

# Triglyceride hydroconversion over alumina-supported and phosphatized-alumina-supported Pd catalysts

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**Project meeting**

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

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

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**Building Partnership**



[www.ttk.hu/palyazatok/bioeconomy](http://www.ttk.hu/palyazatok/bioeconomy)

# Replacing fossil fuels

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## Fossil energy resources

- Depleting resources
- Harmful effect on the environment  
emission of greenhouse gas CO<sub>2</sub> contributes to global warming



## Replacement by inexhaustible and renewable energy sources

- Solar, wind, water, geothermal energy
- **Conversion of waste biomass**, such as, non-edible and waste vegetable oils and animal **fats** to biofuel or fuel blending components

# Diesel fuel production from biomass

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## Biodiesel:

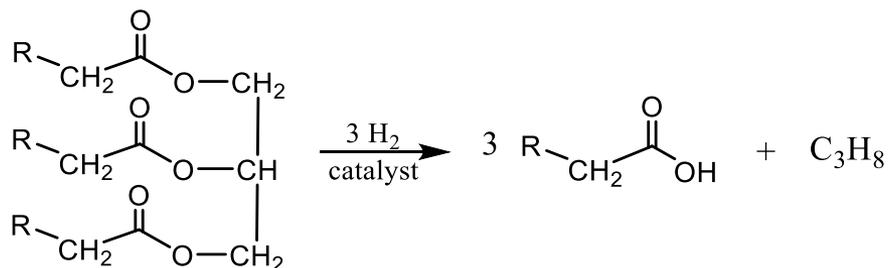
- transesterification of bio-oil triglycerides with methanol or ethanol
- fatty acid methyl or ethyl esters – can be directly blended with conventional diesel fuels
- cannot fully replace conventional diesel oil (lower energy density, higher viscosity, moderate oxidation stability)

## Biogasoil:

- catalytic hydrodeoxygenation (HDO) of bio-oil
- consist of mainly C<sub>15</sub>–C<sub>18</sub> n-alkanes, suitable as an alternative diesel fuel
- no need for the modification of internal combustion engines

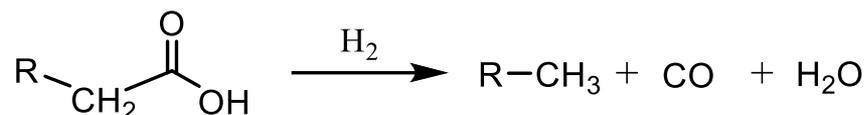
# Hydroconversion of triglycerides to paraffins

First step: hydrogenolysis (HYS) of the ester bonds

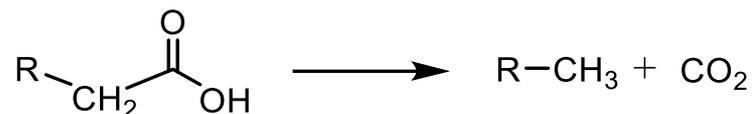


Next step: Conversion of carboxylic acid, not fully understood

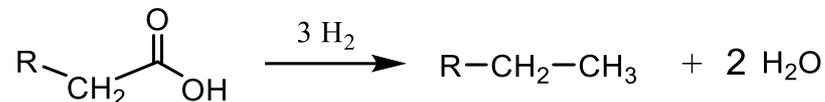
1. hydrodecarbonylation: formation of CO



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



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



# Catalyst preparation and characterisation

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$\gamma$ -Al<sub>2</sub>O<sub>3</sub>-1P,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-2.5P,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-5P supports

1, 2.5 and 5 wt.% P-content by impregnation with H<sub>3</sub>PO<sub>4</sub>

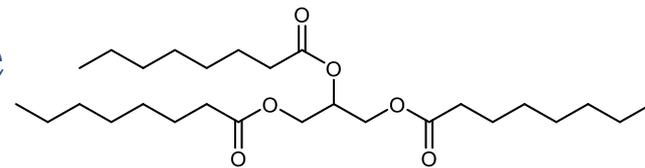
Calcination: 550 °C for 4h

Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-1P, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-2.5P, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-5P catalysts

**0.5 wt.% Pd** by wet impregnation

Calcination: 150 °C for 1h, then 350 °C for 4h

# Tricaprylin (TC) as a model triglyceride



- Caprylic (octanoic acid): highest carboxylic acid, which is liquid at room temperature
- High-pressure fixed-bed flow-through heterogeneous catalytic microreactor system
- Reaction conditions:
  - 140 ml/min H<sub>2</sub> flow
  - 21 bar
  - WHSV=4 g<sub>tricaprylin</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>
  - 300 and 350 °C

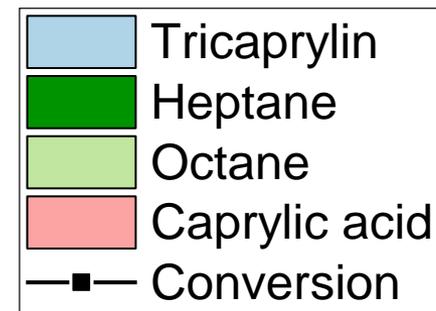
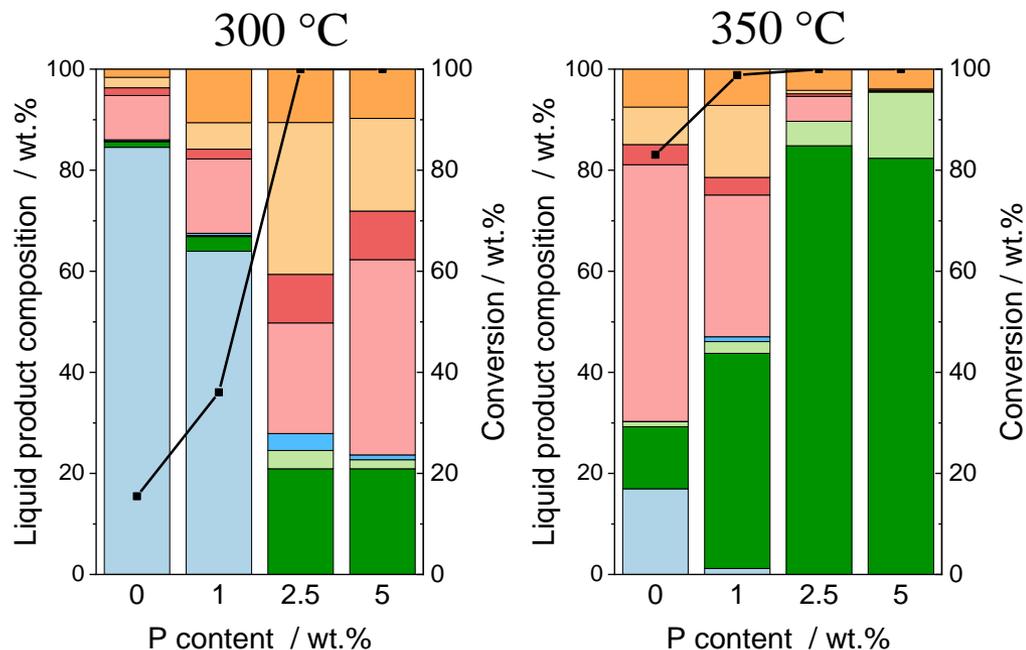
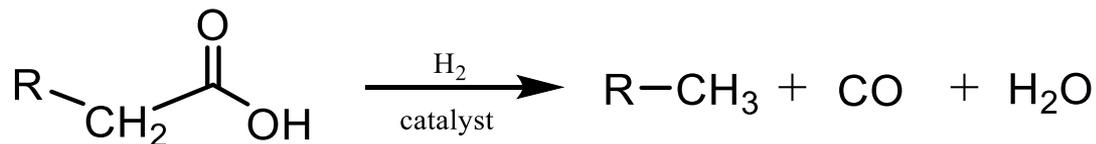


# Product composition of the HDO of tricaprylin

- 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).

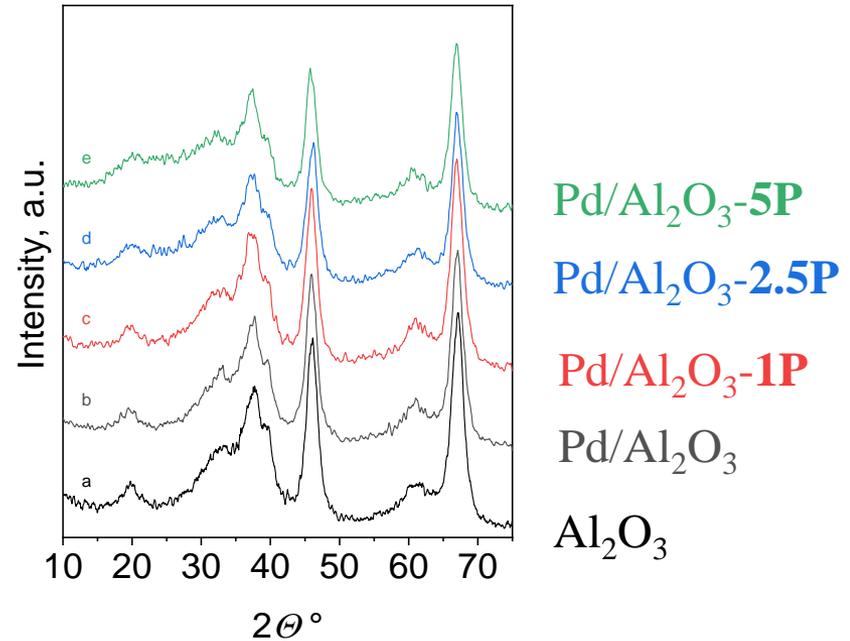


- **Change of catalyst structure**
- **Enhanced HDO (mainly hydrodecarbonylation) activity**



# Catalyst structure

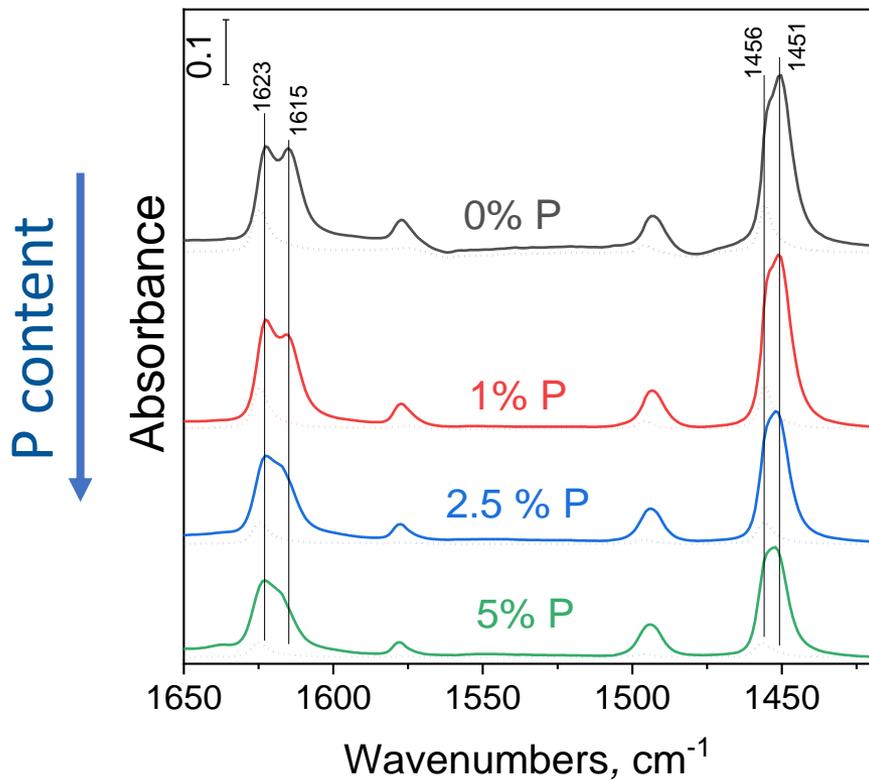
- No new crystalline phase could be detected
- The specific surface area decreased with increasing P-content
- Pd dispersion barely changed with the P-content of catalysts



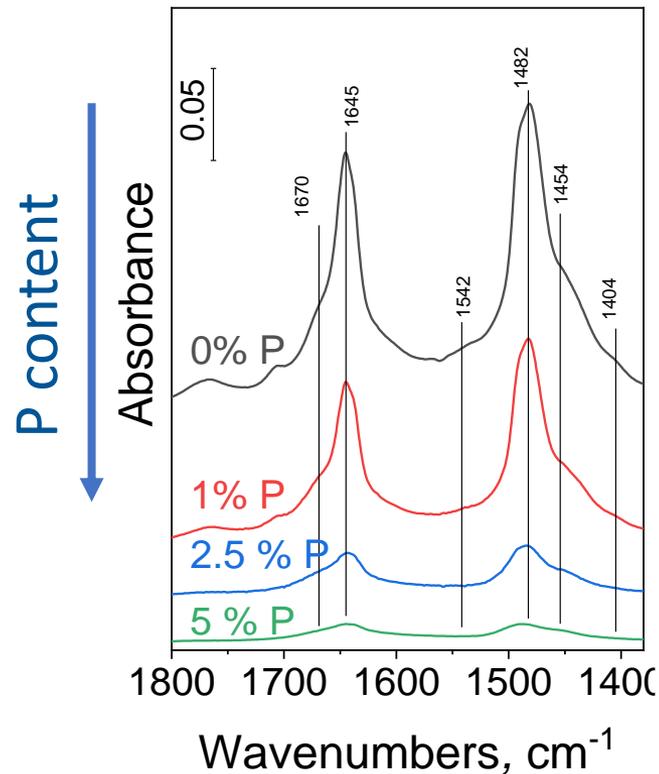
Catalyst	Pd/Al <sub>2</sub> O <sub>3</sub>	Pd/Al <sub>2</sub> O <sub>3</sub> -1P	Pd/Al <sub>2</sub> O <sub>3</sub> -2.5P	Pd/Al <sub>2</sub> O <sub>3</sub> -5P
Specific surface area, m <sup>2</sup> g <sup>-1</sup>	212	183	167	132
Pd dispersion %	86	70	74	74

# Acidic and basic properties of catalyst supports

Pyridine adsorption



$\text{CO}_2$  adsorption



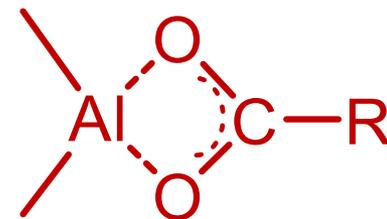
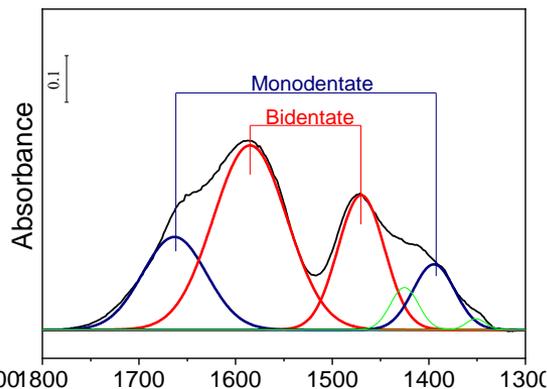
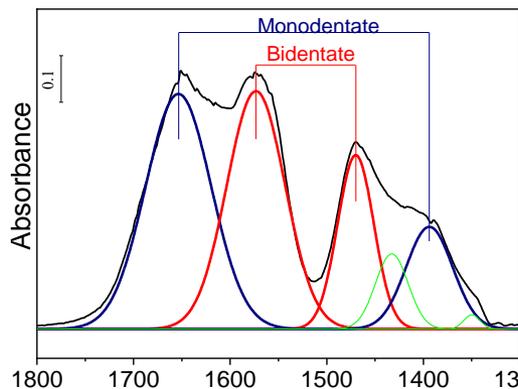
- The intensity of the characteristic absorption bands of the carbonate species as well as the coordinatively bound pyridine species are **inversely proportional to the phosphate loading**.
- The formation of surface phosphate **decreased the concentration of both basic and Lewis acid sites**.

# Quasi-operando DRIFT spectroscopy of valeric acid hydroconversion

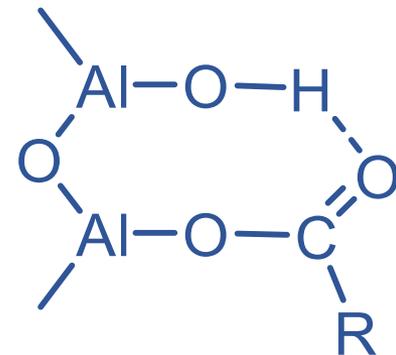
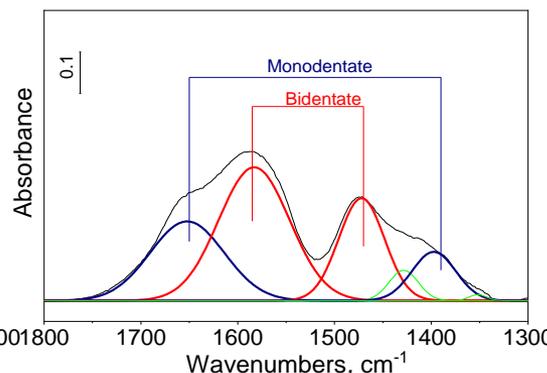
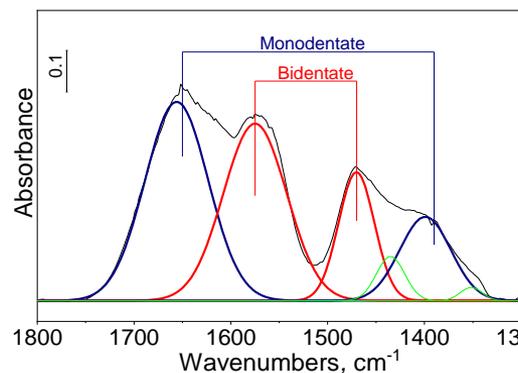
Pd/Al<sub>2</sub>O<sub>3</sub>

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

in He



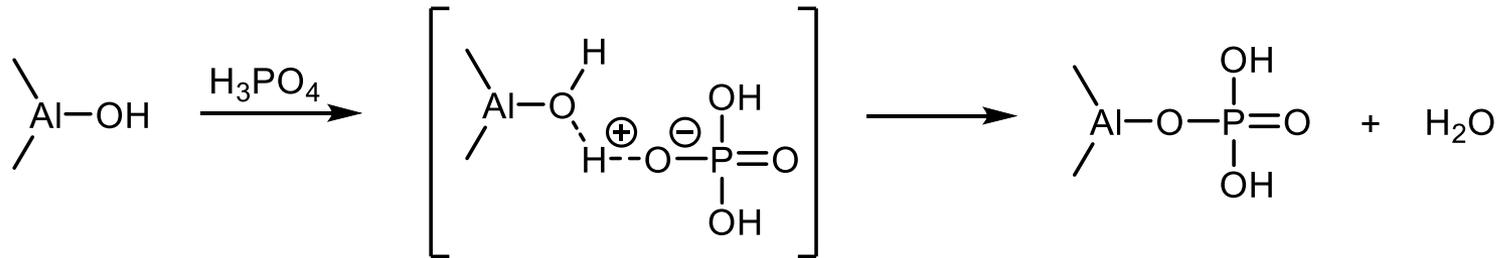
in H<sub>2</sub>



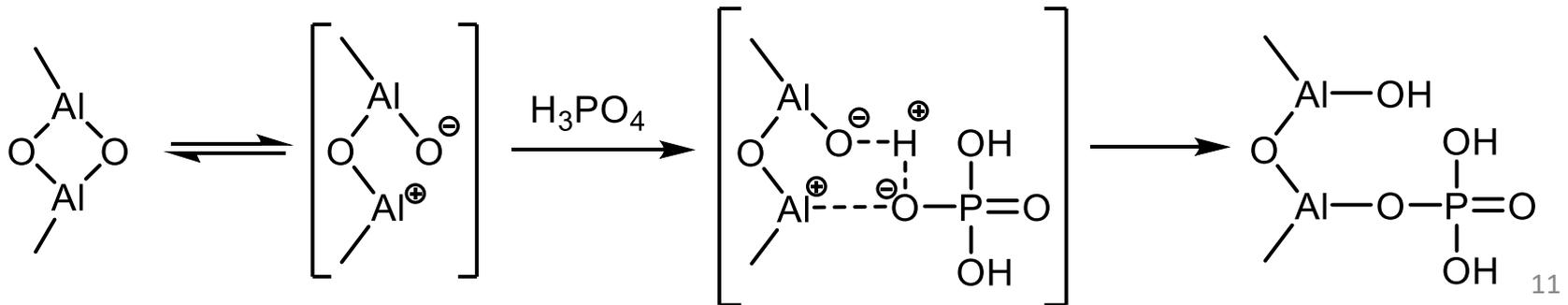
- Phosphatization significantly decrease the concentration of **monodentate** species.
- **Bidentate** carboxylate species are more reactive with H<sub>2</sub> than the **monodentate** species.
- **Bidentate** species, formed in reaction with less basic hydroxyls, are more ready to react.

# Effect of surface phosphatization

## 1. Consumes surface Al–OH groups

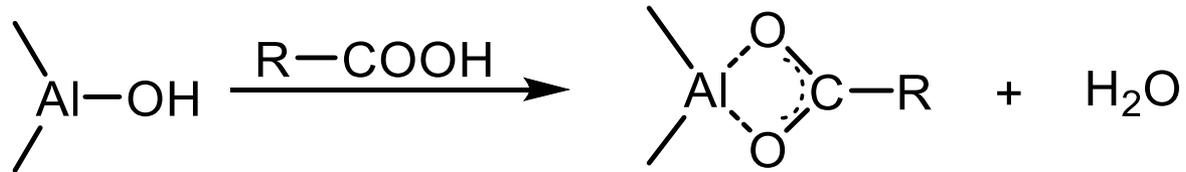


**2. Reduces the concentration of Lewis acid sites and consequently the concentration of the Lewis acid–Lewis base pair sites** (accompanied by the formation of non-reactive terminal Al<sup>IV</sup>-OH groups)

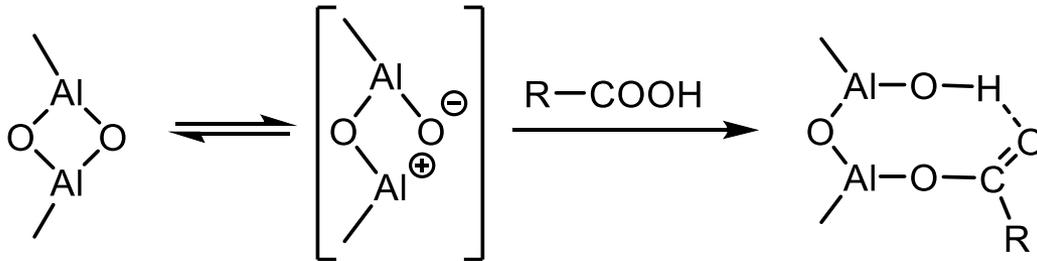


# Formation of carboxylate species on surface

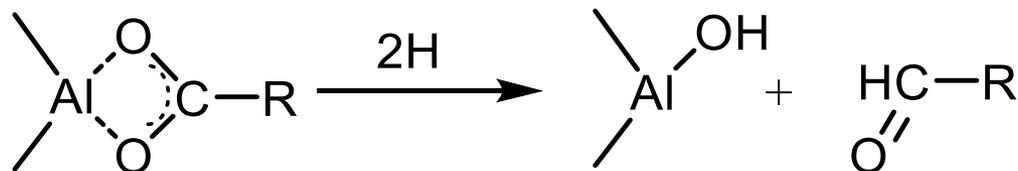
**Bidentate carboxylate** species were formed via acid-base reaction between fatty acid and a surface hydroxyl groups.



**Monodentate carboxylate** species were formed over Lewis acid – Lewis base pair sites.



**Bidentate species** are more ready to react with hydrogen, producing aldehyde intermediate of HDO reaction.



# Conclusions

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- The Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed good activity in the HYS of the ester bonds to convert TC to caprylic acid, but poor activity in the consecutive HDO of the acid to paraffin.
- Surface phosphatization of the  $\gamma$ -alumina support significantly increased the HDO activity of the Pd catalyst.
- The HDO activity was enhanced due to:
  1. the partial replacement of the basic Al–OH groups by weak acid P–OH groups: Bidentate carboxylates bonded to less basic surface sites were found to be more prone to HDO reaction.
  2. the partial elimination of Lewis acid – Lewis base pair sites on the surface of the support:  
Less low-reactivity monodentate carboxylate binds to the surface.

# Acknowledgement

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**[www.skhu.eu](http://www.skhu.eu)**



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