

# Hydroconversion of platform molecules of lignocellulosic origin into renewable fuel components

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**Research Centre for Natural Sciences**

**Project closing meeting**

**„Joint chemical laboratory for the service of bioeconomy in the Slovak-Hungarian border region”**

**Interreg, SKHU/1902/4.1/001/Bioeconomy**

**Faculty of Chemical and Food Technology STU in Bratislava  
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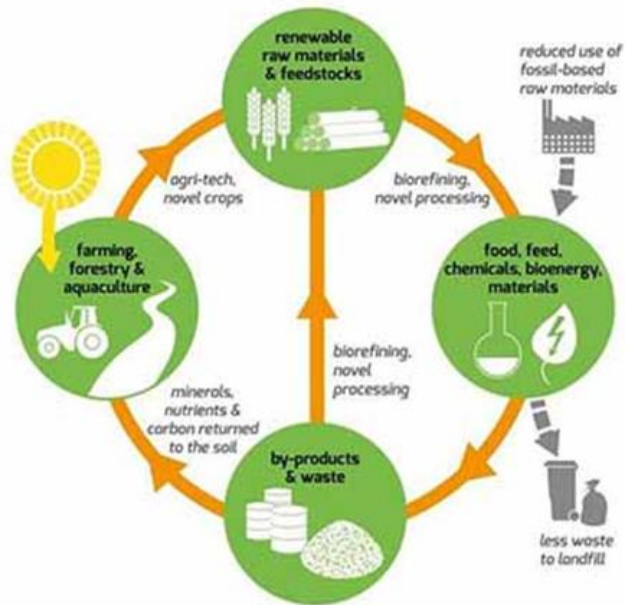
**28 September, 2022**



**Building Partnership**



# Biomass conversion



## Replacing fossil carbon by renewable alternatives

- Depleting resources
- Harmful effect on the environment
- Not carbon neutral, contribute to global warming

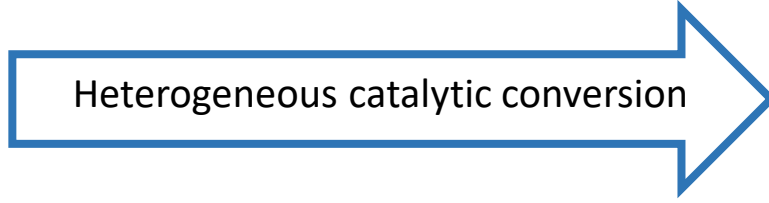
Conversion of waste biomass (non-edible and waste vegetable oils and animal fats) to biofuel or other valuable chemicals

- Carbon neutral: plants capture CO<sub>2</sub> through photosynthesis

# Biomass conversion to biofuels and other chemicals



Ethanol  
 $\gamma$ -Valerolactone (GVL)



Triglycerides  
(Tricaprylin)

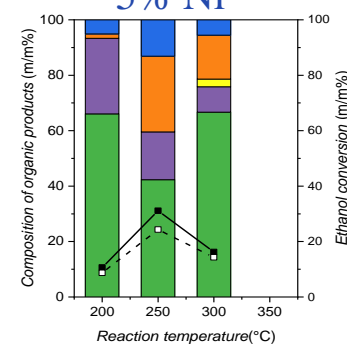
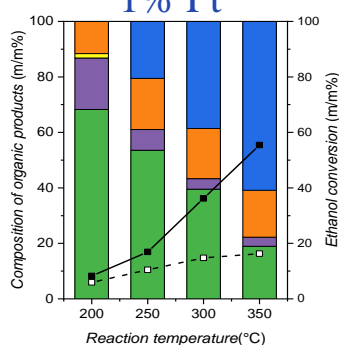
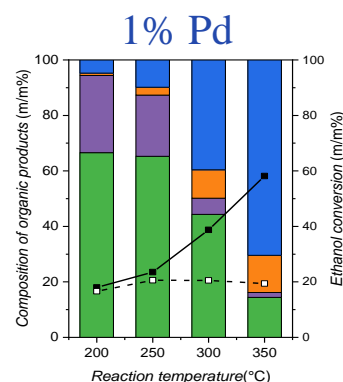
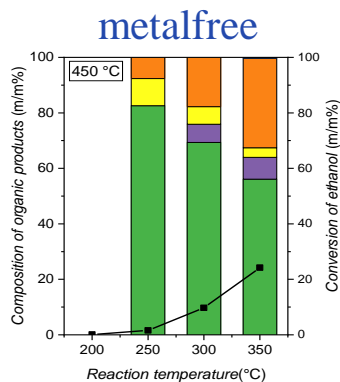




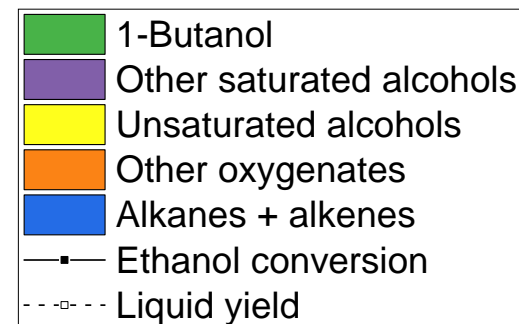
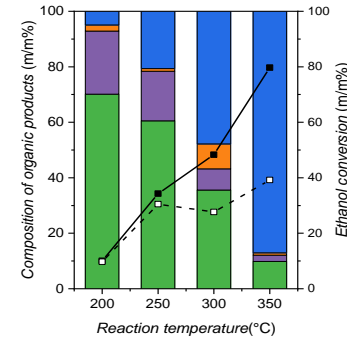
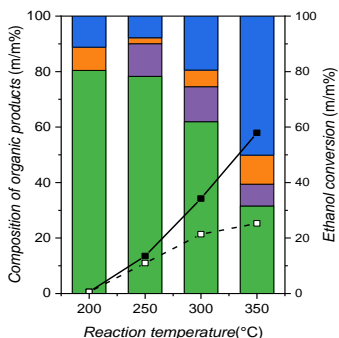
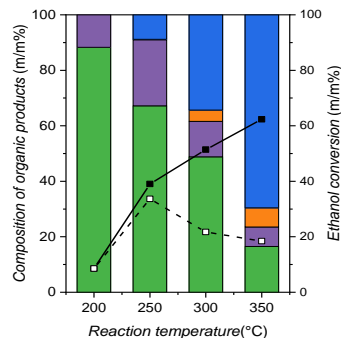
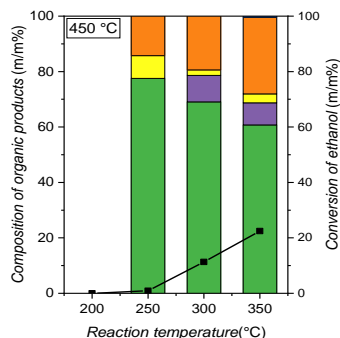
# I. Ethanol conversion on MgO-Al<sub>2</sub>O<sub>3</sub> catalysts

WHSV = 1 g<sub>EtOH</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, p = 21 bar

He flow

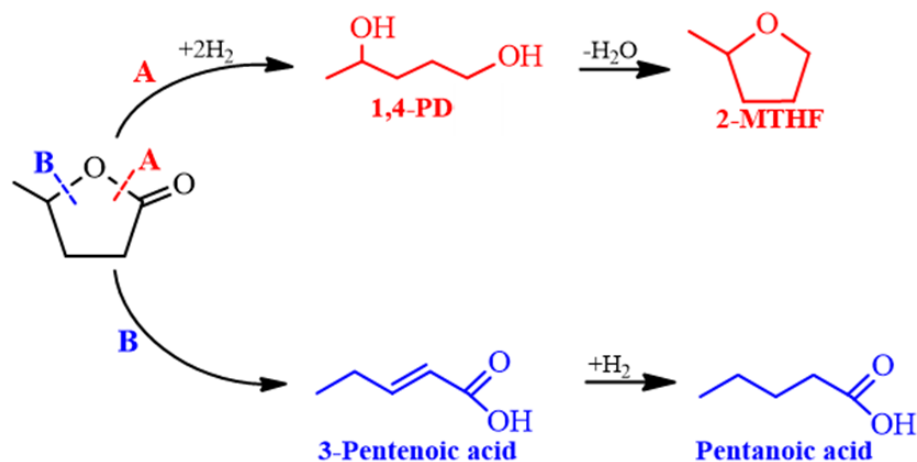


H<sub>2</sub> flow



- Introduction of **metal modifiers** significantly improved the activity, whereas the alcohol yields decreased in the high temperature range.
- The selectivity loss is smaller in **H<sub>2</sub> flow** than in **He flow** over the **Pd-** and **Pt-**containing catalysts.
- At the lowest reaction temperature (200 °C) hydrogen hinders the initial dehydrogenation step of ethanol to acetaldehyde.

## II. Conversion of $\gamma$ -valerolactone to 2-methyltetrahydrofuran



on **8%Co/SiO<sub>2</sub>**

on **0.5%PtCo/  
[Si,Al]Magadiite**

$\gamma$ -Valerolactone (GVL) is produced in large amount from cellulosic biomass

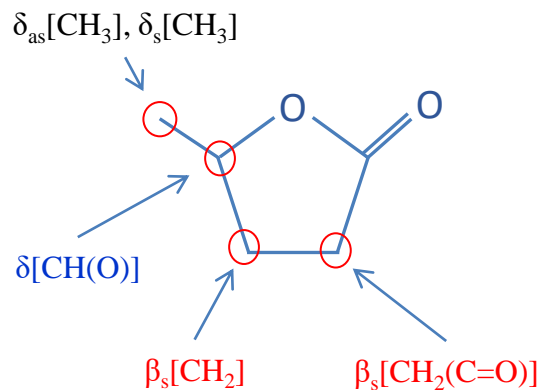
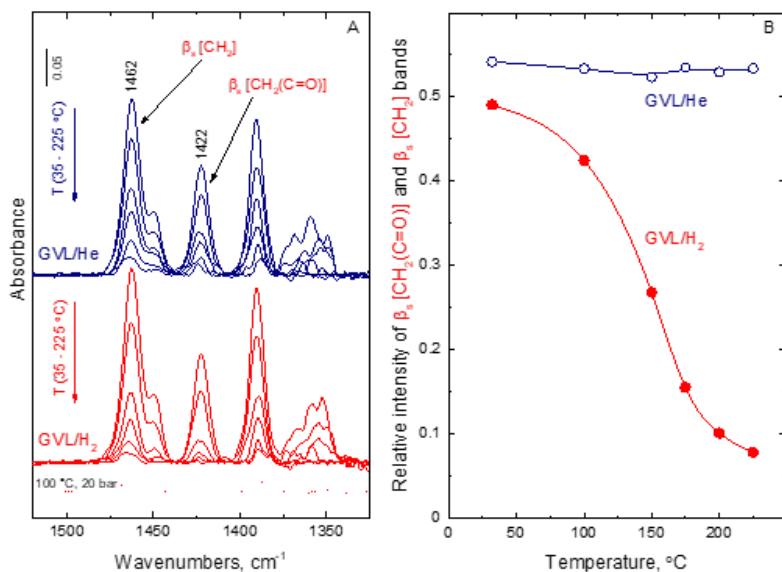
2-Methyltetrahydrofuran is a valuable solvent in chemical industry and can be an additive to gasoline.

**Co/SiO<sub>2</sub>** (contains Lewis acid sites): catalyzes mainly reaction route „**A**”

**Pt/H-MAG** (contains both Lewis and Brønsted acid sites): catalyzes mainly reaction route „**B**”

Catalyst	Reaction temp., °C	Conversion, mol %	Selectivity, mol %				
			2-MTHF <sup>b</sup>	1,4-PD <sup>c</sup>	PA <sup>d</sup>	Pentanol <sup>e</sup>	Others
Co/SiO <sub>2</sub>	200	41.2	69.5	6.0	0	19.6	4.9 <sup>f</sup>
	250	99.0	52.9	0	0	27.5	19.6 <sup>f</sup>
Pt/H-MAG	250	43.5	0.4	0	91.7	0.3	7.6 <sup>g</sup>
	300	90.2	0	0	79.4	0.5	20.1 <sup>g</sup>

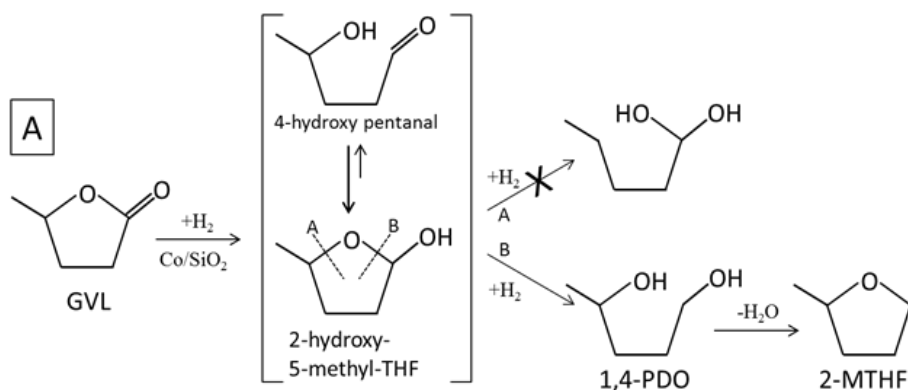
## II. Operando DRIFT spectroscopy of GVL hydrogenation on Co/SiO<sub>2</sub> catalyst



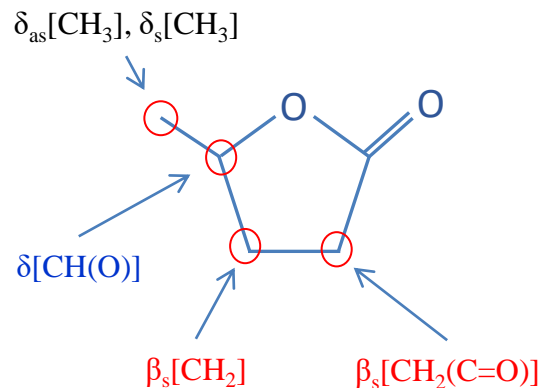
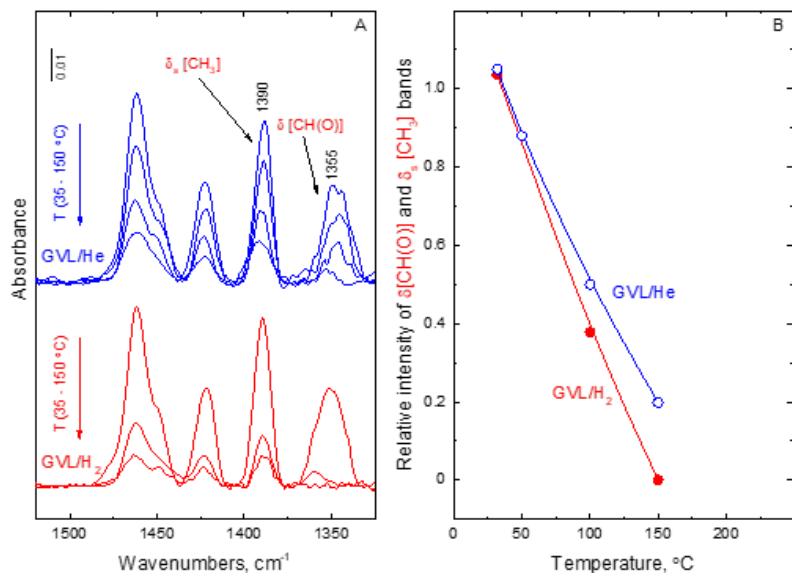
-In contact with **GVL/He** flow:  
only the adsorption coverage of  
the catalyst changes.

-In contact with **GVL/H<sub>2</sub>** flow:  
GVL transformation takes place.

-Hydrogenation reaction  
eliminates the carbonyl group,  
whereas the 5-member ring is not  
affected.

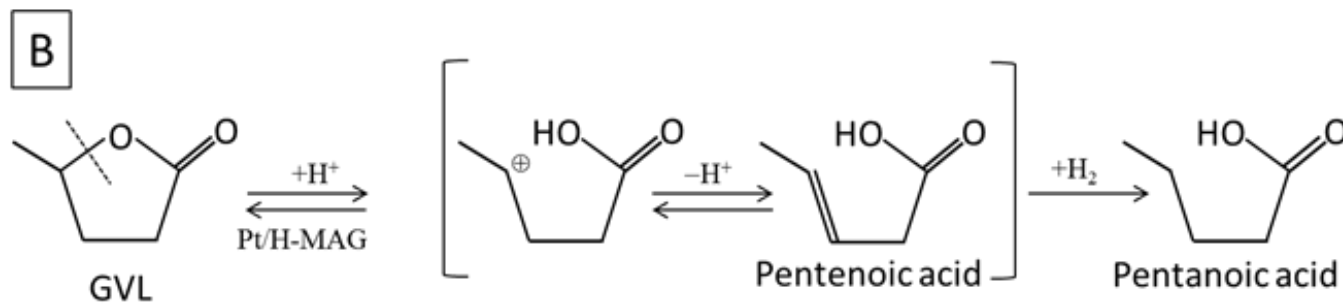


## II. Operando DRIFT spectroscopy of GVL hydrogenation on Pt/H-MAG catalyst



-Regardless of the applied carrier gas (GVL/He or GVL/H<sub>2</sub> flow) GVL transformation takes place.

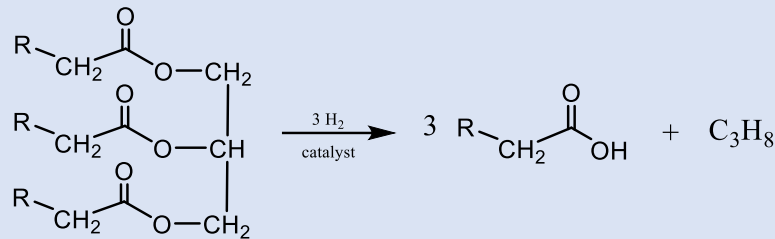
-Results suggest that the cleavage of the C-O bond in the GVL ring occurs on the methyl side. The most probable reaction intermediate is pentenoic acid.





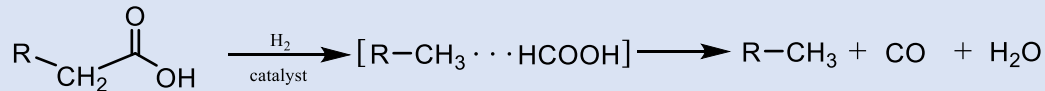
# III. Conversion of triglycerides to diesel fuels

First step: hydrogenolysis of the ester bonds

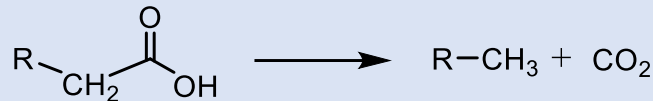


Conversion of carboxylic acid, not fully understood

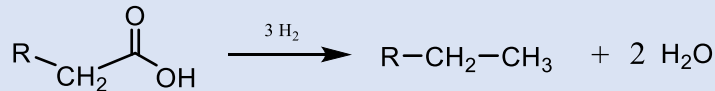
1. hydrodecarbonylation: formation of CO



2. hydrodecarboxylation: formation of CO<sub>2</sub>



2. H<sub>2</sub>-reduction of oxygen: formation of H<sub>2</sub>O via consecutive hydrogen addition and dehydration steps



**Catalytic hydrodeoxygenation (HDO)** of bio-oils is more advantageous than the transesterification with ethanol or methanol.

The product **bio-gasoil** mainly contains C15–C18 alkanes.

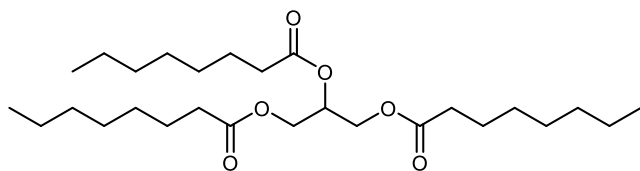
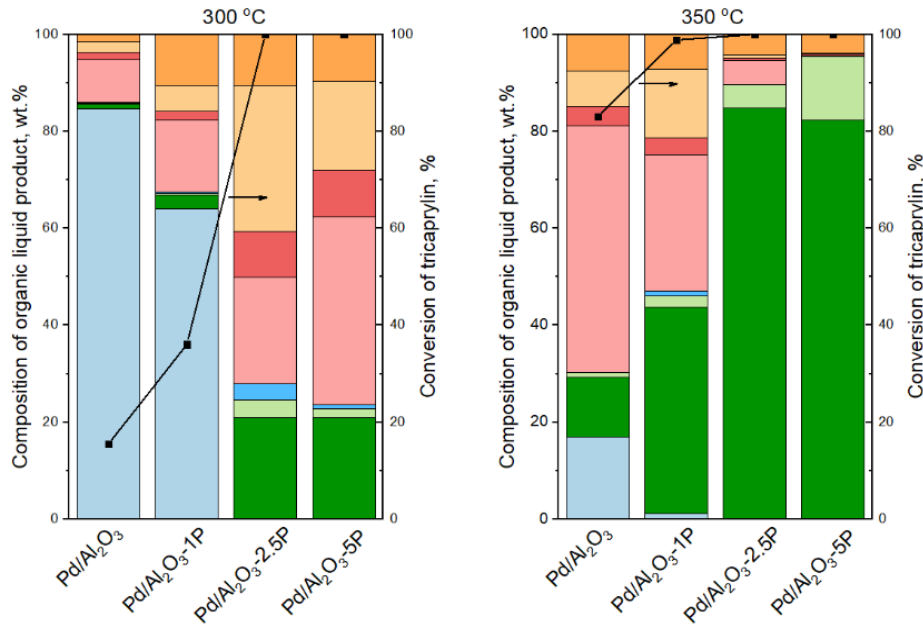
Can be used as an alternative diesel fuel without the modification of internal combustion engines.

# III. HDO reaction of tricaprylin on phosphatized Al<sub>2</sub>O<sub>3</sub>-supported Pd catalysts

Model triglyceride: tricaprylin

20 bar, in H<sub>2</sub> flow,

WHSV=4 g<sub>tricaprylin</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>



■ Tricaprylin  
■ Heptane  
■ Octane  
■ Caprylic acid  
■ Conversion

- Pd/Al<sub>2</sub>O<sub>3</sub> catalysts show high activity in hydrogenolysis of the ester bonds (1<sup>st</sup> step).
- Yield of paraffin products (heptane and octane) dramatically increased with the phosphorous content (nearly 100 % on Pd/Al<sub>2</sub>O<sub>3</sub>-5P).



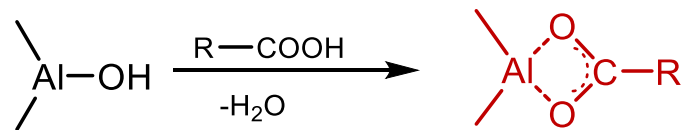
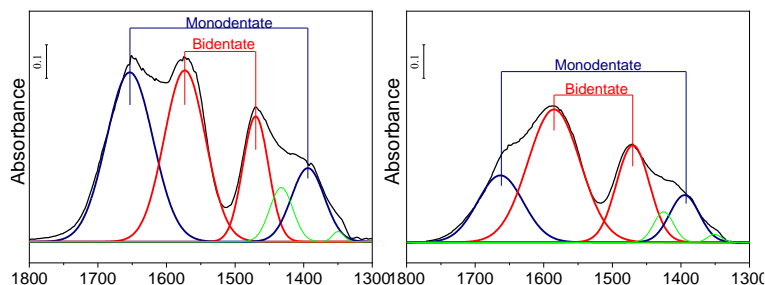
- **Change of catalyst structure**
- **Enhanced HDO (mainly hydrodecarbonylation) activity**



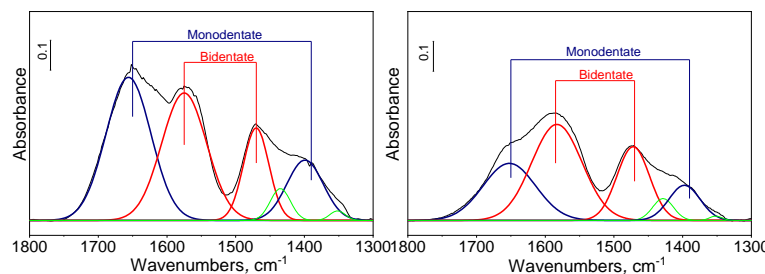
# III. Operando DRIFT spectroscopy of valeric acid hydroconversion

Pd/Al<sub>2</sub>O<sub>3</sub>

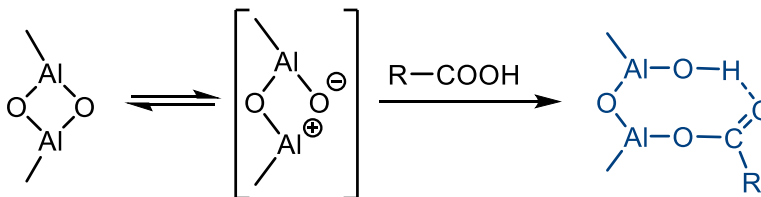
Pd/Al<sub>2</sub>O<sub>3</sub>-5P



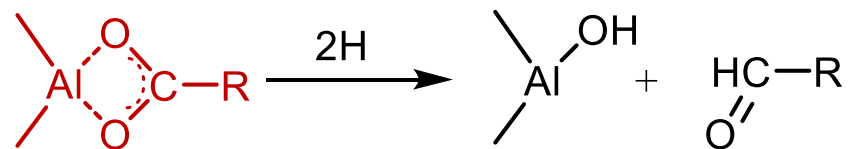
in He



in H<sub>2</sub>



- Phosphatization significantly decrease the concentration of **monodentate** species.
- **Bidentate** carboxylate species are more reactive with H<sub>2</sub> than the **monodentate** species.



# Summary

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- The effect of metal modifiers in Guerbet coupling of bioethanol to butanol was investigated on mixed Mg-Al oxide based catalysts.

Gasoline additive biobutanol was produced in high yields on Pd and Pt modified catalysts.

- Hydrogenation of GVL over 8%Co/SiO<sub>2</sub> catalyst shows high selectivity towards 2-MTHF, whereas 0.5%Pt/H-Magadiite catalyst catalyzed the GVL conversion to pentanoic acid with >90% selectivity.

The results of the operando DRIFT spectroscopic investigations allowed us to propose a plausible reaction mechanism over both bifunctional catalyst.

- Surface phosphatization of the  $\gamma$ -alumina support significantly increased the HDO activity of the Pd catalyst to convert tricaproline into paraffinic hydrocarbons (bio-gasoil).

The operando DRIFT measurements revealed the origin of the increased HDO activity.

# Thank you for your kind attention!

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**Building Partnership**