ChemCatBio
Chemical Catalysis for Bioenergy

Improving Process Durability by Addressing Catalyst Deactivation During Upgrading of Biomass Pyrolysis Vapors

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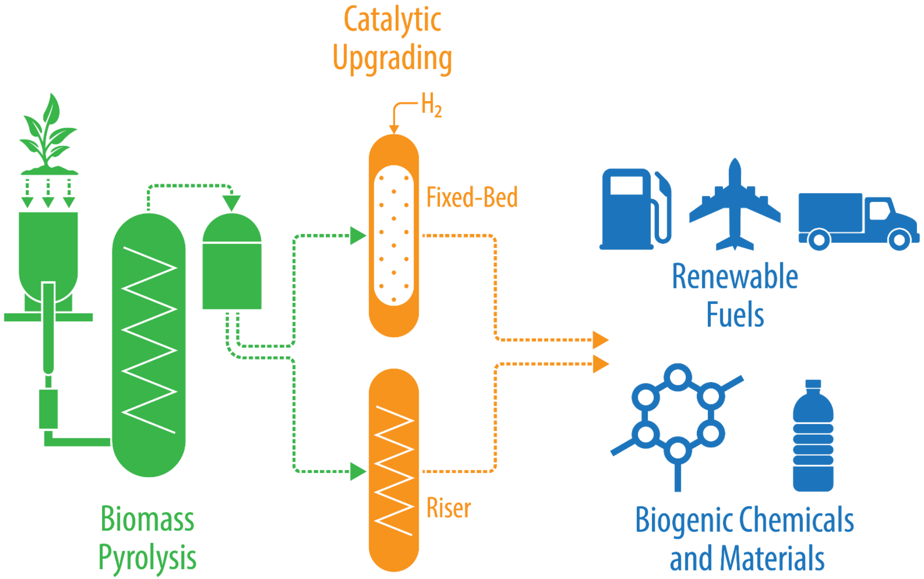
U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Overview

Target Outcome:
Accelerate pathways for the production of distillate-range fuels via catalytic pyrolysis and hydroprocessing

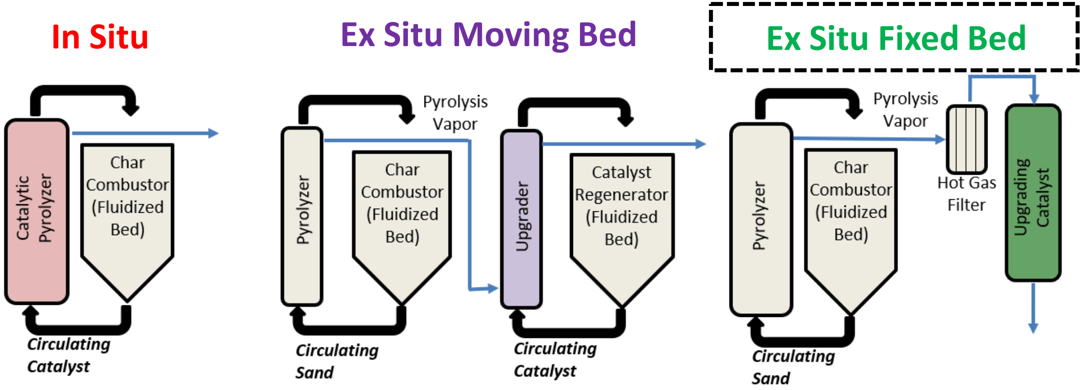
Forest Resources and Woody Wastes	133 Million Dry Tons/Yr	8 BGPY Hydrocarbon Fuel

Sanderson, K., Nature, 2011, 474, S12-S14
2030 Estimates for DOE Billion Ton Report



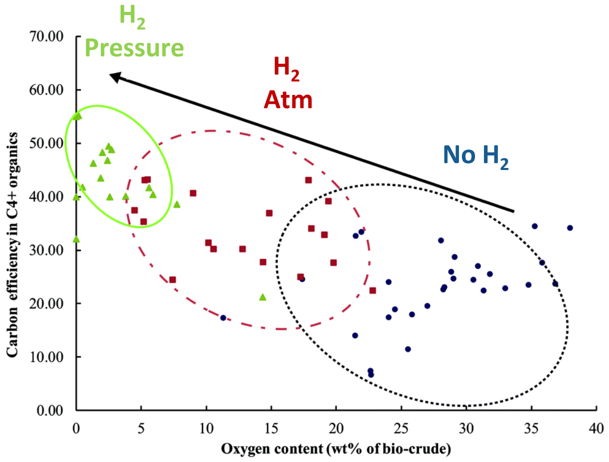
Previous Research

Approaches to CFP have utilized several different catalysts, conditions, and reactor configurations



Low Capex Requirements	**Controlled Upgrading Environment**	**Greater Diversity of Accessible Catalyst and Chemistries**
Harsh Upgrading Environment	**Higher Capex Required**	**Longer Catalyst Lifetime Required**

Co-fed hydrogen can increase carbon yield and reduce bio-oil oxygen content



This research was performed using co-fed hydrogen at atmospheric pressure

K. Wang, et al., *Green Chem.*, 19, 2017

Feedstocks and Reaction Conditions

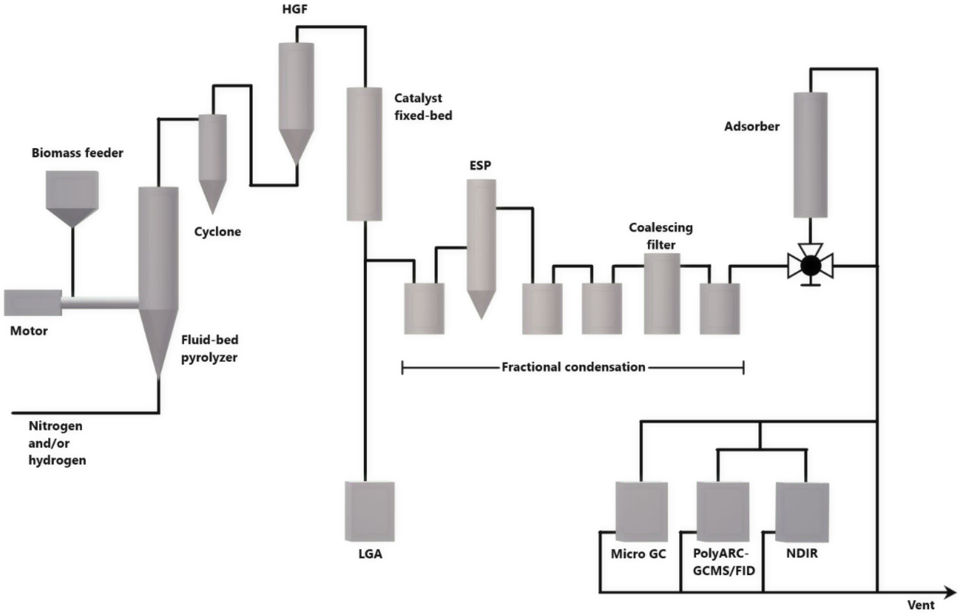
Clean Pine

Debarked stem-wood

Forest Residues

Harvest waste

Feedstock	50/50 Forest Residues + Clean Pine
Composition	Dry wt%
Carbon	50.51
Hydrogen	5.99
Nitrogen	0.17
Sulfur	0.03
Oxygen	41.55
Ash	0.77
Modelled Cost	$67/dry ton



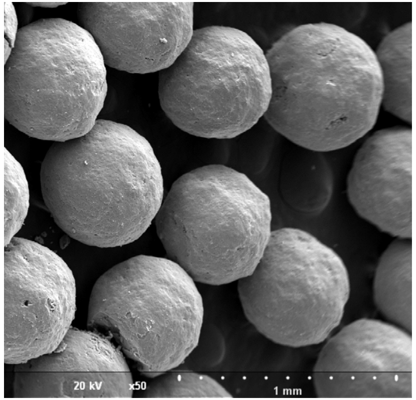
Standard Conditions
Feedstock: Loblolly Pine + Forest Residues
Pyrolysis Temperature: 500 °C
Upgrading Temperature: 435 °C

Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Pressure: ~1 Bar
Hydrogen Concentration: 83%

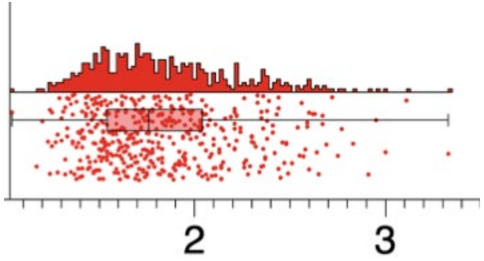
Catalyst Characterization

Catalyst and Synthesis Method	0.5%Pt/TiO_2 Strong Electrostatic Adsorption
Support	0.5 mm TiO_2 Spheres (mixed phase)
Modelled Catalyst cost	$203/kg
Support acidity, NH_3-TPD, µmol/g	156
Support surface area, m^2/g	54
Support pore volume, cm^3/g	0.37
Support median pore diameter, Å	328
Catalyst CO binding site density (µmol/g)	19

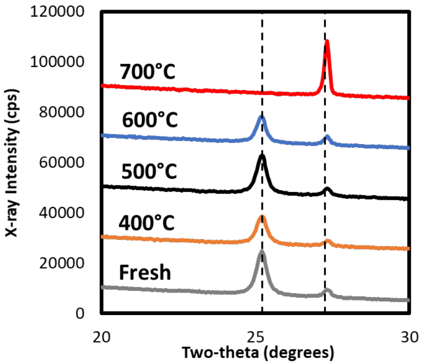
Lin, F., et al. ACS Catal. 2022, 12, 1, 465-480
Griffin, M., et al. ACS Catal. 2016, 6, 2715-2727



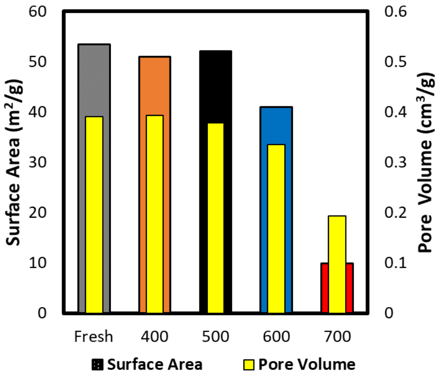
SEM of 0.5 mm TiO_2 support



Pt Particle Size Distribution (nm)



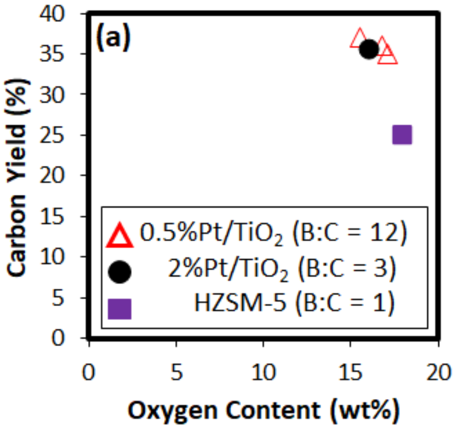
X-Ray Diffraction



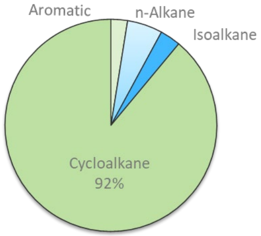
Physisorption

CFP Reaction Testing Results

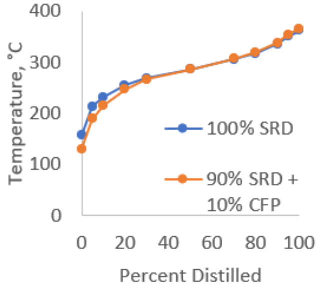
		Process Data	Standard Deviation
Carbon Balances (%)		99	1.5%
Mass Balance		102	0.6%
Process Yields (wt. % of dry biomass unless noted)			
Non-Condensable Gases		30	2.4%
Aqueous Phase (% of biomass C)		1.7	2.3%
Char		11	0.2%
Coke		2	0.5%
Organic Phase	Mass Yield	25	1.3%
	H/C Molar Ratio	1.3	-
	Carbon Yield (%)	36	1.3%
	Oxygen Content (wt% of organic, dry basis)	16.5	0.9%
Carbon Yield to Condensable Light Oxygenates		13	0.2%



High Quality Cycloalkane-Rich SAF Product



Co-Hydroprocessing with Straight Run Diesel



<u>Related Posters/Presentations</u>

Kristiina Iisa: *Hydrotreating to SAF, W-11:15am*

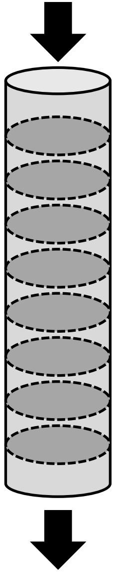
Kristiina Iisa: *Co-Hydrotreating with SRD, Th-2:00pm*

Calvin Mukarakate: *Advancements in CFP, Poster*

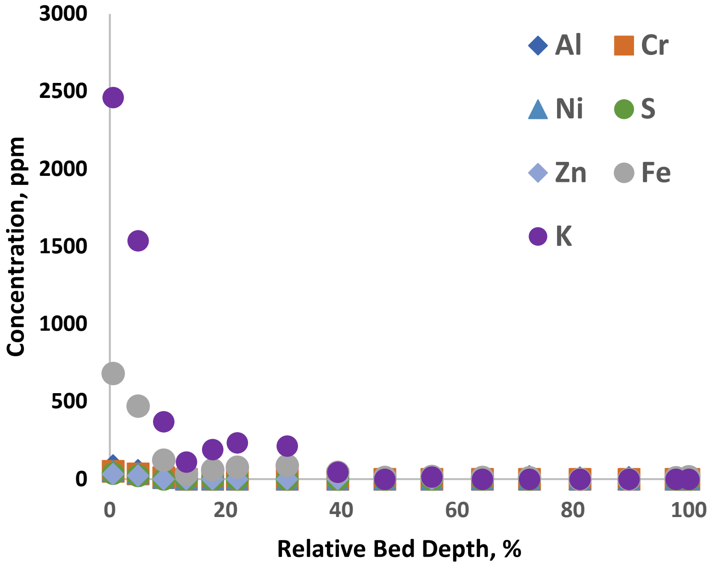
Abhijit Dutta: *TEA/LCA, Poster*

Post-Reaction Catalyst Characterization

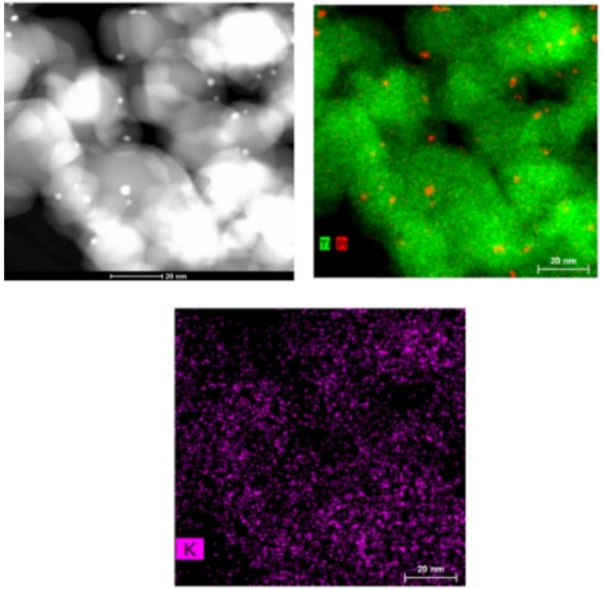
Post Reaction Characterization Revealed Potassium Accumulation Concentrated at the Leading Edge of the Catalyst Bed



Bed Segments: 16
Reaction Cycles: 13
Total TOS: 49 h
Total Biomass Fed: 7.4 kg
Cululative B:C: 74



ICP-OES of Segmented Catalyst Bed



Dark field STEM-EDS From Leading Edge of Bed

Preparation of Potassium-Doped Catalysts

ChemCatBio
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Collaboration with Enabling Projects

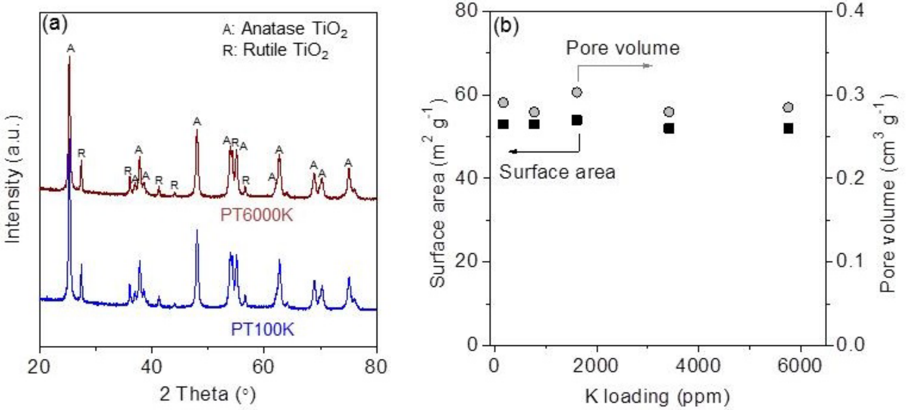
Catalyst Deactivation Mitigation

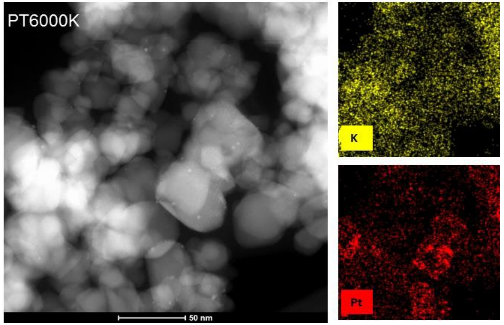
Advanced Catalyst Synthesis and Characterization

Sample	K loading	
	ppm	µmol $g_{cat.}^{-1}$
PT100K	168	4.3
PT800K	774	19.8
PT2000K	1613	41.4
PT4000K	3418	87.6
PT6000K	5757	118

A series of K-doped catalysts were prepared with KNO_3 to achieve K loadings between 100-6000 ppm.

XRD and physisorption reveal no apparent impact of K-loading on crystallinity, surface area, or porosity



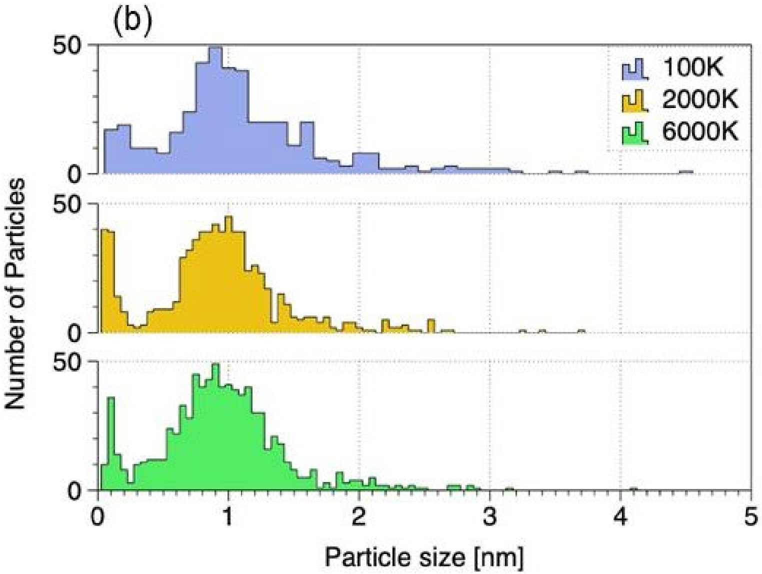


STEM EDS indicates K is well dispersed, consistent with post-reaction catalysts from experiments with whole biomass feedstocks

Lin, F., et al. ACS Catal. 2022, 12, 1, 465-480

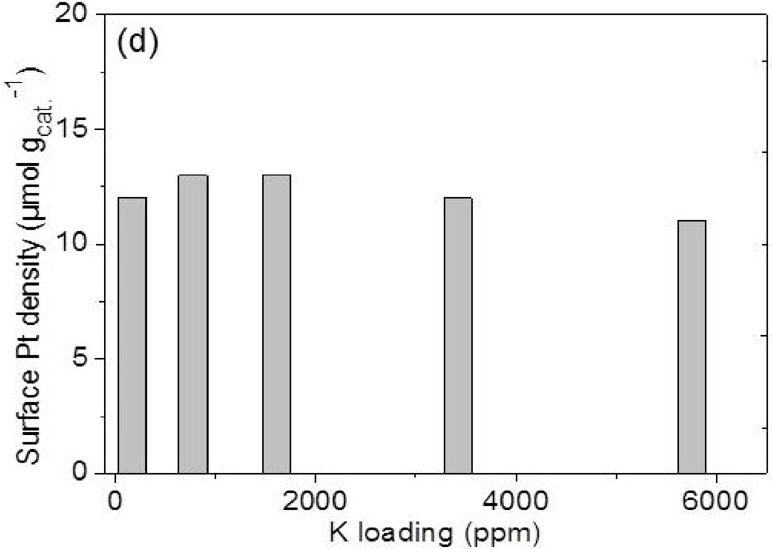
Impact of Potassium on Metal Sites

Particle Size Distribution by TEM



Potassium deposition had minimal impact on Pt particle size distribution

Metal Site Titrations by CO Chemisorption

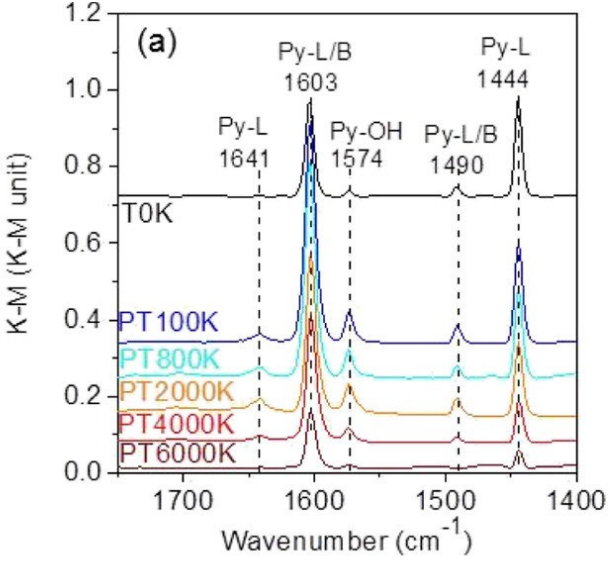


No apparent correlation between CO uptake and K loading

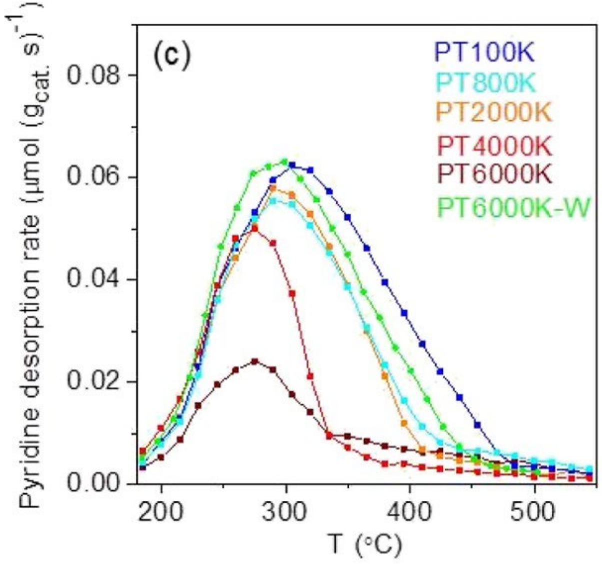
Lin, F., et al. ACS Catal. 2022, 12, 1, 465-480

Impact of Potassium on Acid Sites

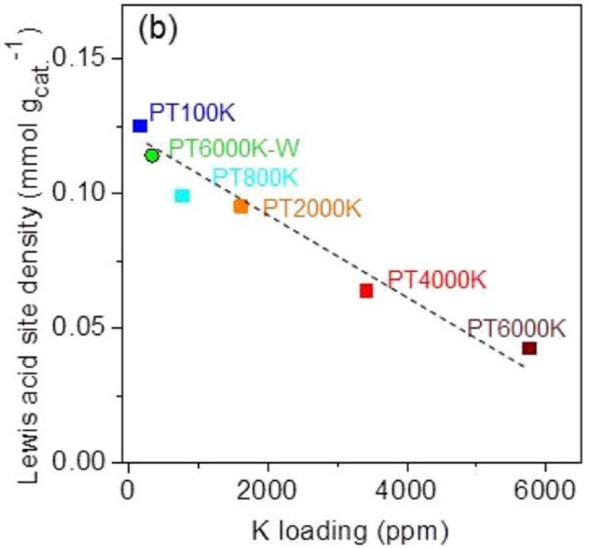
Acid Site Identification by Pyridine DRIFTS



Acid Site Titrations by Pyridine TPD



Correlation Between Potassium Loading and Acid Site Density



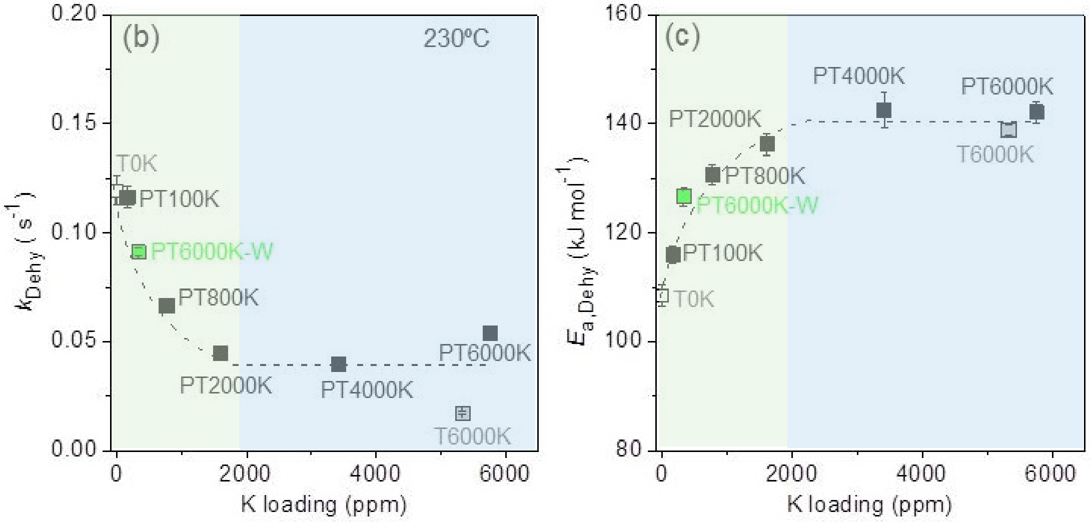
All catalysts exhibited exclusively Lewis acidity

Pyridine TPD reveals a reduction in acid site density and peak desorption temperature with increasing potassium loading

Lin, F., et al. ACS Catal. 2022, 12, 1, 465-480

Impact of K on Activity of TiO_2 Acid Sites

t-Butyl Alcohol Dehydration



<u>0-2000 ppm K</u>

Decrease in rate and increase in apparent activation energy with increasing K-loading

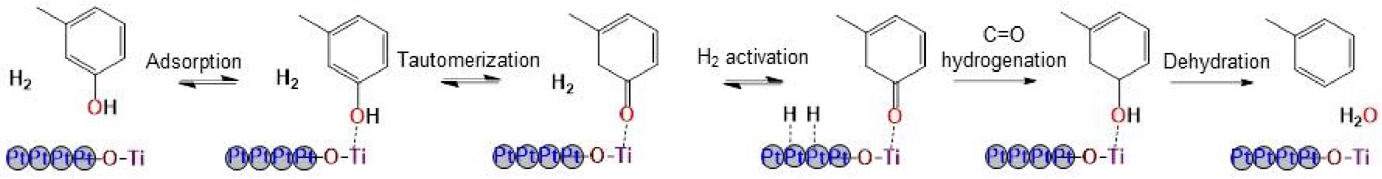
<u>> 2000 ppm K</u>

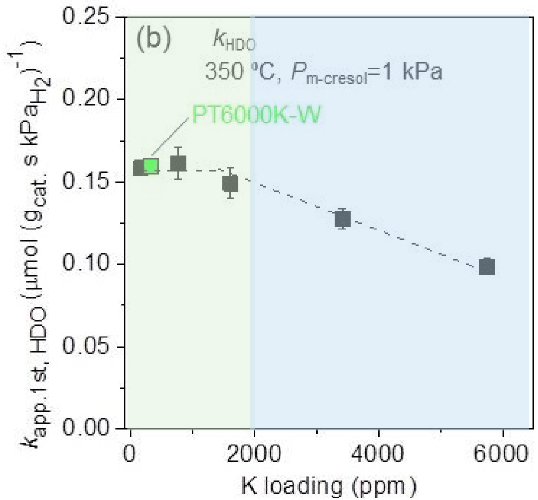
No apparent impact of further K addition

Lin, F., et al. ACS Catal. 2022, 12, 1, 465-480

Impact of K on Activity Near Pt-TiO_2 Interface

m-Cresol Hydrodeoxygenation





<u>0-2000 ppm K</u>
Minimal impact from K addition

<u>> 2000 ppm K</u>
Linear decrease in rate with K addition

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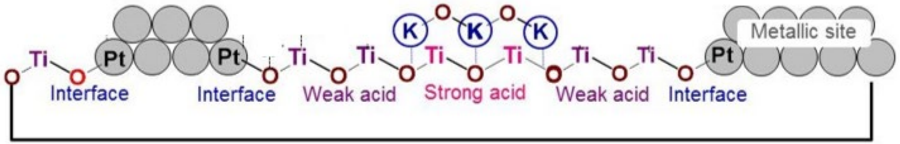
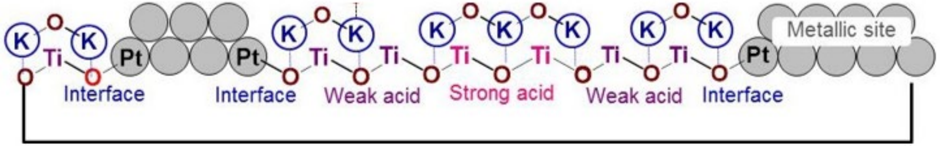
Proposed Mechanism



Low Coverage: Potassium preferentially poisons strong acid sites on the support.



High Coverage: Potassium begins to impact bifunctional sites at the metal-support interface. Metal sites remain largely unaffected.

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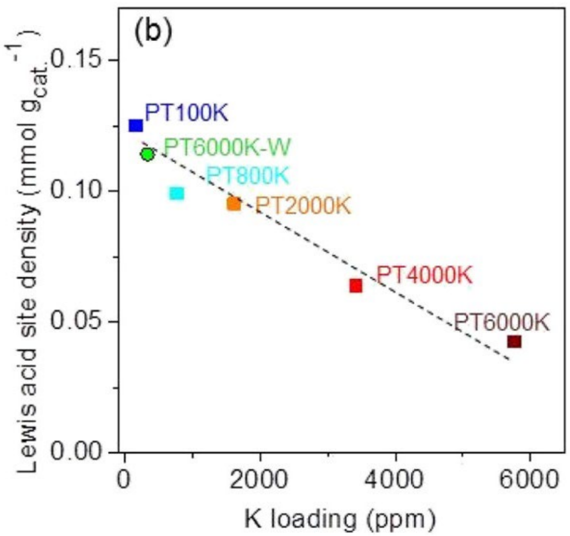
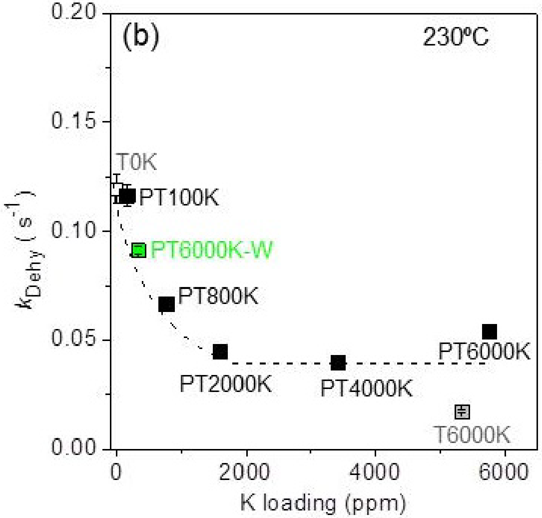
Mitigation Strategy

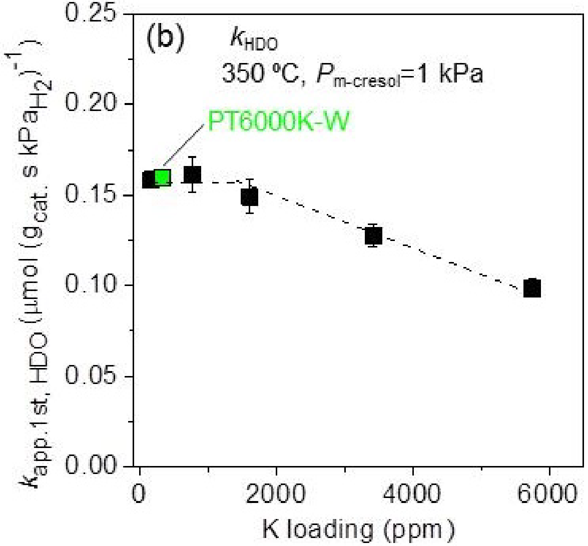
Pyridine TPD



IPA Dehydration



m-Cresol HDO



Sample	K loading	
	ppm	µmol $g_{cat.}^{-1}$
PT100K	168	4.3
PT6000K	5757	118
PT6000K-W	337	8.6

An ex-situ water wash was demonstrated to be an effective regeneration procedure for removing potassium and restoring catalyst activity

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Acknowledgements

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Josh Schaidle (NREL)
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Jessie Glover (BETO)

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