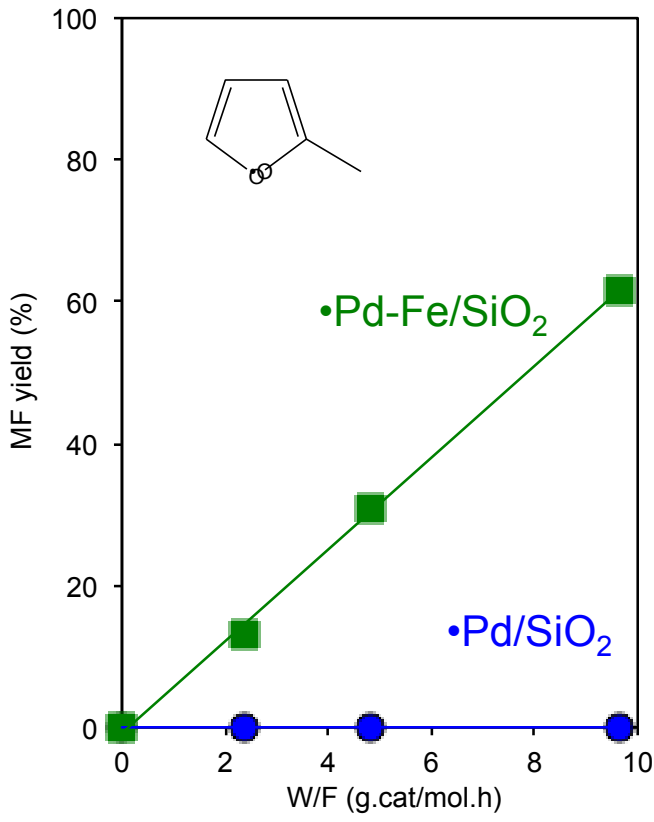
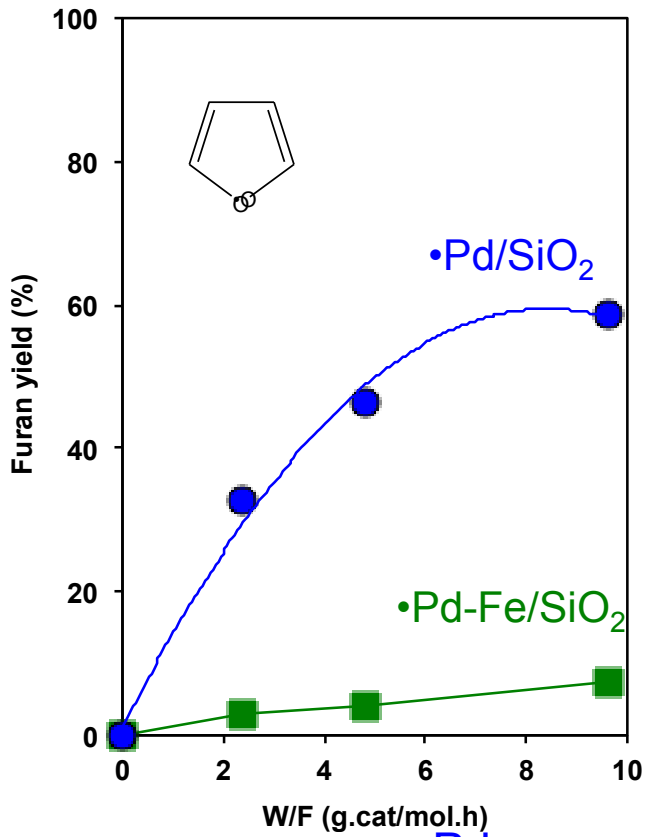


Sitthisa, Pham, Prasomsri, Sooknoi, Mallinson, Resasco, *J. Catalysis*, **280** (2011) 17-27

W/F = 0.1 h, Temp = 230° C, H₂/Feed ratio = 25, H₂ pressure = 1 atm, TOS = 15 min



Pd-Fe/SiO₂: alloy enhances C-O hydrogenolysis



❖ Drop in decarbonylation rate when Fe was added to Pd.

❖ 2-methyl furan became the main product over Pd-Fe catalyst.¹⁷



Strategy No. 3

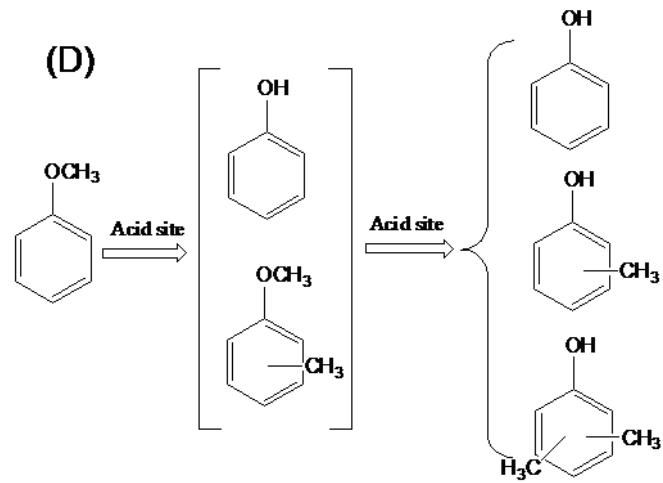
“Eliminate O while keeping C
in the fuel range”

Selective Hydro-Deoxygenation of
Phenolic Compounds



Deoxygenation while preserving C on ring

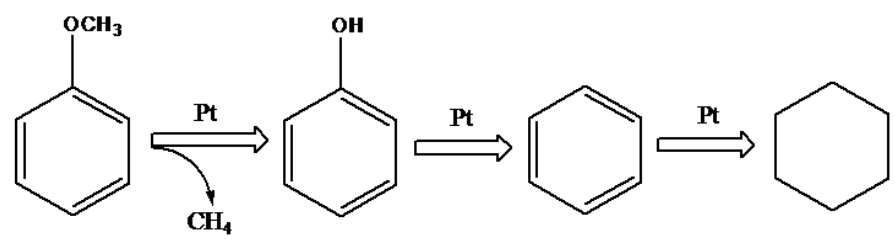
conversion over H-Beta yields branched oxygenates



The major reaction is transalkylation

Very little deoxygenation

conversion over 1% Pt/SiO₂ → HDO with loss of methyl

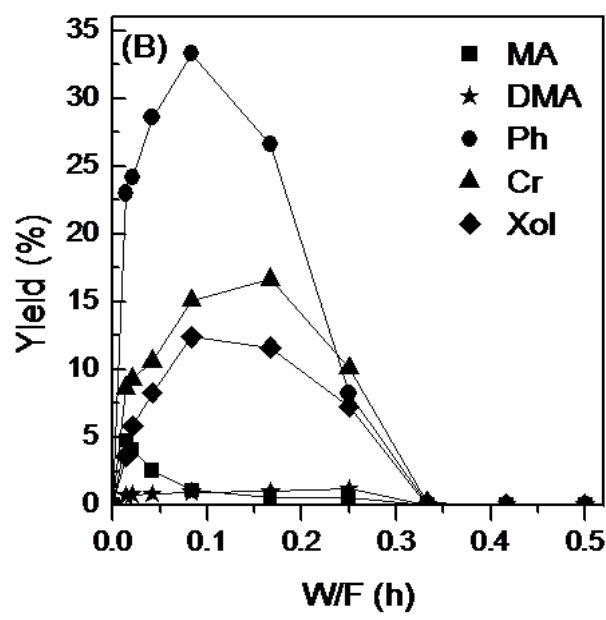
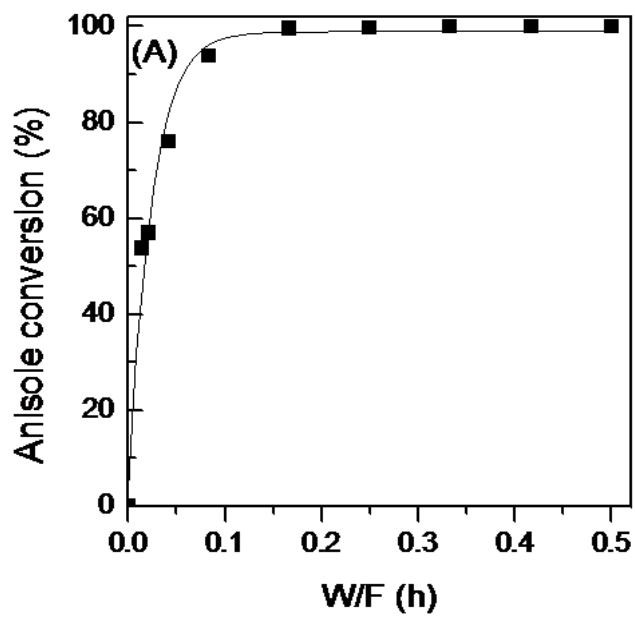


HDO → Methoxy group is lost as methanol and methane

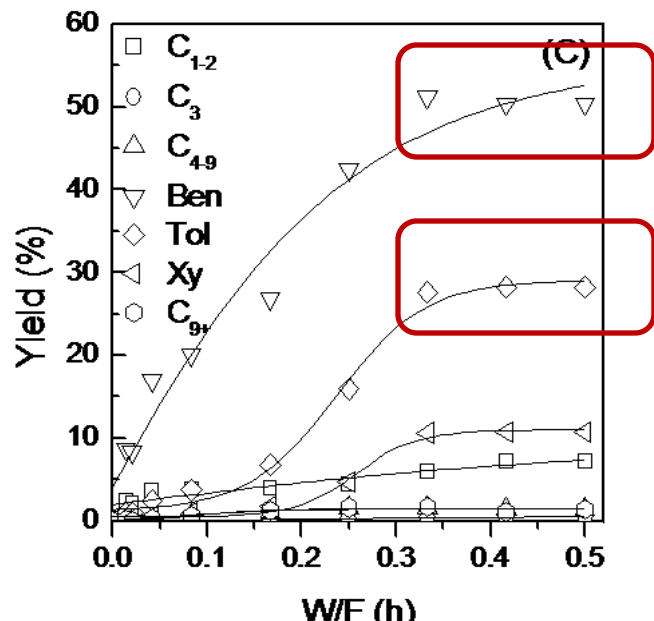
Reaction Conditions: T=400 °C, P=1 atm, H₂/Anisole=50, TOS= 0.5 h.



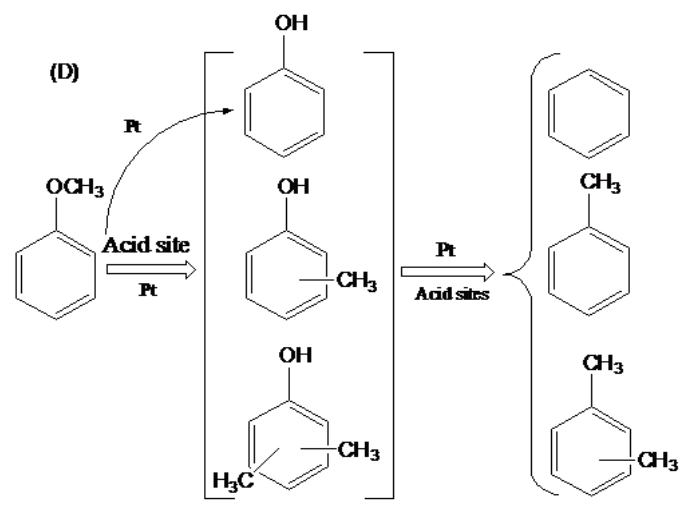
1%Pt/H-Beta deoxygenates while preserving C on ring



Transalkylation and hydrodeoxygenation take place over acid and metal sites, respectively.



Yields of hydrocarbons is enhanced significantly



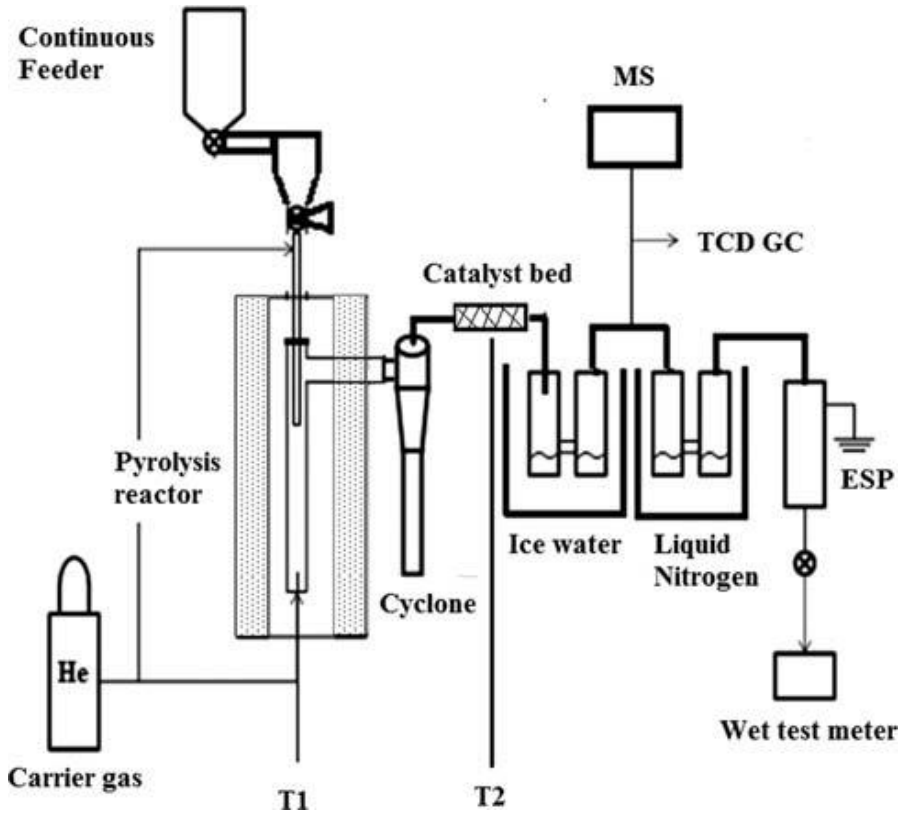
The carbon number is preserved.

•T=400 °C, P=1 atm, H₂/Anisole=50, TOS= 0.5 h.



In situ upgrading of real bio-oil vapors

Ru/TiO₂ conversion of real bio-oil vapors

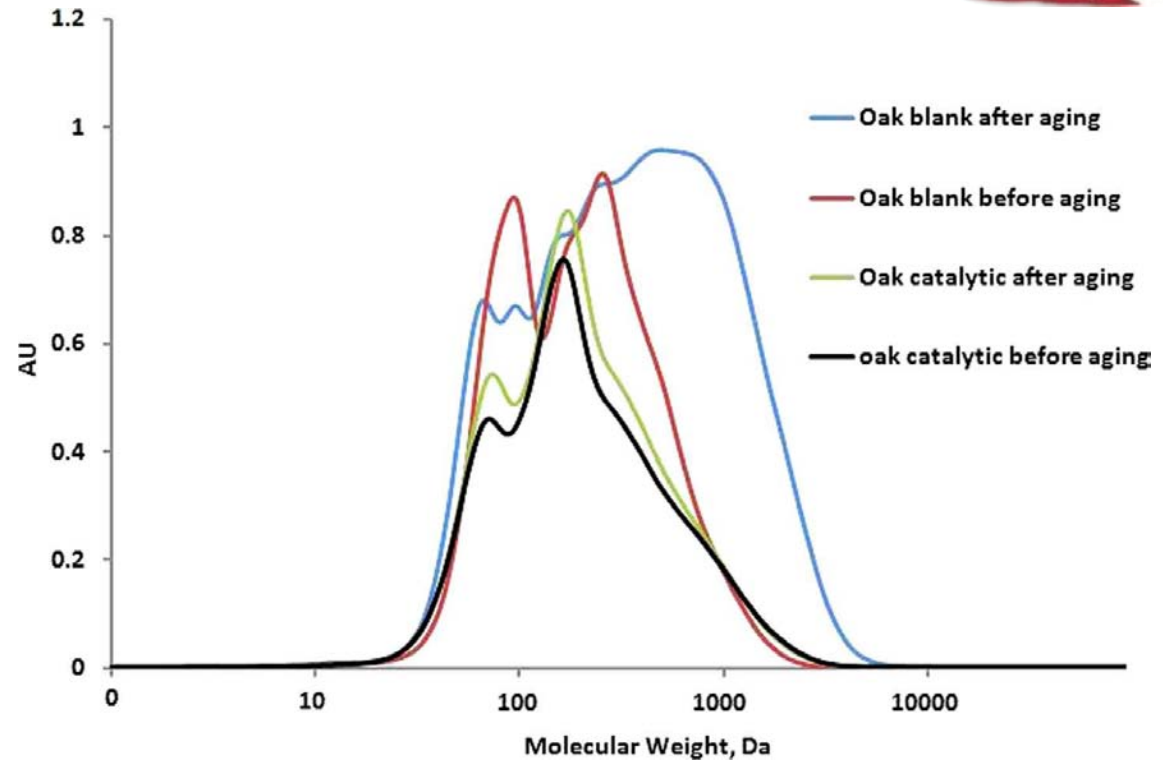




Knowledge from model compound studies applied to real systems

- Acetic acid → acetone
- Bio-oil stability significantly improved

4g Ru/TiO₂
 - 400° C
 - 1Atm H₂
 30g oak/batch



	Oak Blank	Ru-TiO ₂ 1st	Ru-TiO ₂ 3rd
Acetone	0.32 (0.09)*	1.62 (0.17)	0.74 (0.15)
Butanone		0.82 (0.12)	0.57 (0.10)
Acetic acid	6.26 (0.67)	0.84 (0.11)	2.42 (0.31)
Acetol	2.42 (0.29)		0.64 (0.14)
2-cyclopenten-1-one		1.51 (0.16)	1.44 (0.14)
Phenol	0.81 (0.15)	1.58 (0.17)	1.27 (0.16)
Levogluconan	1.75 (0.19)	0.12 (0.04)	1.46 (0.21)

Less change in MW upon aging after Ru/TiO₂ treatment

3 - Relevance

In direct response to barriers Ta-E and Tt-G-

– Conversion Enabling Technologies page 2-48 states:

“Understanding and more accurately measuring catalyst activities, selectivities and deactivation processes, and gaining insights into the synergistic roles of elemental species within the active catalytic sites will enable development of new processes that are more energy, carbon, and cost-efficient.”

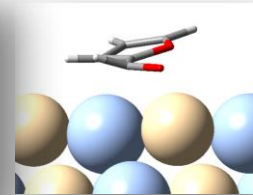
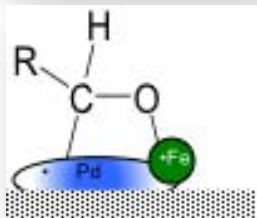
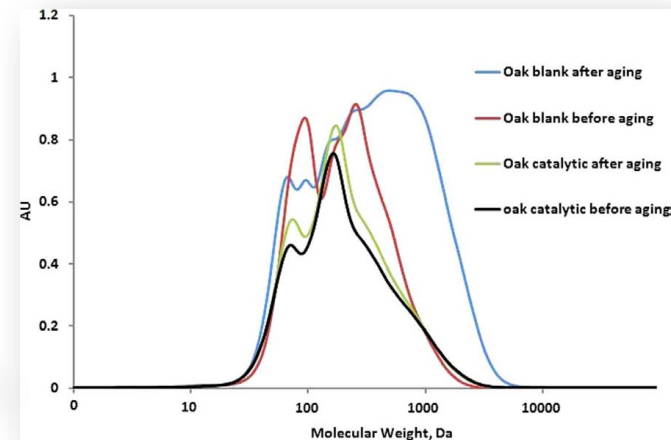
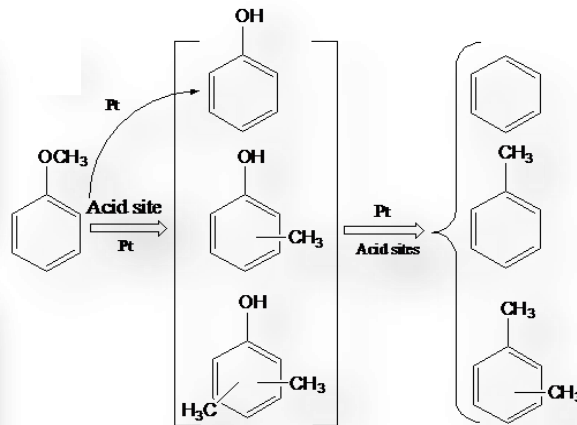
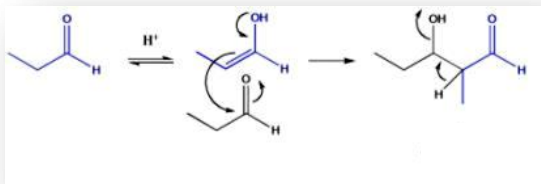
- The fundamental information gained by these model compound results allow the development of novel catalytic strategies that are critical to improving carbon yields while minimizing cost and hydrogen consumption critical to the advancement of the field of thermochemical conversion of biomass.
- Results from the studies supported by this project have led to several more advanced follow up projects utilizing real bio-oil fractions to improve the overall cost, liquid yields, and carbon efficiency while producing feedstocks amenable for refinery insertion.

Success Factors and Challenges

- Success factors:
 - Higher carbon retention and lower hydrogen consumption versus bio-oil hydrotreating
 - Improved catalyst life
 - Identified fundamental knowledge necessary to design strategies necessary for refinery insertion → topic of current and future projects
- Challenges:
 - Control of reaction selectivity in complex mixtures
 - Mitigating catalyst deactivation by specific catalyst and operating condition design
 - Reactor engineering of the cascade
- Relevance to the state of technology and commercial viability
 - Catalyst knowledge (activity, selectivity, reaction pathways) vital for any upgrading strategy
 - Improving carbon retention (liquid fuel yield) and decreasing hydrogen consumption very relevant to cost competitiveness and commercial viability
 - Improved carbon retention and decreased hydrogen consumption improve process sustainability and impact on petroleum substitution
 - Catalysts and conditions have been identified using model compounds; mixture and bio-oil studies have been initiated
 - Studies of catalyst deactivation and regeneration are planned

Summary

- “Catalytic cascade” upgrading has potential advantages over hydrotreating:
 - Carbon retention (biofuel liquid yield)
 - Hydrogen consumption
 - Product selectivity
- Several C retention strategies have been identified with model compounds
 - Aldol condensation of light oxygenates to produce aromatics at rates much faster than olefin oligomerization and dehydrocyclization
 - Selective C-O cleavage via the introduction of bimetallic alloys for the conversion of furanics
 - Carbon retention on the ring by incorporating acid catalyzed transalkylation prior to hydrodeoxygenation
- Research is relevant to biomass program goals of cost competitiveness, petroleum substitution, sustainability, and integration
- Model compound studies have identified catalysts and conditions that have been tested with bio oil vapors to improve stability
- Significant challenges: catalyst deactivation, selectivity control, reactor engineering



Responses to Previous Reviewers' Comments

A common theme among reviewer's comments was the good fundamental work, but more interaction with industry and applied research with real systems while incorporating TEA is necessary to increase the impact.

Response:

We agree with the comments and agree that these elements are necessary for the project to have more significant impact. We are partnering with Iowa State University and PNNL (DOE funded) on a project aimed at developing feedstocks for refinery insertion; we believe this may be the most immediate possible use of stabilized pyrolysis oil. We are also teaming with USDA and several other universities (South Carolina, Delaware, many others) to study the catalyst deactivation rates. Both projects apply the knowledge we have gained through model compounds to real systems. In both projects, we have support from refiners as well as collaborators in TEA to help evaluate our results. We have also submitted grants in collaboration with national labs aimed at advancing the knowledge gained through model compound studies to develop novel conversion routes using real feedstocks while collaborating with other universities to incorporate LCA and TEA. These projects would not have been possible without the support from the current grant.



1. Teerawit Prasomsri, Roberto E. Galiasso Tailleux, Walter E. Alvarez, Tawan Sooknoi, Daniel E. Resasco, "Conversion of 1-tetralone over HY zeolite: An indicator of the extent of hydrogen transfer" *Applied Catalysis A*, **389**, 140-146, **2010**
2. Surapas Sitthisa, Trung Pham, Teerawit Prasomsri, Tawan Sooknoi, Richard G. Mallinson, Daniel E. Resasco, "Conversion of furfural and 2-methylpentanal on Pd/SiO₂ and Pd-Cu/SiO₂ catalysts" *Journal of Catalysis*, 280 (2011) 17–27, **2011**
3. Xinli Zhu, Lance L. Lobban, Richard G. Mallinson, Daniel E. Resasco, "Bifunctional hydrodeoxygenation of phenolic model compound over Pt/HBeta catalyst." *Journal of Catalysis* 281 (1) p. 21-29 (2011).
4. Surapas Sitthisa, Tawan Sooknoi, Yuguang Ma, Perla B. Balbuena, Daniel E. Resasco, "Kinetics and mechanism of hydrogenation of furfural on Cu/SiO₂ catalysts," *Journal of Catalysis*, **277**, 1-13, **2011**,
5. Chiappero M., Do PTM, Crossley S, Lobban LL, Resasco DE, "Direct conversion of triglycerides to olefins and paraffins over noble metal supported catalysts." *Fuel*, **90**, 1155-1165, **2011**
6. Love, N. D., Parthasarathy, R. N. and Gollahalli, S. R. "Concentration Measurements of CH and OH Radicals in Laminar Biofuel Flames," *International Journal of Green Energy*, Vol. 8, pp. 113-120.
7. Surapas Sitthisa and Daniel Resasco, "Hydrodeoxygenation of furfural over supported metal catalysts: a comparative study of Cu, Pd and Ni," *Catalysis Letters* 141, p. 784-791 (2011).
8. Sequera, A., Parthasarathy, R. N. and Gollahalli, S. R. "Effects of Fuel Injection Timing in the Combustion of Biofuels in a Diesel Engine at Partial Loads," *Journal of Energy Resources Technology*, Vol. 133, pp. 022203-022209.
9. Tanate Danuthai, Tawan Sooknoi, Siriporn Jongpatiwut, Thirasak, Rirksomboon, Somchai Osuwan, Daniel E Resasco "Effect of extra-framework cesium on the deoxygenation of methylester over CsNaX zeolites," *Appl. Catal. A-General*, 409, 74–81, **2011**
10. Daniel E. Resasco "What Should We Demand from the Catalysts Responsible for Upgrading Biomass Pyrolysis Oil?" Guest Commentary, *J. Phys. Chem. Lett.*, 2, 2294–2295, **2011**



11. Miguel Ángel González-Borja and Daniel E. Resasco “Anisole and Guaiacol Hydrodeoxygenation Over Pt-Sn on Monolithic Catalyst Supports,”, *Energy Fuels*, 25, 4155-4162, **2011**
12. Surapas Sitthisa, Wei An, and Daniel E. Resasco “Selective Conversion of Furfural to Methylfuran over Silica-supported Ni-Fe Bimetallic Catalysts,”, *Journal of Catalysis* 284, 90–101, **2011**
13. Paula A. Zapata, Jimmy Faria, M. Pilar Ruiz, Daniel E. Resasco “Condensation/hydrogenation of biomass-derived oxygenates in water/oil emulsions stabilized by nanohybrid catalysts,” *Topics in Catal.* (in press)
14. Ruiz M. Pilar; Faria Jimmy; Shen Min; Drexler, Santiago; Prasomsri, Teerawit; Resasco, Daniel E. “Nanostructured Carbon-Metal Oxide Hybrids as Amphiphilic Emulsion Catalysts,”, *ChemSusChem* 4, 964-974, **2011**
15. Heng Fan, Daniel E. Resasco, and Alberto Striolo, “Amphiphilic silica nanoparticles at the decane-water interface: Insights from atomistic simulations,” *Langmuir*, 27, 5264 -5274, **2011**
16. Nie, L. and Resasco, D.E., “Improving carbon retention in biomass conversion by alkylation of phenolics with small oxygenates,” *Applied Catalysis A – General*, 447, p 14-21 **2012**.
17. Pham, T.N., Shi, D.C., Sooknoi, T. and Resasco D.E., “Aqueous-phase ketonization of acetic acid over Ru/TiO₂/carbon catalysts,” *J. Catalysis*, 295, p 169-178 **2012**.
18. Wan, S., Pham, T., Zhang, S., Lobban, L., Resasco, D. and Mallinson, R, “Direct catalytic upgrading of biomass pyrolysis vapors by a dual function Ru/TiO₂ catalyst.” *AIChE J.* doi: 10.1002/aic.14038 . **2013**.



1. Daniel E. Resasco, "Model compound studies towards the catalytic upgrade of bio-oil in vapor and liquid phases." *Invited Speaker*, 21th ACS National Meeting & Exposition, Anaheim, California, March 27-31, 2011.
2. Daniel E. Resasco, "Solid nanoparticles to stabilize water/oil emulsions and catalyze reactions at the liquid/liquid interface." *Invited Speaker*, Symposium in Honor of Harold Kung, 21th ACS National Meeting & Exposition, Anaheim, California, March 27-31, 2011.
3. Lance Lobban "Heterogeneous catalytic upgrading of biomass-derived oils," invited speaker, Total Catalysis Club, Brussels, Belgium Jan 27-28, 2011.
4. Mendez, C. J., Parthasarathy, R. N. and Gollahalli, S. R. "Performance and Emission Characteristics of Alcohol/Jet A Blends in a Small Scale Gas Turbine Engine," 49th AIAA Aerospace Sciences Meeting, AIAA2011-0619, January 4-7, 2011, Orlando, FL.
5. Aldana, C., Gollahalli, S. R. and Parthasarathy, R. N. "Combustion Characteristics of Spray Flames of Soy Methyl Ester and Diesel Blends," 49th AIAA Aerospace Sciences Meeting, AIAA2011-0618, , January 4-7, 2011, Orlando, FL.
6. Grisanti, M. A., Parthasarathy, R. N. and Gollahalli, S. R. "Measurement of Flash Points of Biofuels and Their Blends," 31st AIAA/ASME Symposium, University of Oklahoma, April 2011, Norman, OK.
7. Singh, V., Gollahalli, S. R. and Parthasarathy, R. N. "Effects of Equivalence Ratio on Temperature and Soot Volume Fraction in Laminar Partially Premixed Flames of CME/Diesel Blends," 31st AIAA/ASME Symposium, University of Oklahoma, April 2011, Norman, OK .
8. Daniel E. Resasco, "Catalytic Upgrade of Pyrolysis Bio-oil Components in Vapor and Liquid Phases," *Keynote Lecture*, 22nd North American Catalysis Society Meeting, June 5-10, 2011. Detroit Marriott at the Renaissance Center, Detroit, MI
9. Daniel E. Resasco, "Model compound studies towards the catalytic upgrade of pyrolysis oil in vapor and liquid phases", Brookhaven National Laboratory, August 1, 2011.
10. Daniel E. Resasco, "Model compound studies towards the catalytic upgrade of pyrolysis oil in vapor and liquid phases", Pacific Northwest National Laboratory, Institute for Integrated catalysis, August 15-17, 2011.

Presentations cont.



11. Daniel E. Resasco, "Catalytic Upgrading of Vapors and Liquids from Pyrolysis of Biomass." The *D. B. Robinson Distinguished Speaker*, University of Alberta, Edmonton, Canada, September 15, 2011
12. Grisanti, M. C., Parthasarathy, R. N. and Gollahalli, S. R. (2011) "Physical and Combustion Properties of Biofuels and Biofuel Blends with Petroleum Fuels," *Proceedings of the 9th International Energy Conversion Engineering Conference and Exhibit*, Paper No. AIAA 2011-6012, San Diego.
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Presentations cont.



21. Faria, Jimmy A., Rattiya Saetang and Daniel E. Resasco, "Catalytic Isomerization/Dehydration of Sugars On Functionalized CNT-Metal Oxide Hybrids At the Liquid-Liquid Interface of Water/Oil Emulsions" AIChE Annual Meeting, Minneapolis, MN October, 2011.
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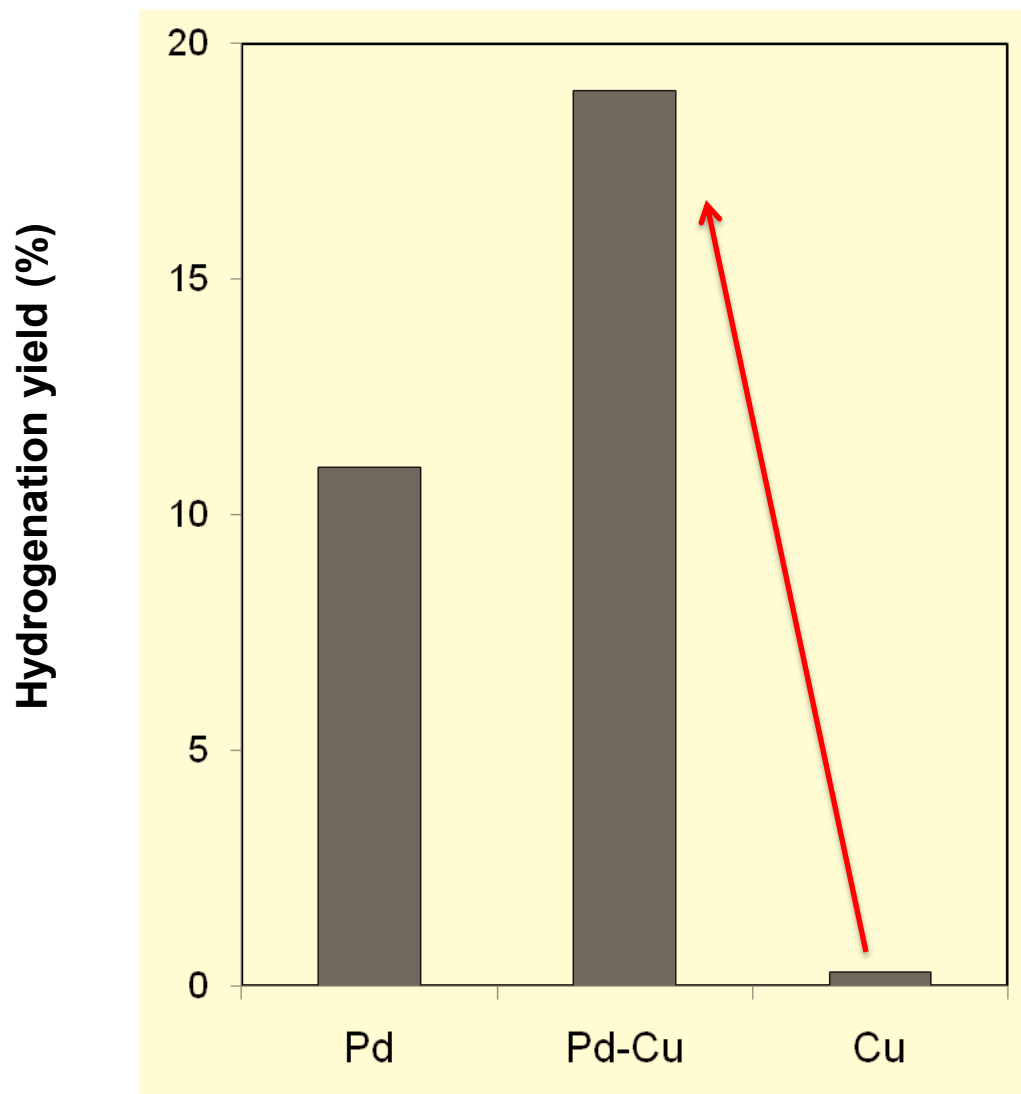
Presentations cont.



31. Tran, V., Morton, C., Parthasarathy, R. N. and Gollahalli, S. R. (2012) "Combustion Characteristics of Pool Fires of Biofuel/Jet A Blends," *10th International Energy Conversion Engineering Conference and Exhibit*, AIAA 2012-3722, Atlanta.
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Backup Slides

Pd-Cu alloy enhances yield of furfuryl alcohol



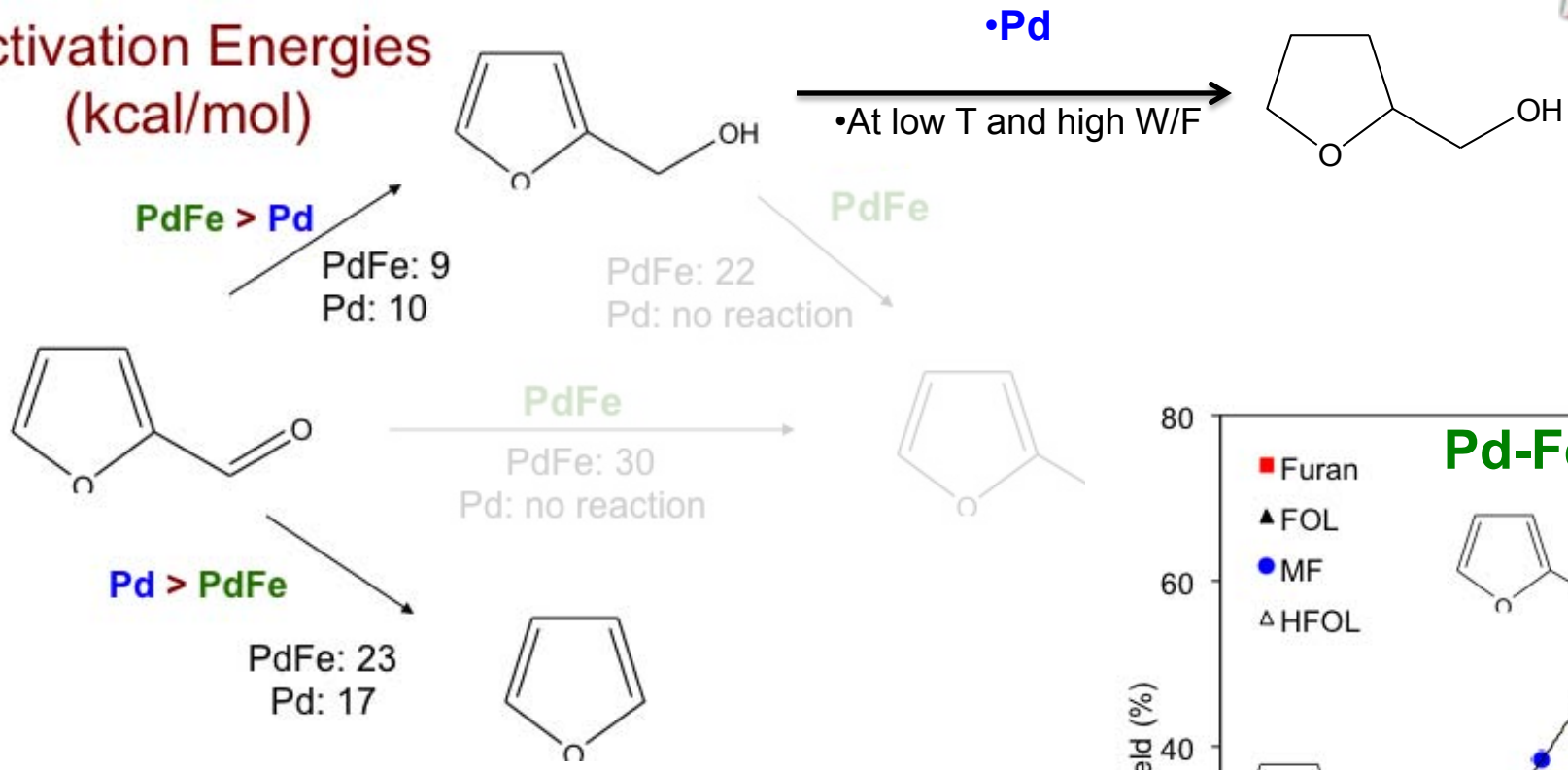
Dramatic increase in **yield** of furfuryl alcohol on the Pd-Cu catalyst with high **selectivity**.

W/F = 0.2 h, Temp = 250°C,
H₂/Feed ratio = 25,
Pressure = 1atm,
TOS = 15 min.

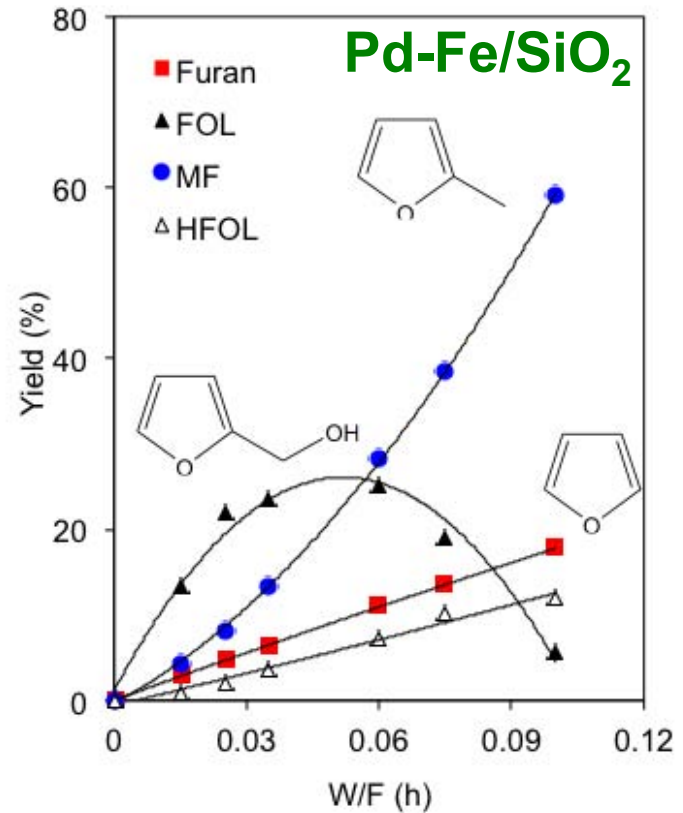


Product selectivity control by modifying surface intermediates

Activation Energies (kcal/mol)



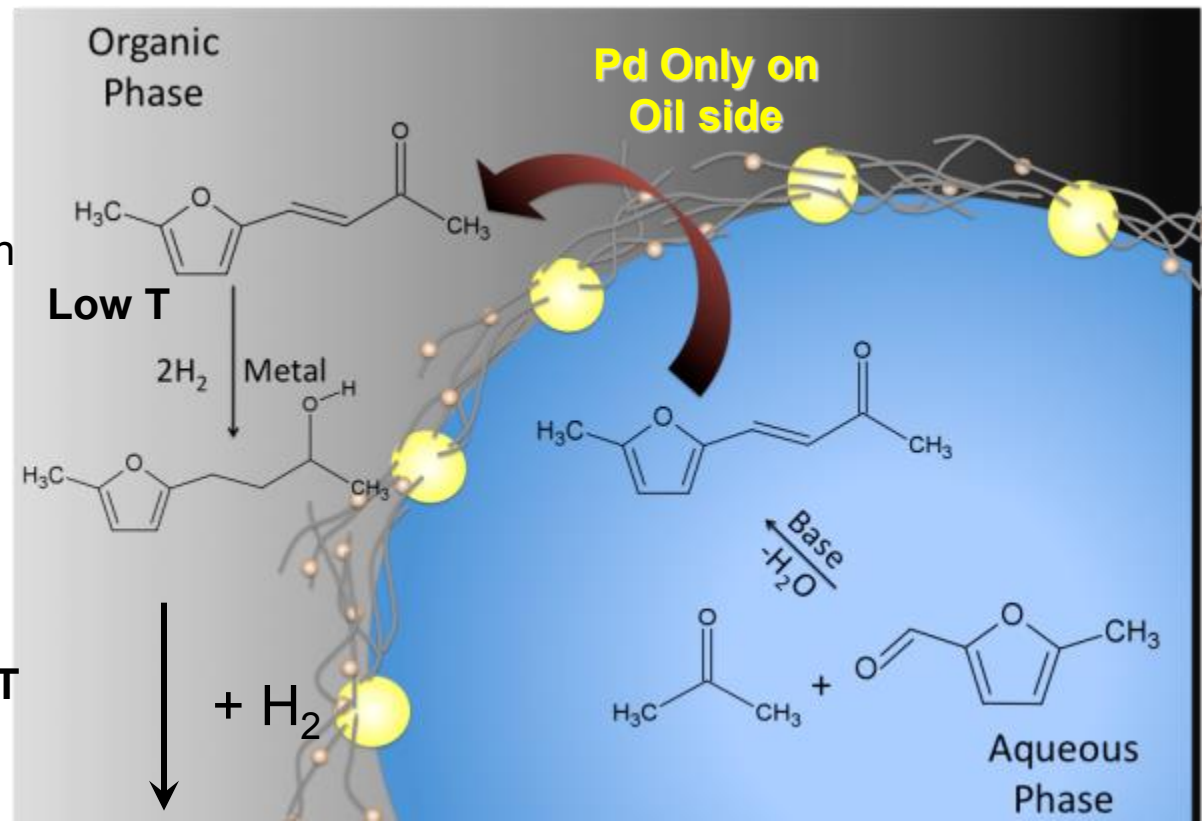
- ❖ Decarbonylation drastically decreased when Fe was added to Pd.
- ❖ FAL hydrogenolysis goes mostly through FOL – via hydrogenation.



Liquid Phase Biphasic condensation over MgO/CNT/Pd



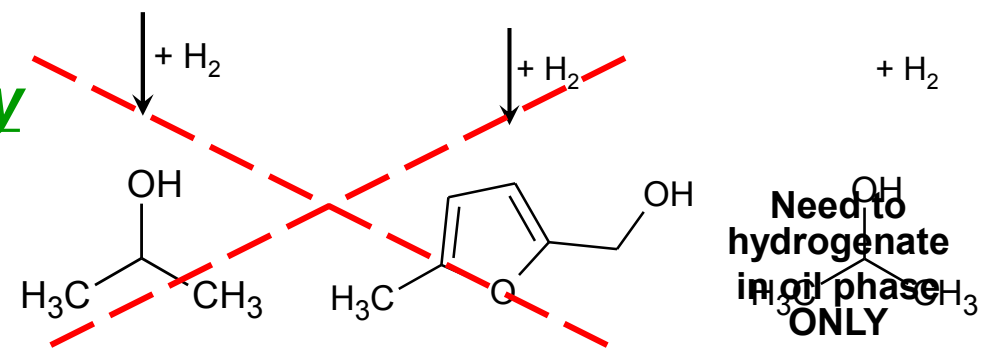
STEP 2:
Temperature
Staged
Hydrogenation



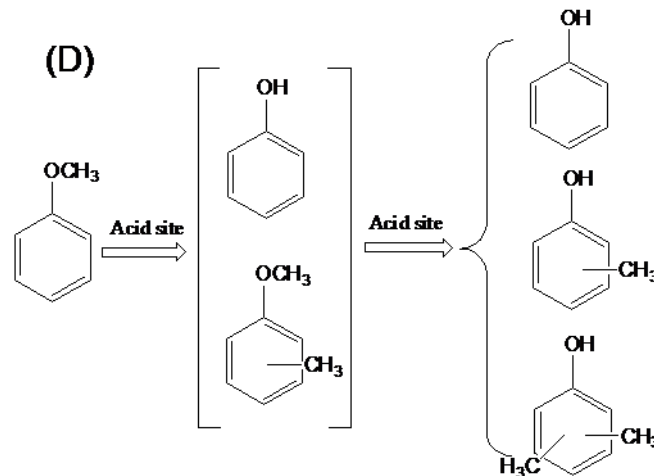
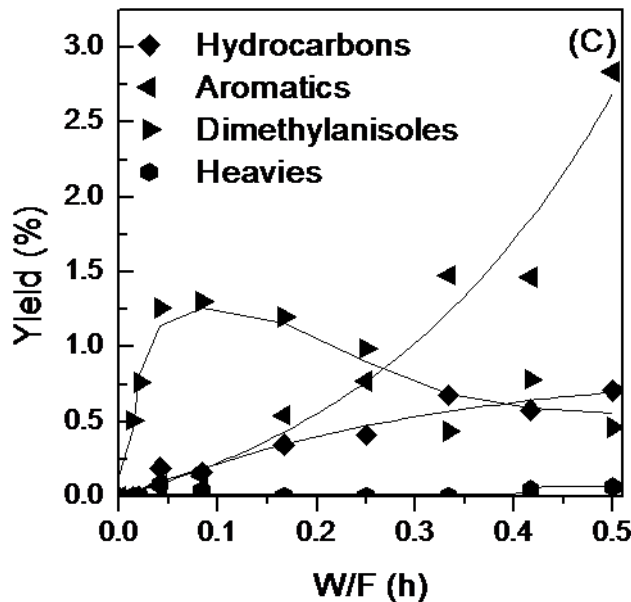
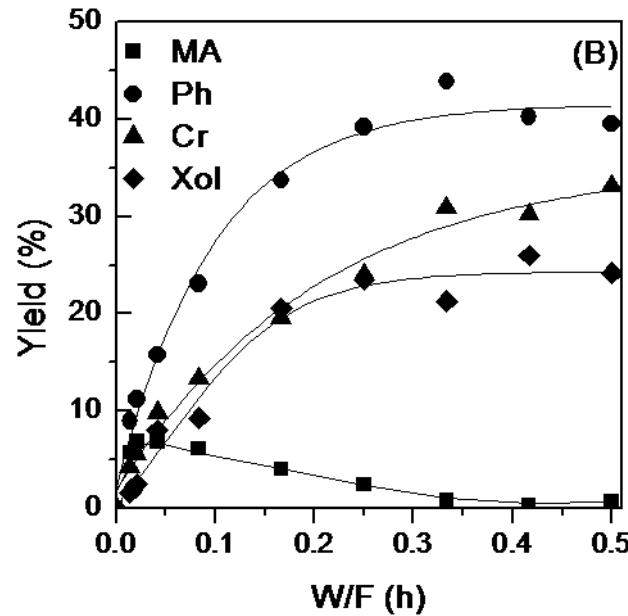
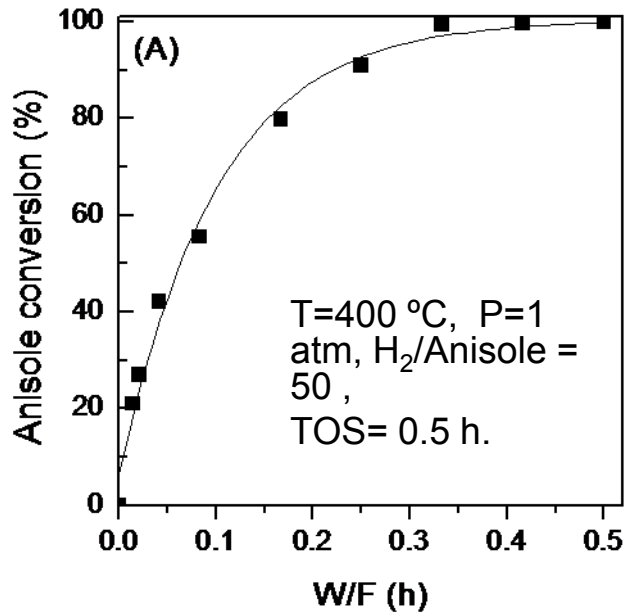
STEP 1:
Based-
catalyzed
aldol
condensation:
- MgO
nanoparticles

Importance of Phase Selectivity
To Maximize Yield

Crossley, Sen, Faria, Resasco
SCIENCE, 327, 68-72 (2010)



conversion over H-Beta yields branched oxygenates



Yield of hydrocarbons is very small.

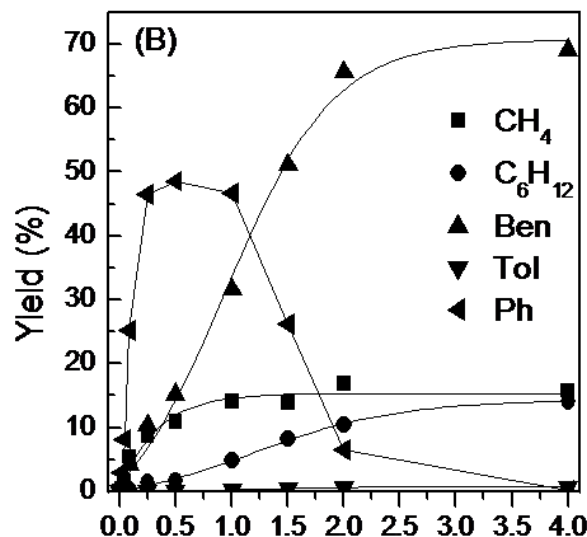
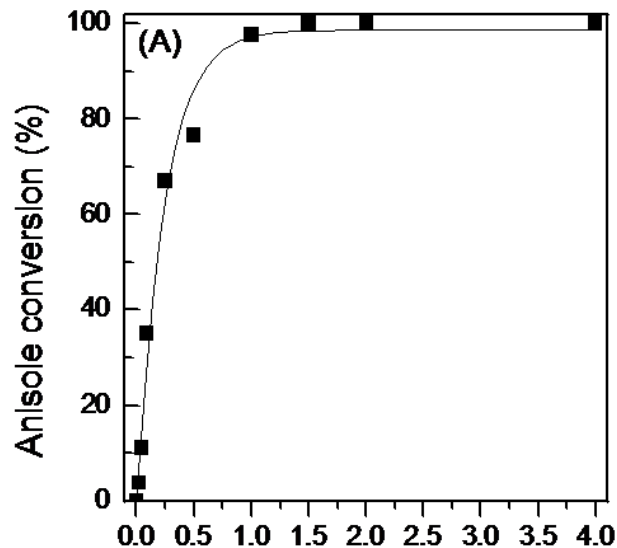
The major reaction is transalkylation alkylation.

**PHENOL
 CRESOL
 AND XYLENOL
 ARE
 DOMINANT
 PRODUCTS**

Bifunctional transalkylation and hydrodeoxygenation of anisole over a Pt/HBeta catalyst **J. Catalysis, (2011)**

X. Zhu, L. Lobban, R.G. Mallinson, D.E. Resasco

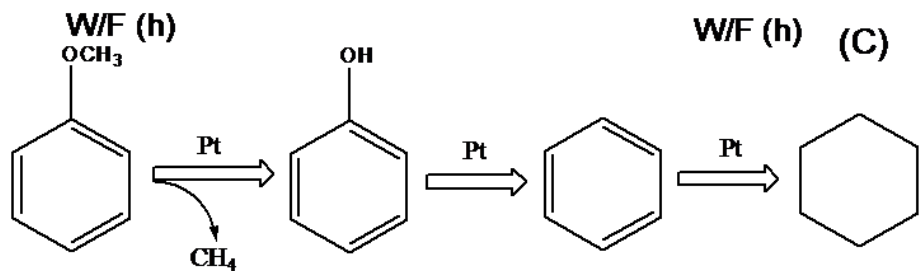
conversion over 1% Pt/SiO₂ → HDO with loss of methyl



One carbon is lost by methane formation.

Phenols is the primary product, and can be hydrodeoxygenated to benzene.

Benzene can be further hydrogenated to cyclohexane which is undesirable.



Bifunctional transalkylation and hydrodeoxygenation of anisole over a Pt/HBeta catalyst **J. Catalysis**, (2011)

X. Zhu, L. Lobban, R.G. Mallinson, D.E. Resasco



Reaction conditions: T=400 °C, P=1 atm, H₂/Anisole=50, TOS= 0.5 h.