Supported palladium catalyst structure and acidity effects on liquid phase hydrodeoxygenation

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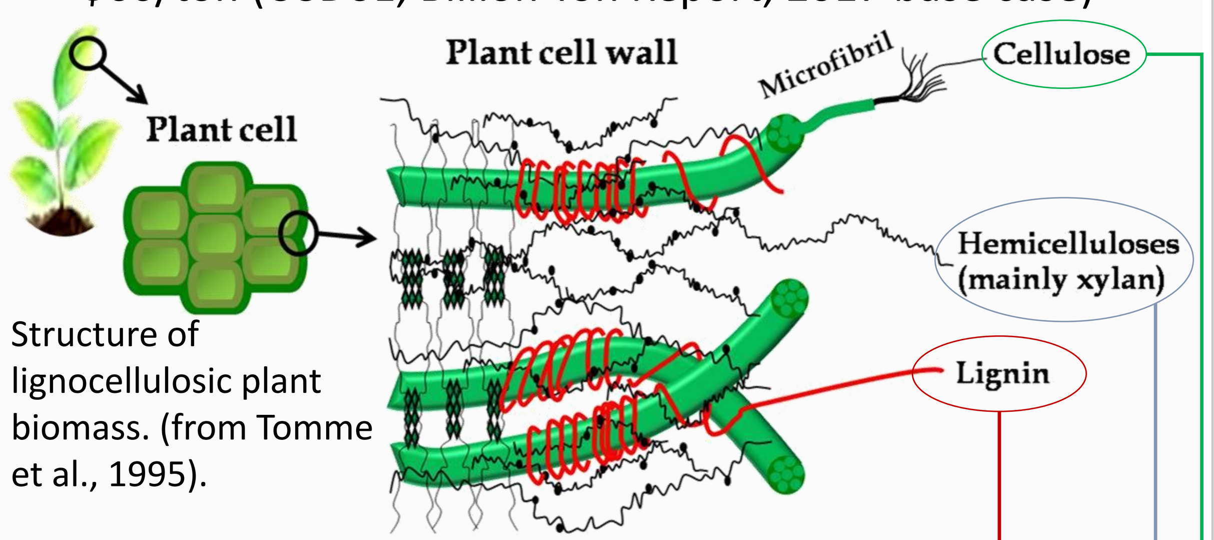
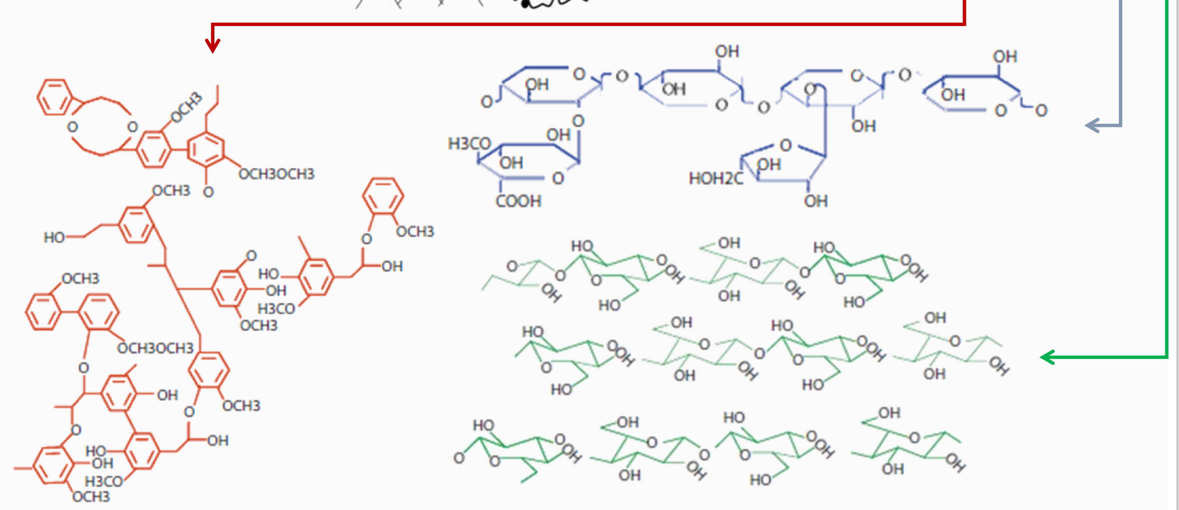
Lignocellulosic Biomass

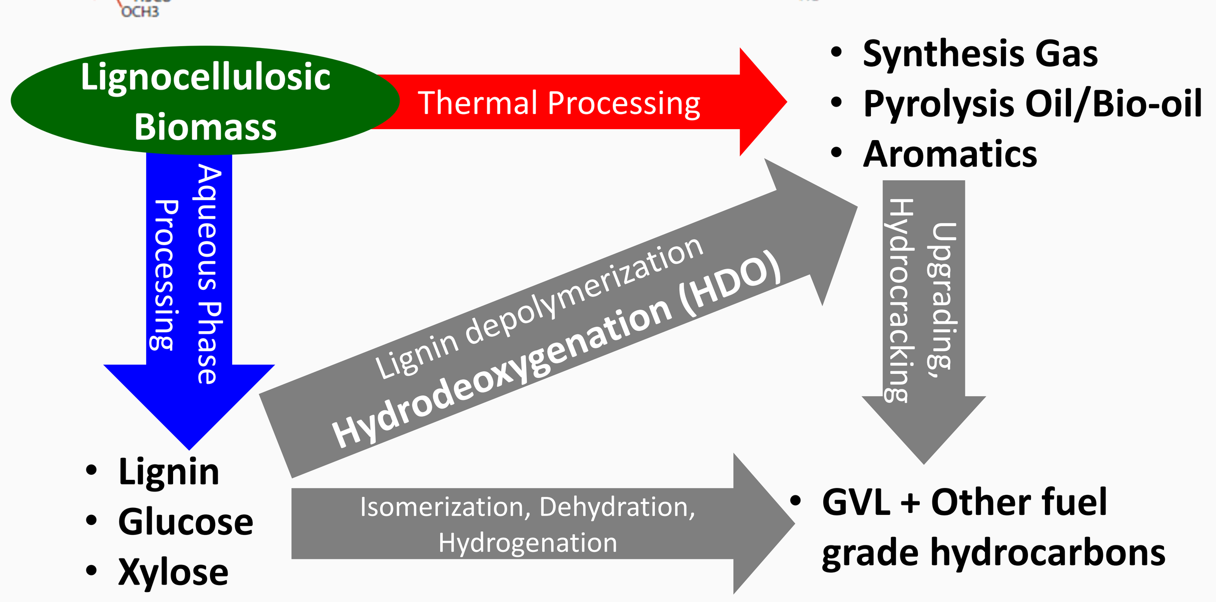
- Plant matter
- Agricultural residue (corn stover, bagasse, grass/weed clippings, straw)
- Forest byproducts
- Waste (household, food, businesses)

~ 709 million tons per year of dry biomass available at $60/ton (USDoE, Billion Ton Report, 2017 base case)



Structure of lignocellulosic plant biomass. (from Tomme et al., 1995).





- Well tuned multifunctional catalysts needed for conversion

Catalysis for Renewables: Applications, Fundamentals and Technologies (CRAFT)

PROJECT 1: Metal/ Acidic Zeolite Nanocrystals for Tandem Depolymerization/Hydrodeoxygenation of Lignin Molecules

PROJECT 2: Molecular Layer Deposition (MLD) and Metal Modified Mesoporous Silica for Lignin Depolymerization

PROJECT 3: Molecular catalysts on acidic or basic supports for lignin deconstruction

What is the effect of the Pd size, acid site density, and Zeolite crystal size on HDO?

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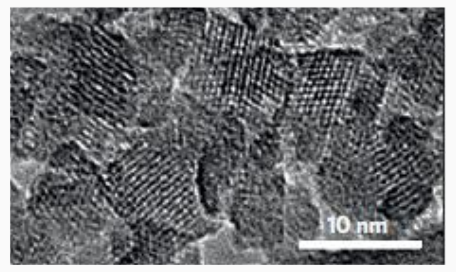
Catalyst Synthesis

- Effect of acid site density: use commercial Zeolite Y5.1, Y12, Y30, Silica KIT-6
- Effect of zeolite size: Use Y30 and NanoY
- Effect of Pd Size: Change of synthesis method



NanoY (Nano FAU) Zeolite

Effect of Acid Site Density and Metal Loading

- Ion Exchange of Pd (from $Pd(NH_3)_4Cl_2$) with promotion of Strong Electrostatic Adsorption (SEA-IE)

Zeolite	SiO_2 : Al_2O_3	Surface Area (m^2/g)	Pd loading (% w/w)	Treatment
Y5.1	5.1 : 1	730	2.5	Calc. 300°C Red. 180°C
			0.075	Calc. 300°C
Y12	12 : 1	730	2.5	Calc. 300°C Red. 180°C
			0.075	Calc. 300°C
Y30	30 : 1	780	2.5	Calc. 300°C Red. 180°C
			0.075	Calc. 300°C

Thermal treatments

- Calc. = Calcined in 20% O_2/bal.He, 250sccm
- Red. = Reduced in 20% H_2/bal.He, 250sccm

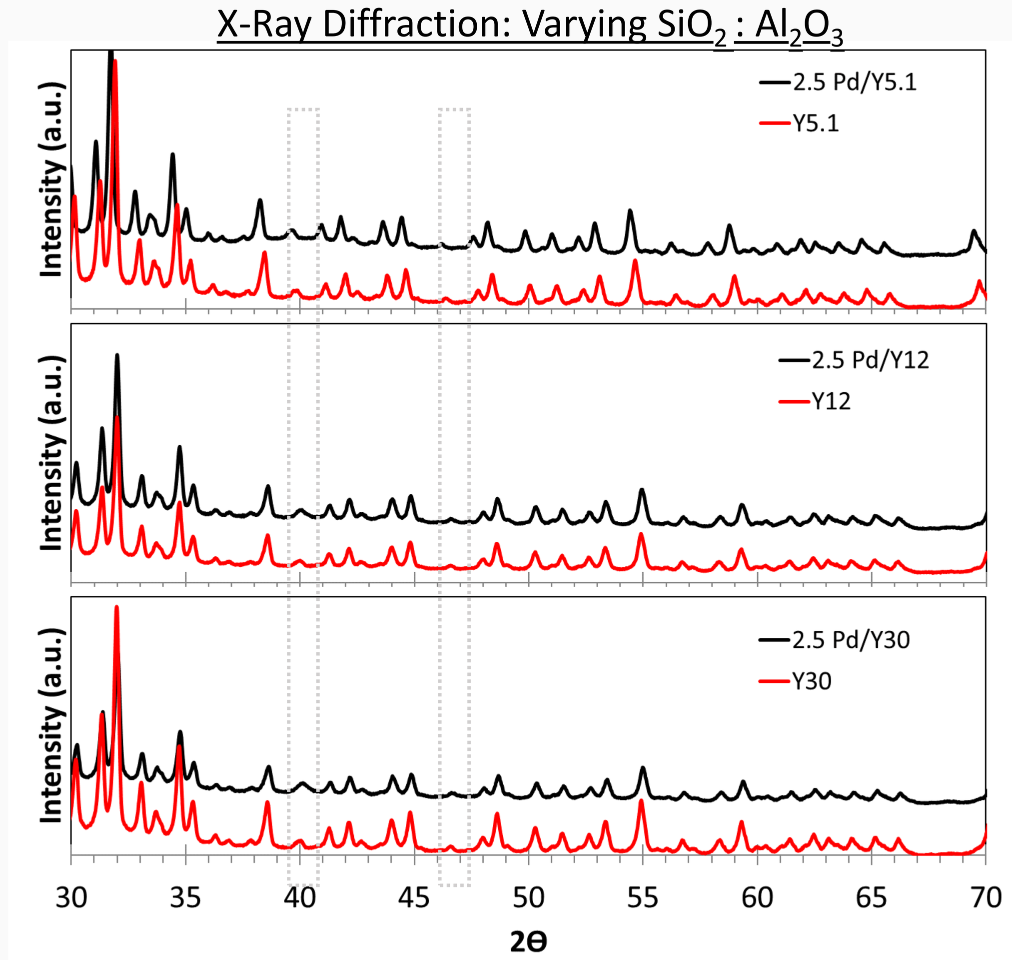
Effect of Metal Particle Size and Zeolite Crystallite Size

Target Size: 2.5 wt% Pd	SMALL D<2nm	SMALL D ~ 4 nm	LARGE D>15nm
Y30	SEA+IE, small batch Calc. 300°C Red. 180°C	SEA+IE, large batch Calc. 300°C Red. 180°C	DI Calc. 300°C Red. 180°C
NanoY		SEA+IE Calc. 300°C Red. 180°C	DI Calc. 300°C Red. 180°C
KIT-6	SEA Red. 180°C	CEDI+NaCl (NaCl:Pd = 0.25:1) Red. 180°C	DI Red. 180°C

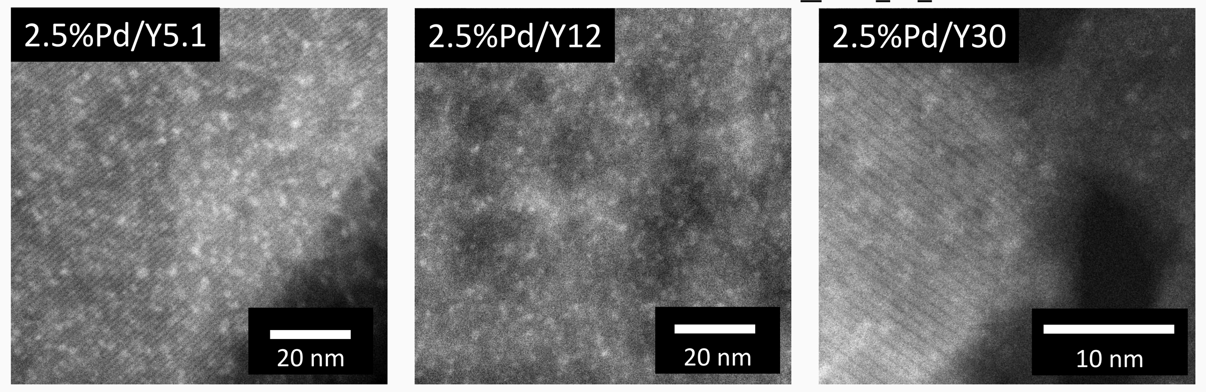
- DI = Dry Impregnation
- CEDI = Charge Enhanced Dry Impregnation, a DI variant of SEA

Catalyst Characterization

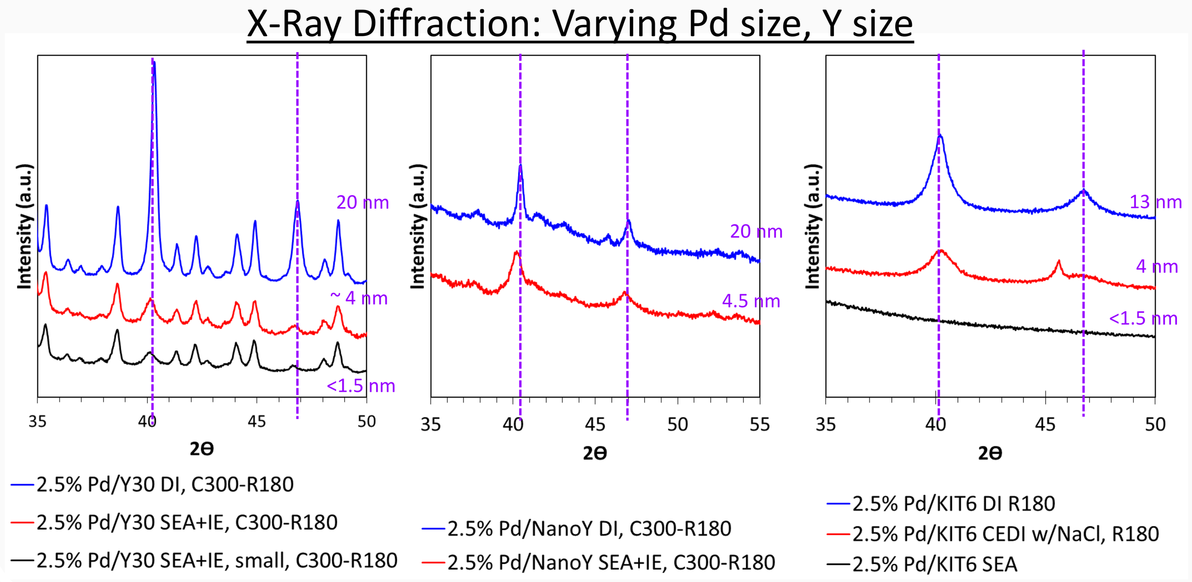
X-Ray Diffraction: Varying SiO_2 : Al_2O_3



Electron Microscopy: Varying SiO_2 : Al_2O_3

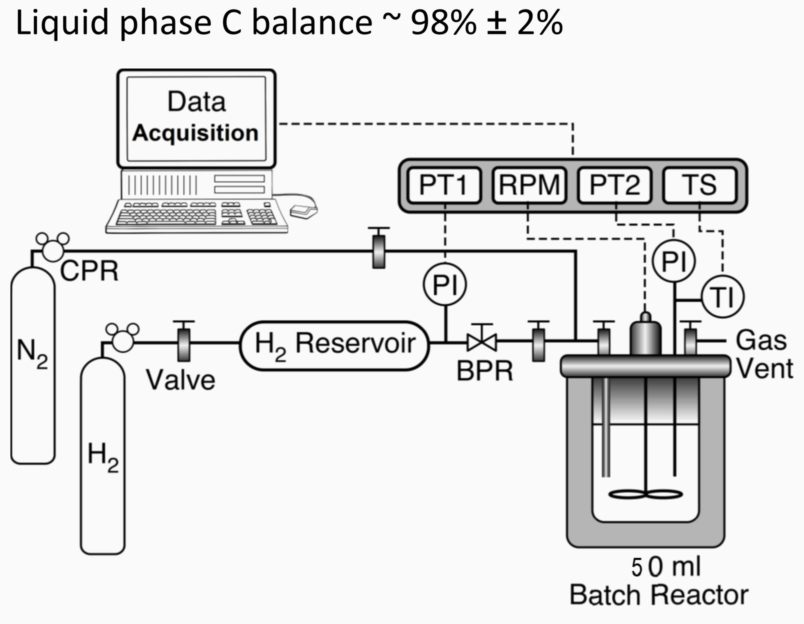


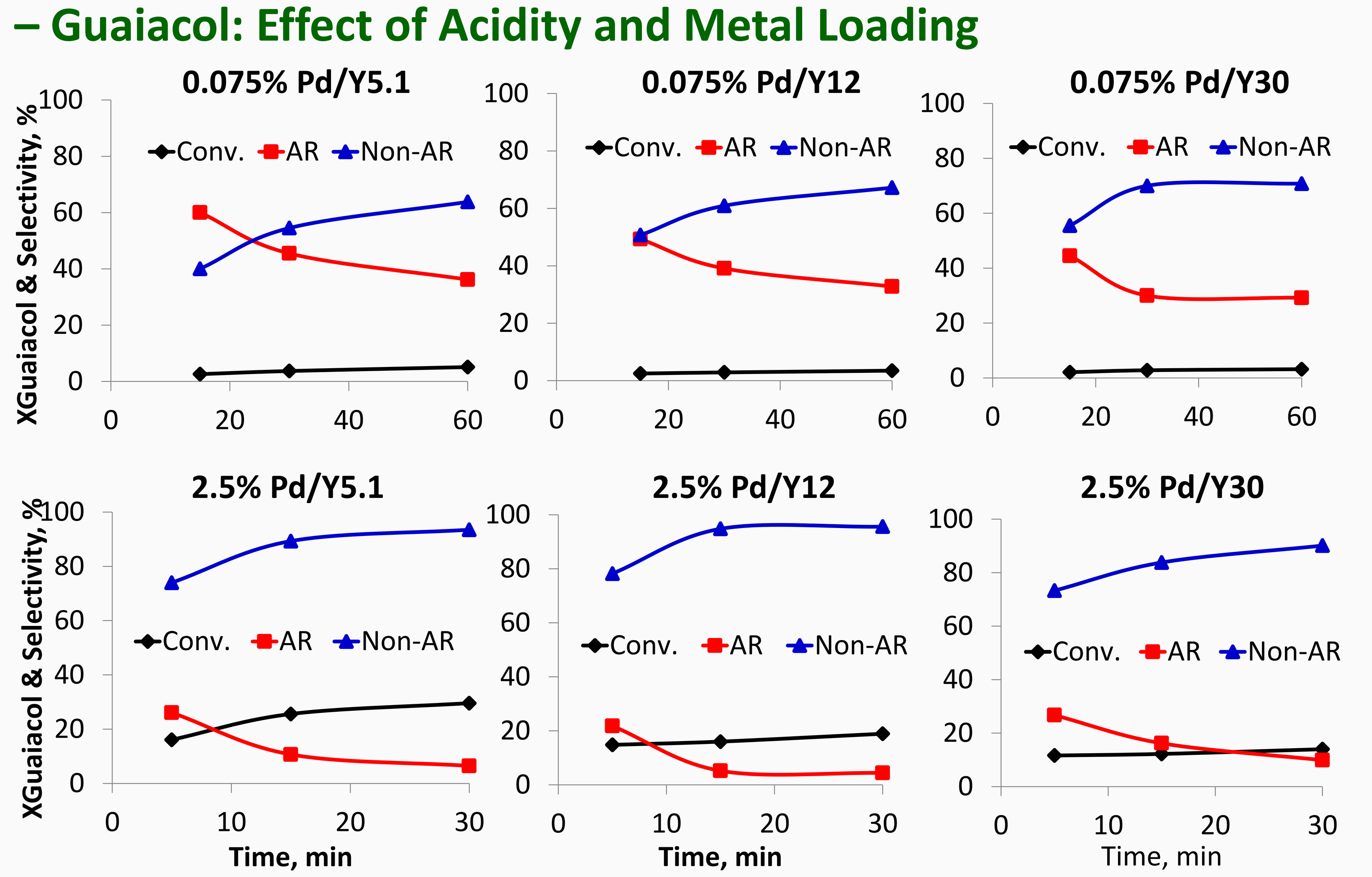
X-Ray Diffraction: Varying Pd size, Y size



HDO of Lignin Model Compound – Guaiacol: Effect of Acidity and Metal Loading

Reaction conditions: Guaiacol = 7.5 mmol (0.93 g),
Water = 20 g,
Dodecane = 200 μL (internal standard)
catalyst = 100 mg,
T = 110 °C, 900 RPM,
Initial H_2 partial pressure/Total P(psi) ~180/225
Liquid phase C balance ~ 98% ± 2%





- At similar support acidity, low Pd loading (0.075 wt %) favors aromatic selectivity (~60% maximum) than high loading (2.5 wt %).
- Higher Pd loading (2.5 wt %) favors ring hydrogenated (Non-AR) over aromatic (AR) products.

HDO of Guaiacol: Control Experiments

Catalyst Name	SiO_2/Al_2O_3	Reaction Time (min)	Conversion (%)	Selectivity (%) AR	Selectivity (%) Non-AR	Acidity mmol/g
Base treated Y Calcined at 500°C	5.1	30	No rxn	-	-	1.35
	12	30	No rxn	-	-	0.92
	30	30	No rxn	-	-	0.65
0.075 % Pd/Y	5.1	15	2.6	60.0	40.0	1.37
0.075 % Pd/KIT-6	-	15	3.5	22.8	77.2	NM

- Aromatic products are favored on acidic supports

HDO of Benzyl Alcohol – Effect of Pd particle size, Acidity, and Zeolite Y size

Reaction Condition: Benzyl alcohol = 22.4 mmol, External standard = 200 μL dodecane, Solvent (H_2O) = 20 ml, Reaction temperature 110 °C, H_2 partial pressure = 90 psi, Catalyst, 25 mg, 1100 rpm, Reaction hour 30 minutes. Carbon balance= 98 -99.9 %. H_2 consumption from external reservoir.

Activity of BZOH HDO on 2.5%Pd/KIT-6

Catalyst: 2.5%Pd/KIT-6	Time, min	Conv., % GC, H_2	Selectivity, % Deoxygenated	Selectivity, % Oxygenated	Selectivity, % Others
<1.5 nm	30	No- activity			
4 nm	30	26.0 (26.8)	96.5	3.4	0.1
13 nm	30	25.6 (26.2)	93.8	6.1	0.1

- The similar HDO activity of reaction data indicate that within the KIT-6 support, there is no Pd particle size effect.
- Pd particles maybe all on the external surface.

Activity of BzOH HDO on 2.5%Pd/Y30

Catalyst: 2.5%Pd/Y30	Time, min	Conv., % GC, H_2	Selectivity, % Deoxygenated	Selectivity, % Oxygenated	Selectivity, % Others
<1.5 nm	30	26.2 (25.6)	95.6	3.3	1.1
4 nm	30	27.0 (27.2)	96.8	3.1	0.1
20 nm	30	28.4 (26.8)	92.1	7.4	0.5

Activity of BzOH HDO on 2.5%Pd/NanoY

Catalyst: 2.5%Pd/NanoY	Time, min	Conv., % GC, H_2	Selectivity, % Deoxygenated	Selectivity, % Oxygenated	Selectivity, % Others
4 nm	30	5.1 (4.4)	92.4	7.5	0.1
20 nm	30	3.6 (2.3)	96.1	3.8	0.1

- No observed particle size effect on Pd/Y30 samples for BzOH HDO.
- NanoY supported catalysts have lower activity, due to rapid deactivation.
- Higher external surface area may have caused coking, resulting in deactivation of NanoY catalysts.
- Increased acidity may have a role in deactivation (NanoY SiO_2/Al_2O_3 ~ 2:1). However, Y5.1 support did not show similar deactivation in earlier experiments.

Summary and Conclusions

- Pd catalysts on acidic (Y Zeolite) and neutral (KIT-6) supports were made and Pd size and loading were effectively varied
- Effects of acidity, particle size, loading, and support crystallite size (external surface area) were studied for Guaiacol and Benzyl Alcohol HDO.
  - ➢ Lower metal loading favored aromatic selectivity at the expense of activity.
  - ➢ Higher acidity favored aromatic products.
  - ➢ No observed particle size effect for BzOH HDO.
  - ➢ Larger external surface on acidic support may lead to rapid deactivation.

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