Co-Optimization of Fuels & Engines

NATIONAL RENEWABLE ENERGY LABORATORY

Conversion, stability, and selectivity improvements through catalyst development for the reductive etherification reaction

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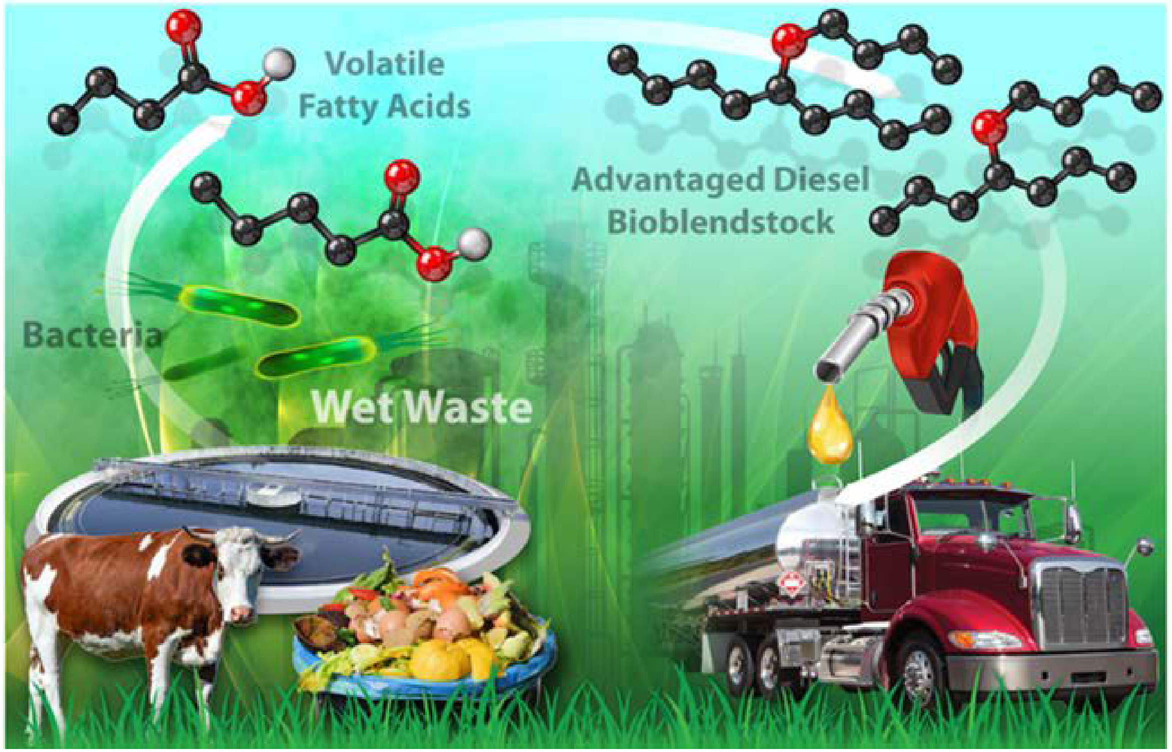
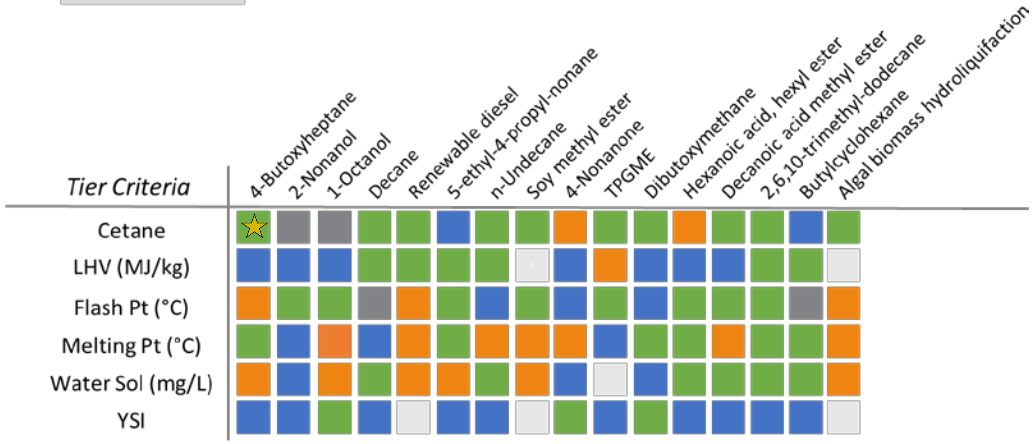
ACS Fall 2019 National Meeting
Division of Catalysis Science and Technology,
San Diego, CA
August 27th, 2019

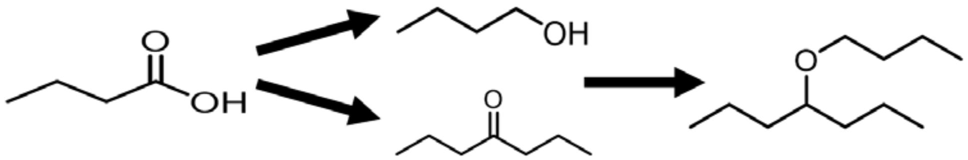
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Waste-to-biofuel upgrading



Tier Criteria	Greatly Exceeds	Exceeds Criteria	Meets Criteria	Barriers Exist
Cetane	> 50	46 to 50	40 to 45	< 40
LHV (MJ/kg)	> 40	31 to 40	25 to 30	< 25
Flash Pt (°C)	> 70	61 to 70	52 to 60	< 52
Melting Pt (°C)	< -50	-50 to -26	-25 to 0	> 0
Water Sol (mg/L)	< 5	5 to 501	500 to 1000	> 1000
YSI	< 50	50 to 151	150 to 200	> 200

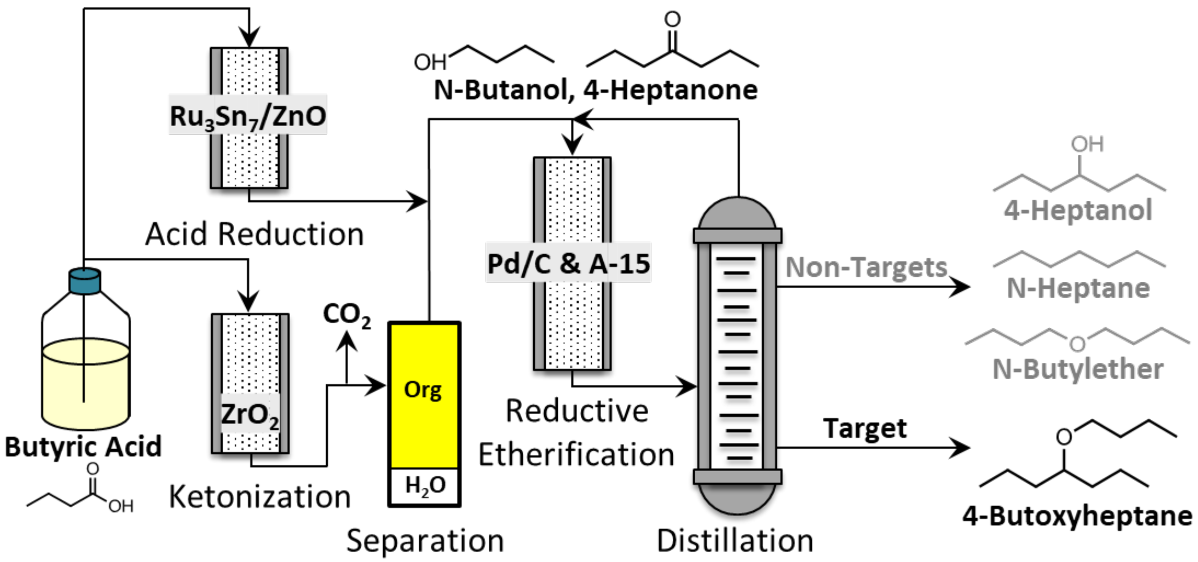


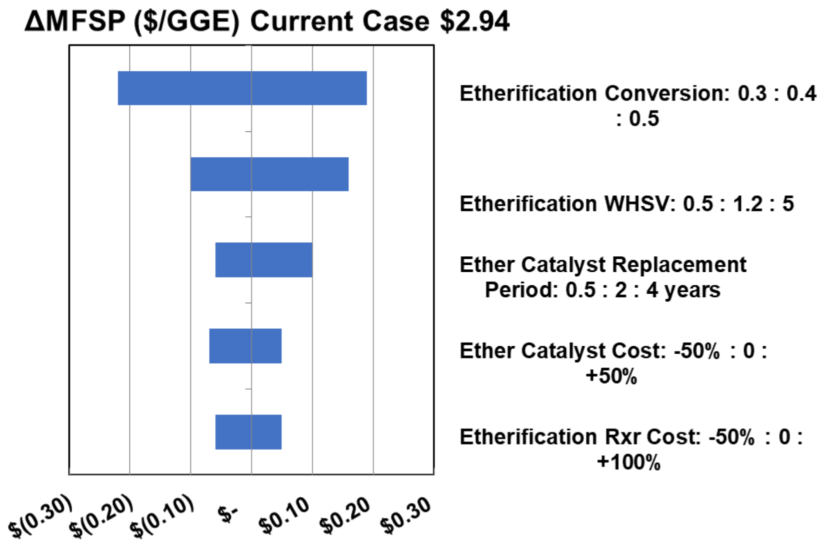


4-butoxyheptane

Goal of upgrading low or negative cost feedstocks into targeted bioblendstocks

Ether production process

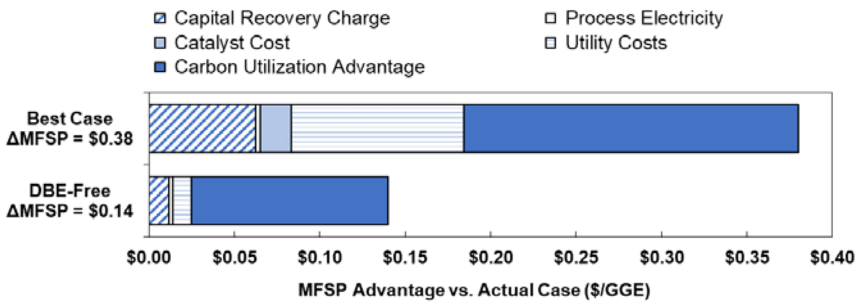




Tornado plot showing impact of various sensitivities on MFSP for the "Current Case."

Iteration on technoeconomic analysis (TEA):

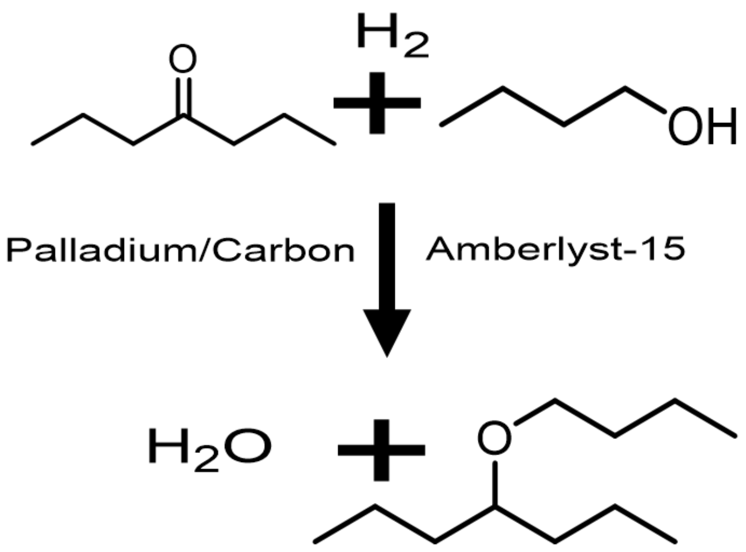
- Major TEA cost drivers include conversion, space velocity, selectivity-specifically dibutyl ether (DBE)
- Assumptions on catalyst stability and regenerability



Cost comparison for DBE-Free (neglecting dibutyl ether formation) and Best Case (100% selectivity to the target) scenarios relative to the experimentally based Current Case analysis.

Collaboration with TEA shows cost drivers and critical assumptions

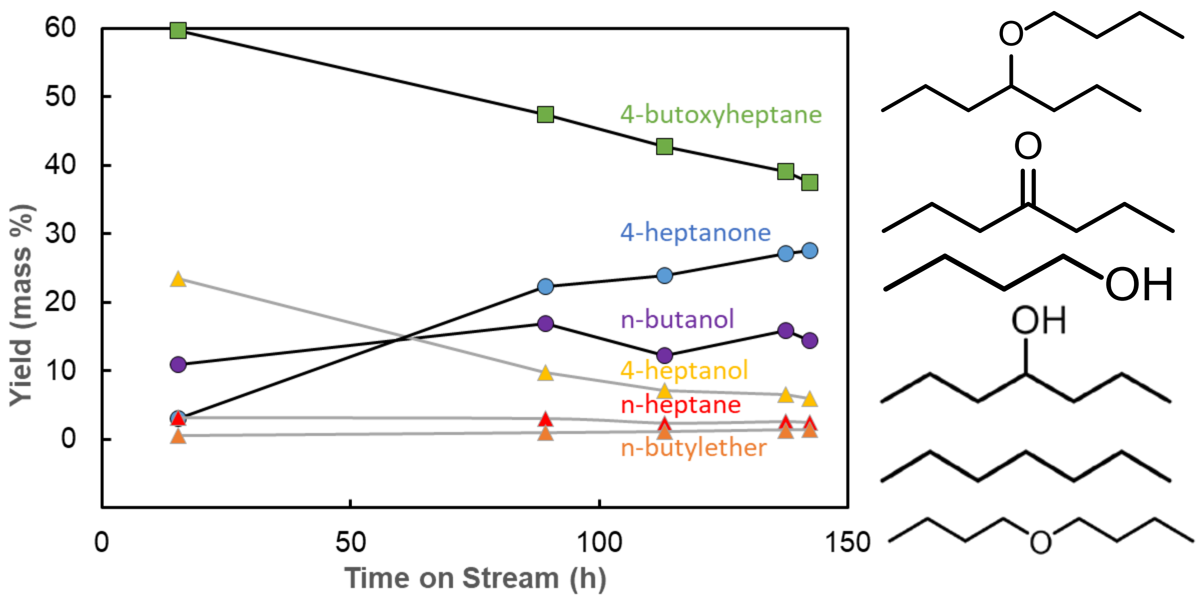
Reductive etherification



Dual Catalyst System:

- Pd expected to be fairly stable
- Solid acids are known to absorb water and deactivate
- Side reactions on acidic surfaces can form inhibitory coking

Continuous flow reaction:

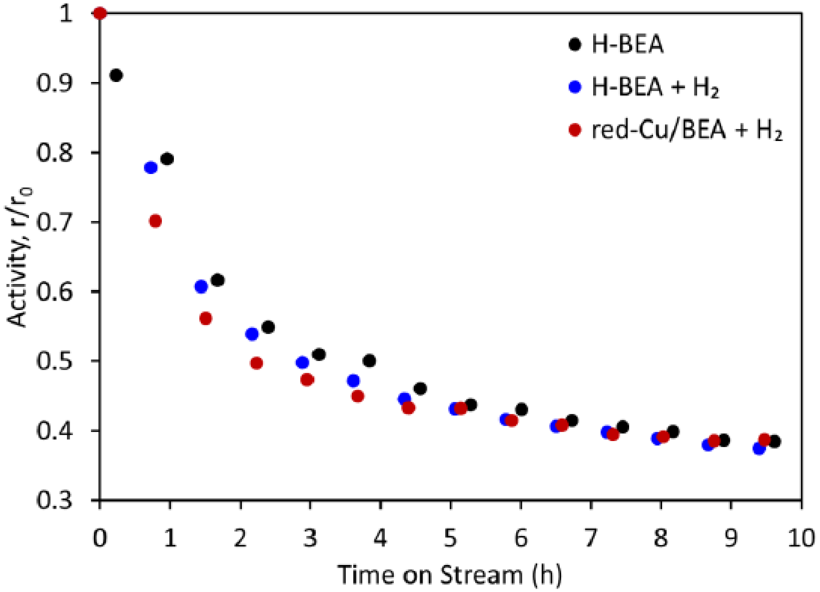


Continuous flow test: 0.25 mL/min of equimolar 4-heptanone & n-butanol, 2.2 g Pd/C, 6.6 g A-15, 120 °C, 1000 psig H_2 (3-4 fold excess)

Continuous flow reaction seems to show catalyst deactivation

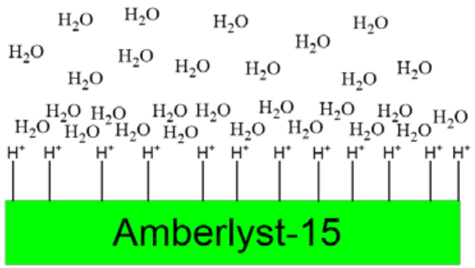
Solid acid deactivation

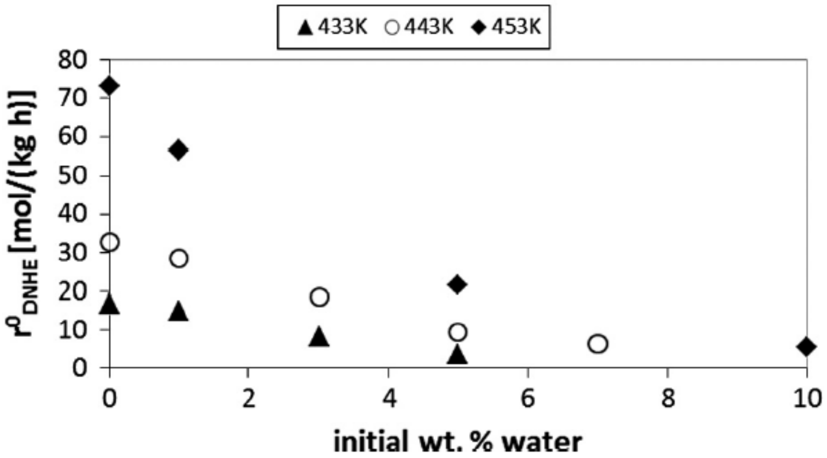
Carbon deposition:



Decrease in reaction rate of dimethylether over zeolite-based catalysts
ACS Catalysis **2015**, 5, 1794−1803

Water adsorption:

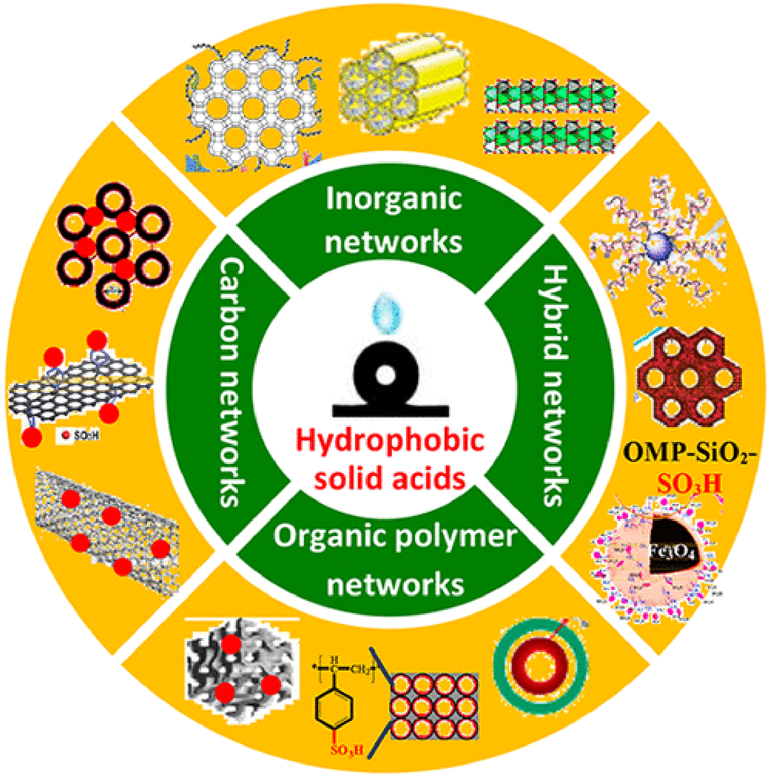




Comparison of initial etherification rate and water concentration over Amberlyst-70
Chemical Engineering Journal **2014**, 246, 71–78

Deactivation can occur through carbon deposition or water adsorption

Tailored solid acids



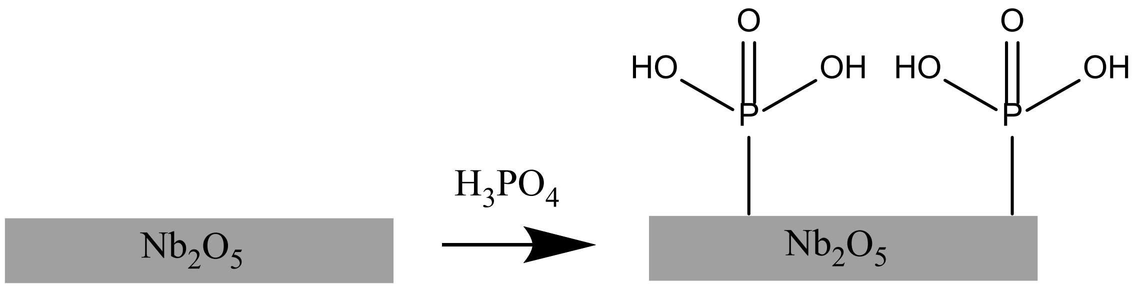
ACS Catal., **2018**, *8* (1), pp 372–391

Overall goal:

- Improved aqueous stability
- Improved thermal stability
- High acid site density
- Low cost materials

Phosphated metal oxides:

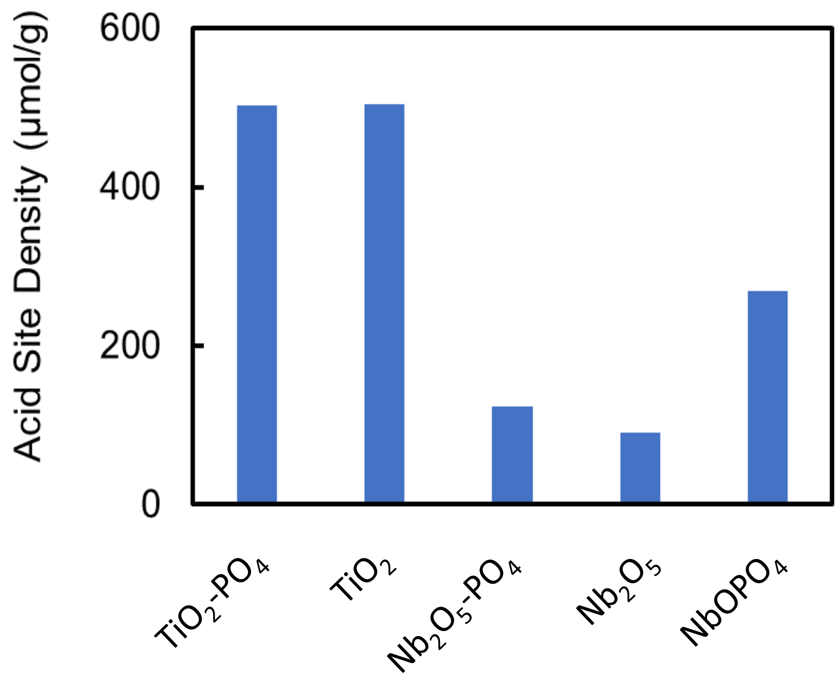
- Reported to be water-tolerant
- Thermally stable
- Varied acidities and material costs



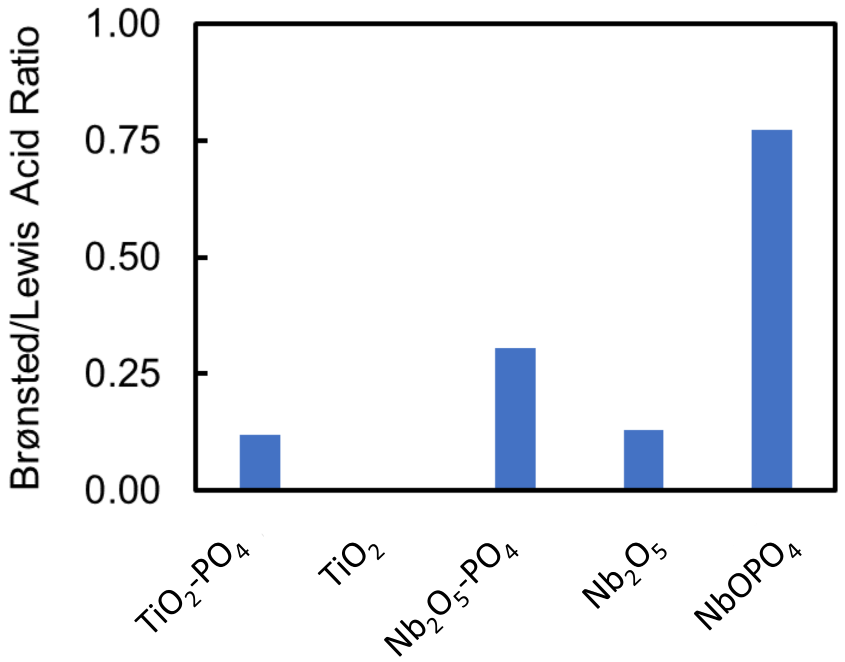
Metal oxide surface modification with phosphoric acid

Water-tolerant acids could lead to increased stability and facile regenerability

Acidity characterization



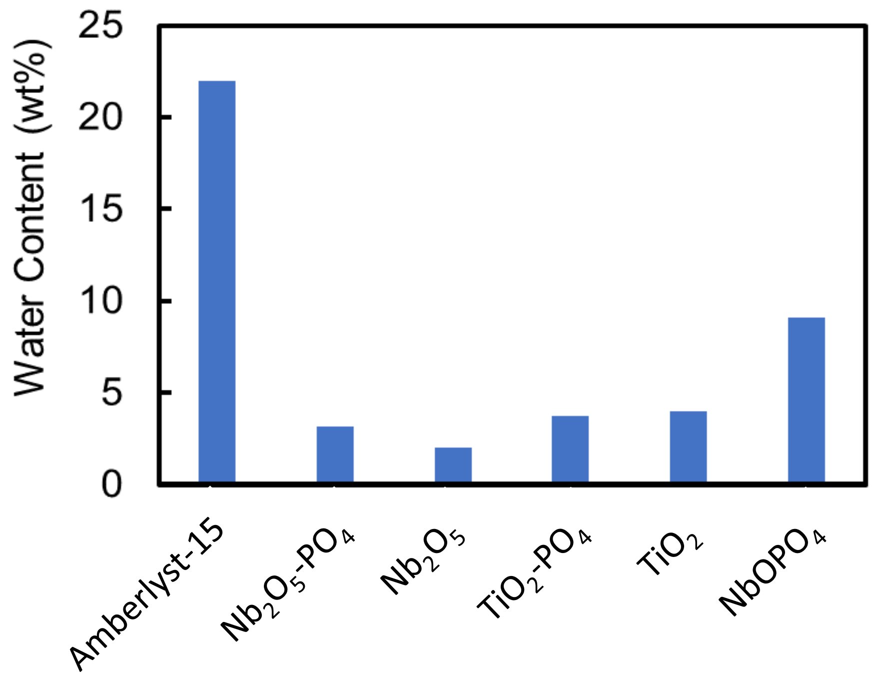
NH$_3$-TPD results for total acidity measurements (Amberlyst-15 reported to be 4600 µmol/g)

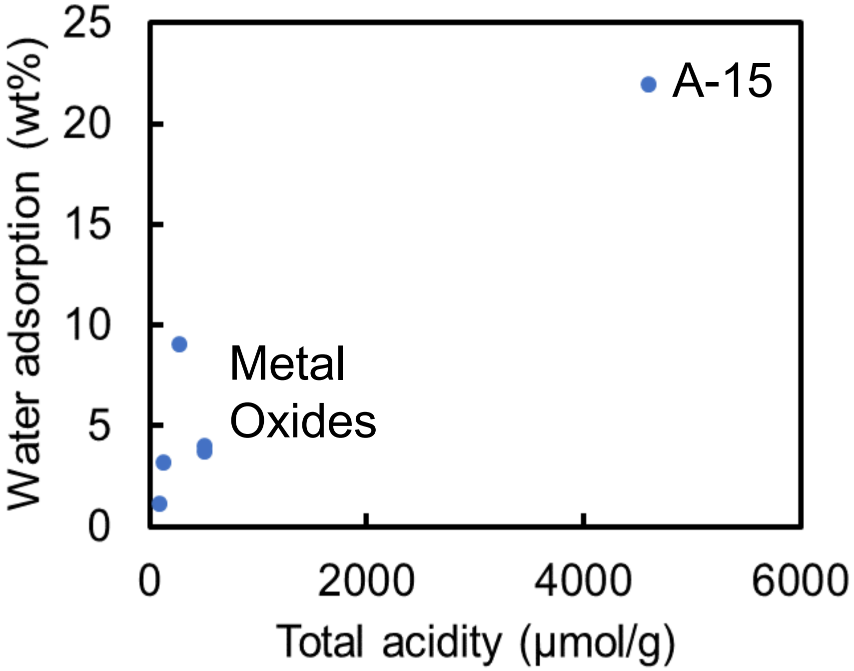


Pyridine-DRIFTS spectra showing the relative amounts of Brønsted and Lewis acid sites.

Phosphating procedure increases Brønsted/Lewis ratio and possibly total acidity

Hydrophobicity evaluation





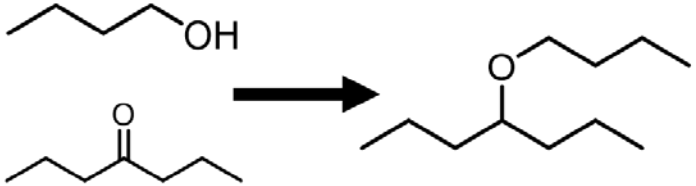
Thermogravimetric analysis of catalysts after treatment in saturated water chamber for 72 h.

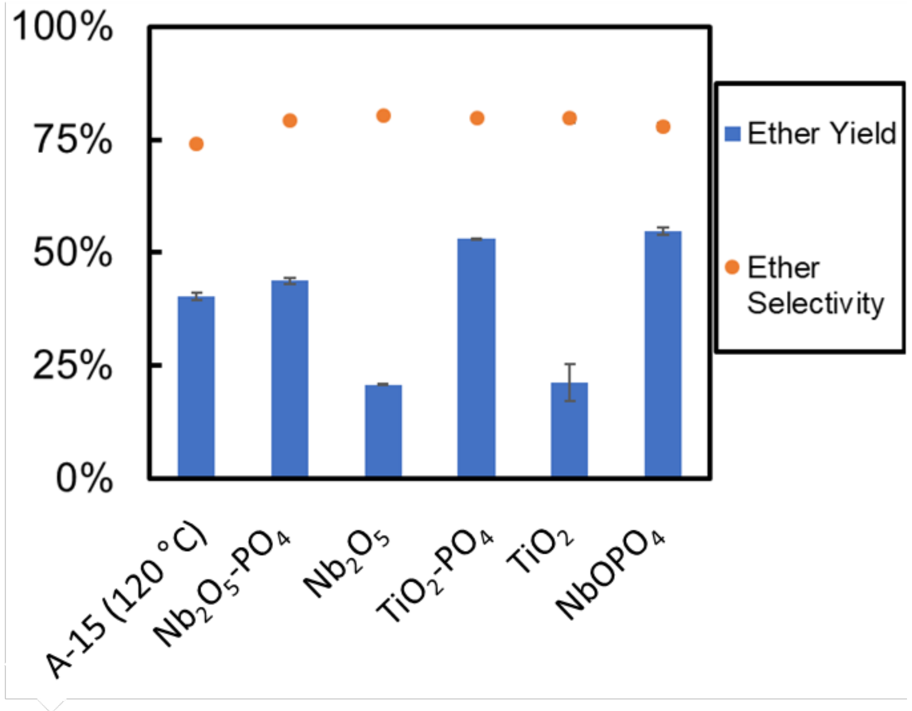
Little effect on acidity vs. hydrophobicity but reported to maintain catalytic efficiency

Acidity and water adsorption results show little change in hydrophobicity

Metal oxide batch testing

High-pressure batch reactors



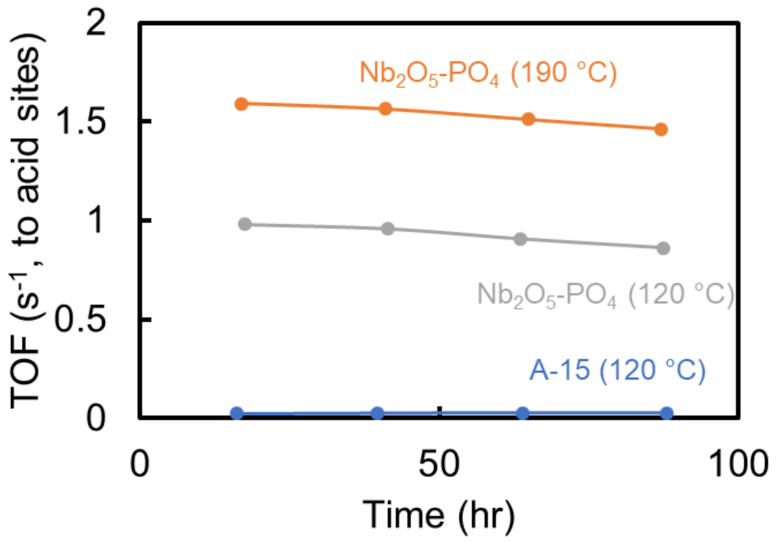


20 mL equimolar 4-heptanone & n-butanol, 231 mg Pd/Carbon, 681 mg solid acid, 120 or 190 °C, 1000 psig H_2,1 h.

Increasing temperature improves ether yield and selectivity but A-15 is limited

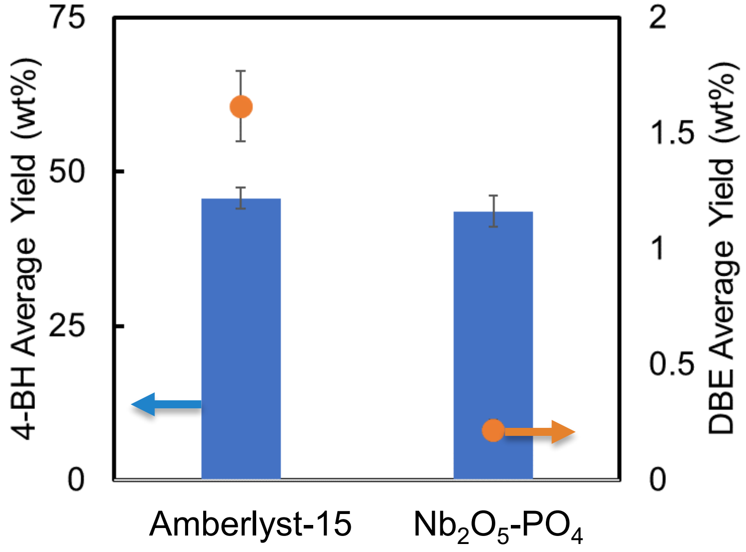
Flow reaction tests

C3PO: a high-pressure trickle bed flow reactor



Significantly higher turnover (to acid sites) from metal oxide catalysts

Metal oxide stability was roughly double of the previous A-15 run

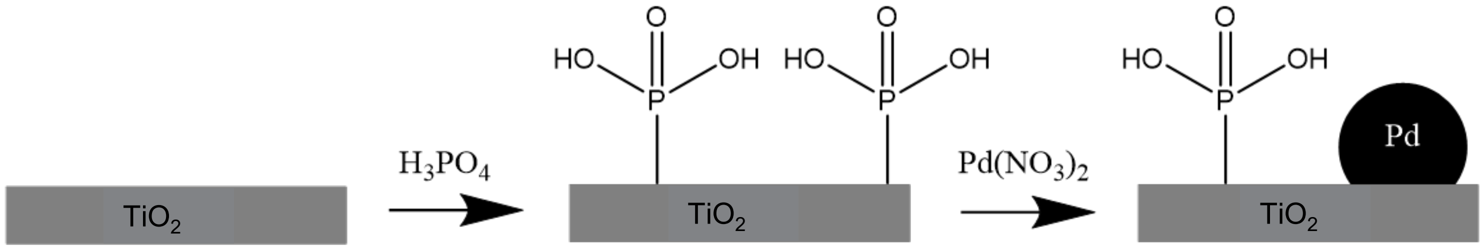


Increase in 4-BH Yield of 5%, increase in DBE yield of 7.5-fold

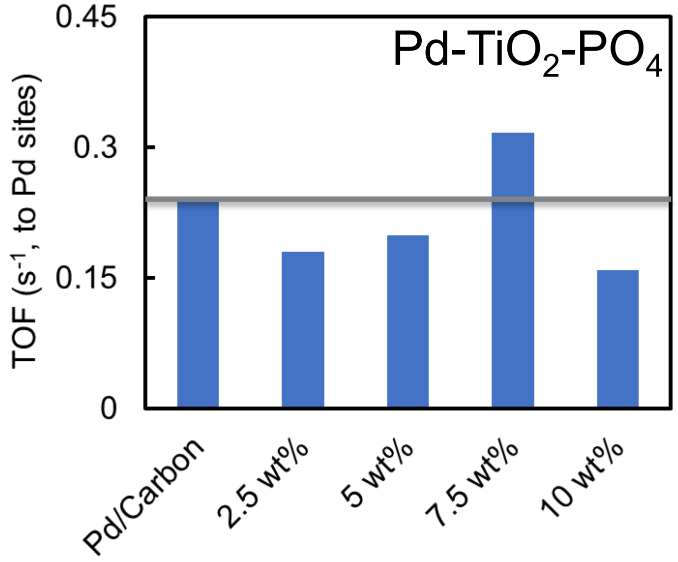
0.05 mL/min of equimolar 4-heptanone & n-butanol,
0.5 g Pd/C, 1.5 g acid catalyst, 1000 psig H_2

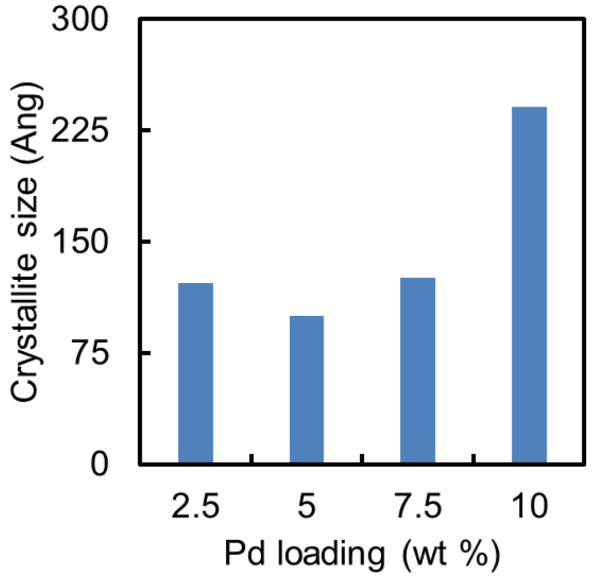
Preliminary flow tests show increased turnover and selectivity to diesel targets

Single-phase catalyst



Incipient wetness deposition of Pd onto metal oxides





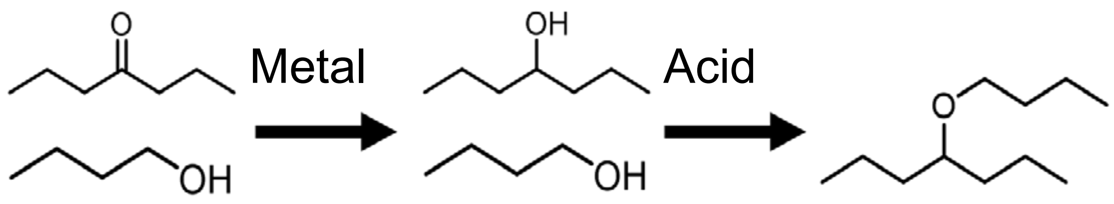
20 mL equimolar 4-heptanone & n-butanol, 231 mg Pd/Carbon, 681 mg solid acid, 1000 psig H_2, 1 h.

Pd crystallite size from X-Ray Diffraction spectroscopy using FWHM of 40° Pd peak

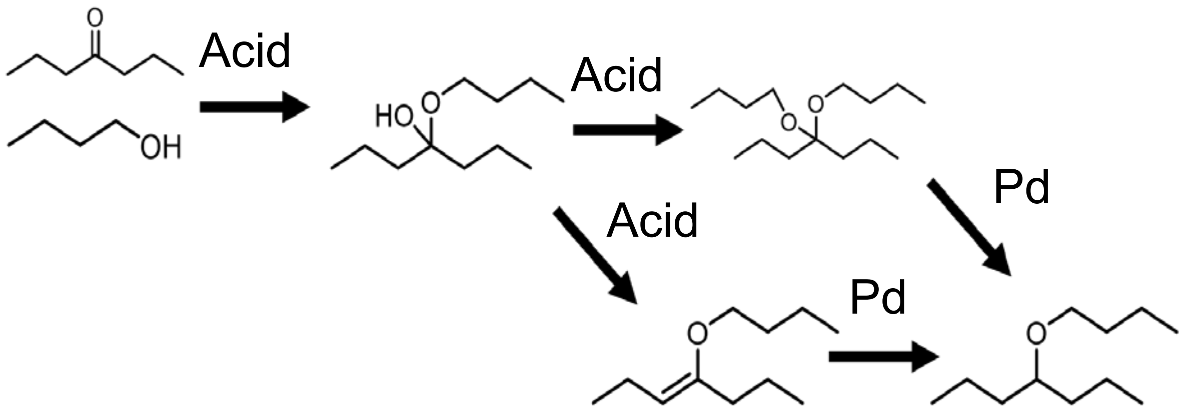
Single-phase catalysts show superior results in batch testing

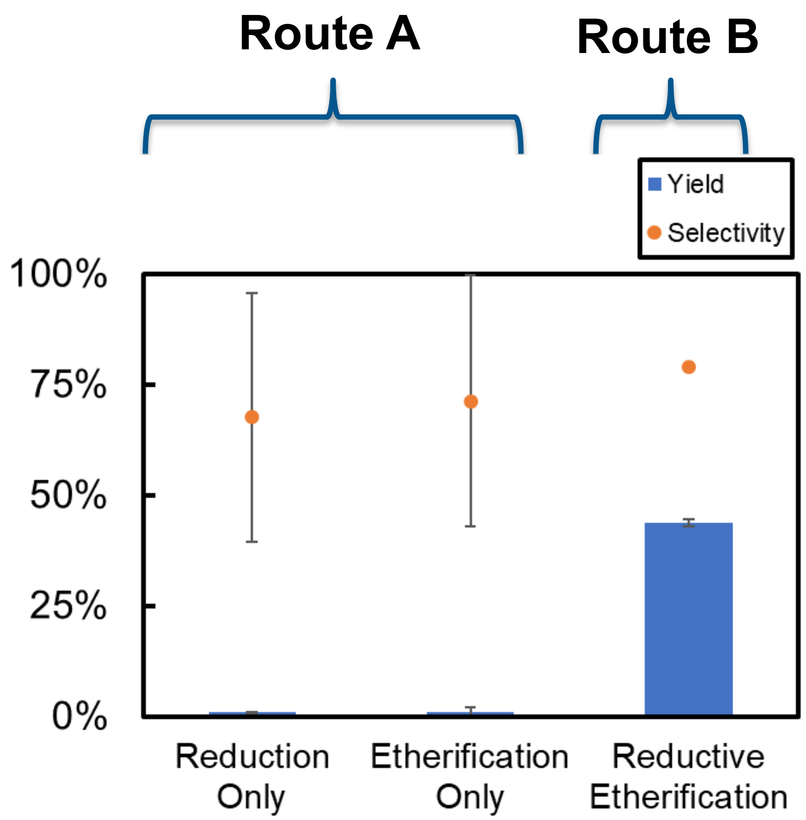
Reaction pathway

Route A: Reduction, then etherification



Route B: Ketalization, then etherification



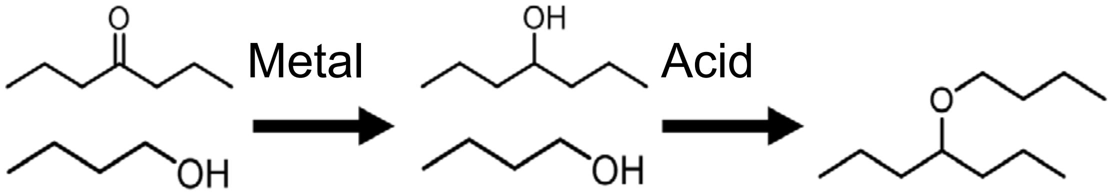


20 mL equimolar 4-heptanone (or 4-heptanol) & n-butanol, 231 mg Pd/Carbon, 681 mg solid acid, 1000 psig H_2 (or He), 1 h.

Reaction seems to proceed through ketalization pathway of reductive etherification

Reaction pathway

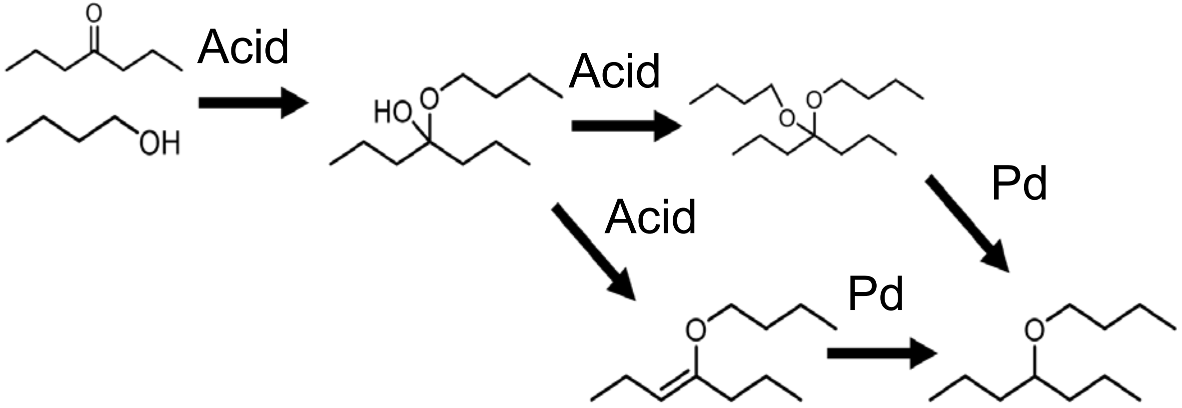
Route A: Reduction, then etherification



Metal & Acid:

Applied Catalysis A: General **2000**, 191,153–162
Catalysts **2015**, 5 (4), 2244-2257
Green Chemistry **2018,** *20* (5), 1095-1105
Applied Catalysis B: Environmental **2019,** *258*, 117793
Energy Technology **2019,** *7* (5), 1801071
Etc.

Route B: Ketalization, then etherification



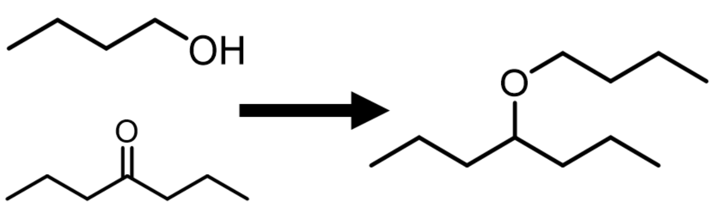
Palladium & Acid:

Tetrahedron Letters, **1995**, 36 (24), pp. 4235-4236
Journal of Molecular Catalysis A: Chemical **2000,** *152* (1-2), 133-140.
Bulletin of the Chemical Society of Japan **2005,** *78* (3), 456-463
Synlett **2006,** 20, 3489-3491.
***Green Chem.,* **2012**, 14, 1626
ACS Sustainable Chem. Eng. **2016**, 4, 4089−4093
ChemSusChem **2017**, 10, 2527 – 2533
Green Chemistry **2018,** *20* (9), 2110-2117
ChemSusChem **2018,** *11* (21), 3796-3802
RSC Advances **2019,** *9* (44), 25345-25350

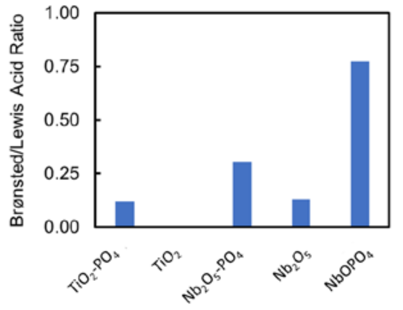
Palladium is heavily favored for acetal/ketal pathway of ether formation

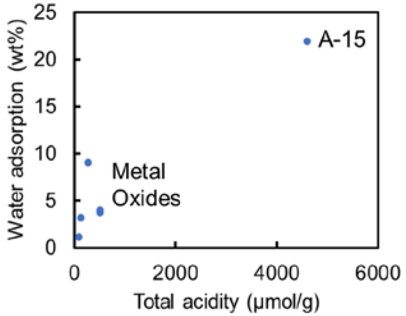
Key takeaways

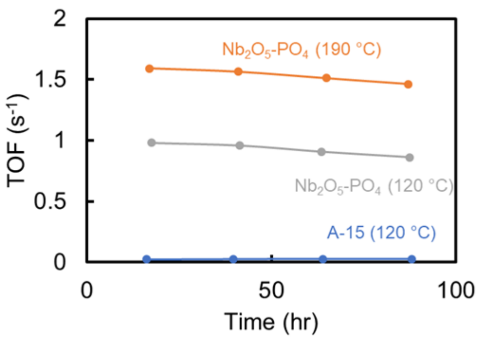
Reductive etherification for targeted bioblendstocks

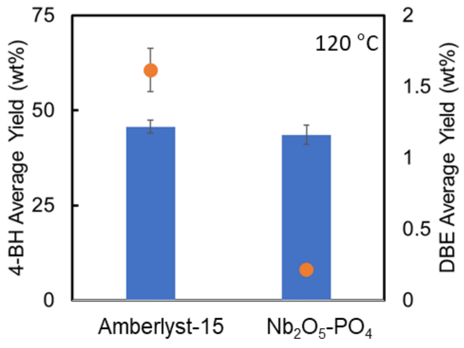


- Phosphated metal oxides show increased Bronsted acidity but similar hydrophobicity

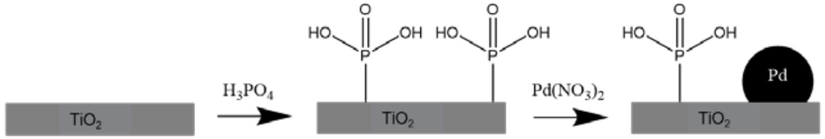




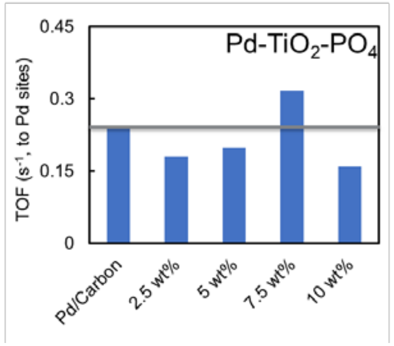




- Nb_2O_5-PO_4 shows increased turnover and selectivity in flow reaction tests



- Palladium-deposited onto TiO_2-PO_4 at 7.5 wt% shows optimized yields enabling stronger regeneration conditions



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