

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

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Project meeting

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Interreg, SKHU/1902/4.1/001/Bioeconomy

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Building Partnership



www.ttk.hu/palyazatok/bioeconomy

Replacing fossil fuels

Fossil energy resources

- Depleting resources
- Harmful effect on the environment
emission of greenhouse gas CO₂ 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

Biodiesel:

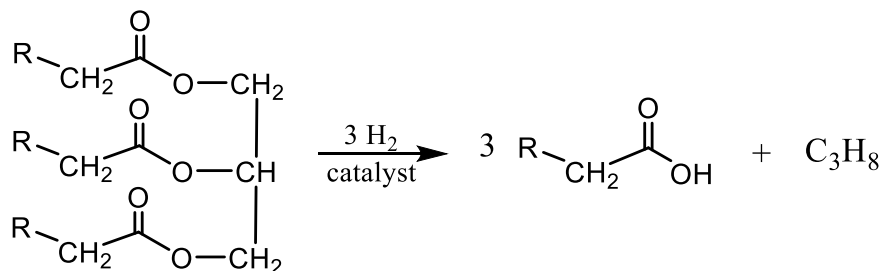
- transesterification of bio-oil triglycerides with methanol or ethanol
- fatty acid methyl or ethyl esters – can be directly blended with conventional diesel fuels
- cannot fully replace conventional diesel oil (lower energy density, higher viscosity, moderate oxidation stability)

Biogasoil:

- catalytic hydrodeoxygenation (HDO) of bio-oil
- consist of mainly C₁₅–C₁₈ n-alkanes, suitable as an alternative diesel fuel
- no need for the modification of internal combustion engines

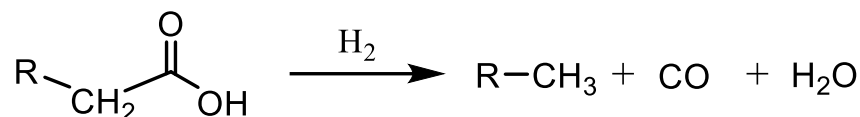
Hydroconversion of triglycerides to paraffins

First step: hydrogenolysis (HYS) of the ester bonds

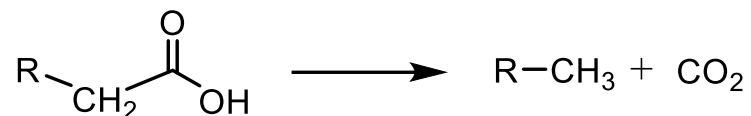


Next step: Conversion of carboxylic acid, not fully understood

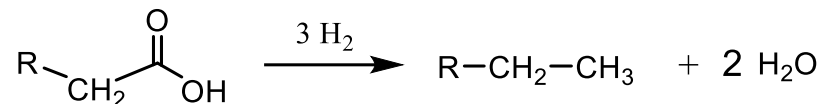
1. hydrodecarbonylation: formation of CO



2. hydrodecarboxylation: formation of CO₂



3. H₂-reduction of oxygen: formation of H₂O via consecutive hydrogen addition and dehydration steps



Catalyst preparation and characterisation

γ -Al₂O₃-1P, γ -Al₂O₃-2.5P, γ -Al₂O₃-5P supports

1, 2.5 and 5 wt.% P-content by impregnation with H₃PO₄

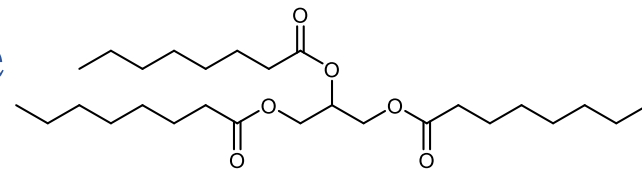
Calcination: 550 °C for 4h

Pd/ γ -Al₂O₃, Pd/ γ -Al₂O₃-1P, Pd/ γ -Al₂O₃-2.5P, Pd/ γ -Al₂O₃-5P 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 H₂ flow
 - 21 bar
 - WHSV=4 g_{tricaprylin} g_{catalyst}⁻¹ h⁻¹
 - 300 and 350 °C

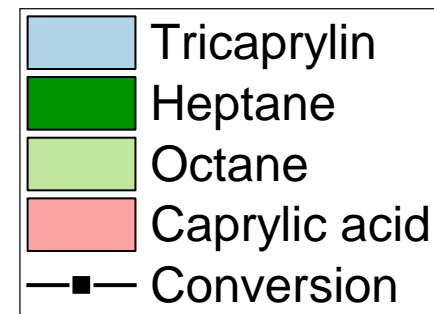
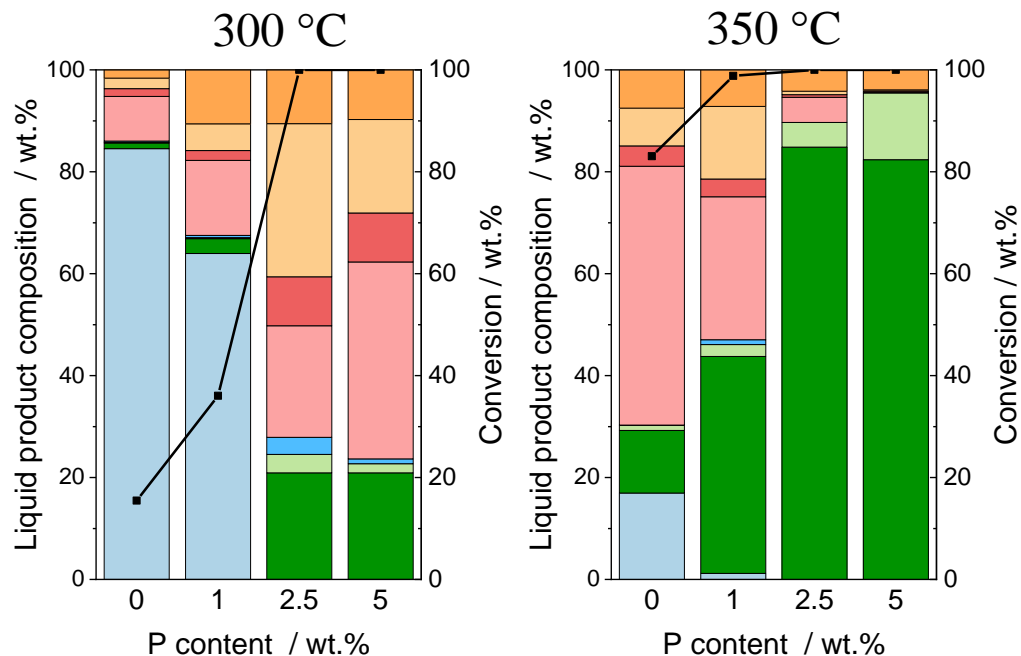
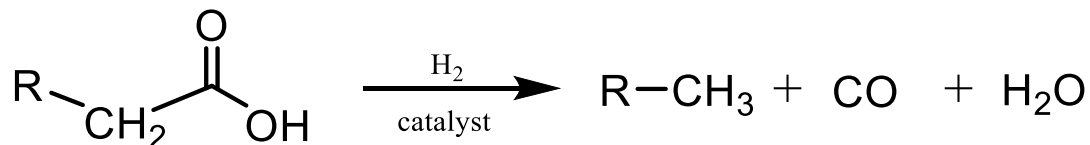


Product composition of the HDO of tricaprylin

- Pd/Al₂O₃ catalysts show high activity in hydrogenolysis of the ester bonds (1st step).
- Yield of paraffin products (heptane and octane) dramatically increased with the phosphorous content (nearly 100 % on Pd/Al₂O₃-5P).

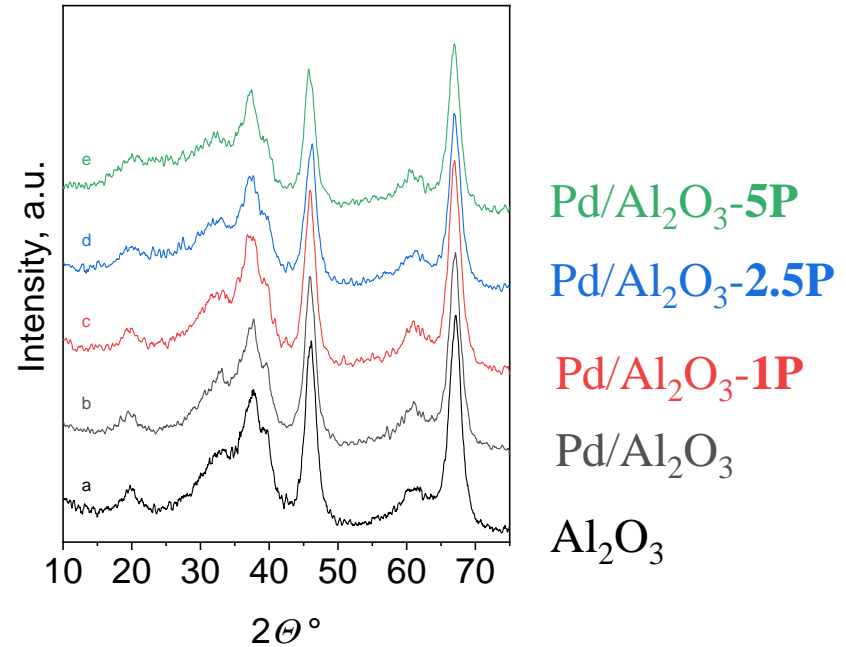


- **Change of catalyst structure**
- **Enhanced HDO (mainly hydrodecarbonylation) activity**



Catalyst structure

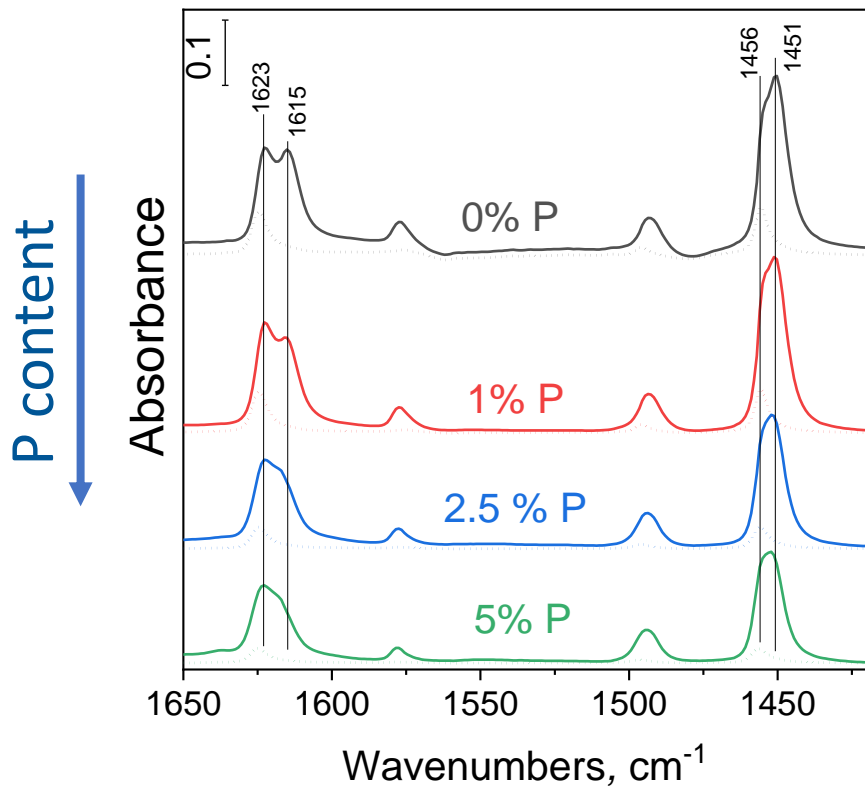
- No new crystalline phase could be detected
- The specific surface area decreased with increasing P-content
- Pd dispersion barely changed with the P-content of catalysts



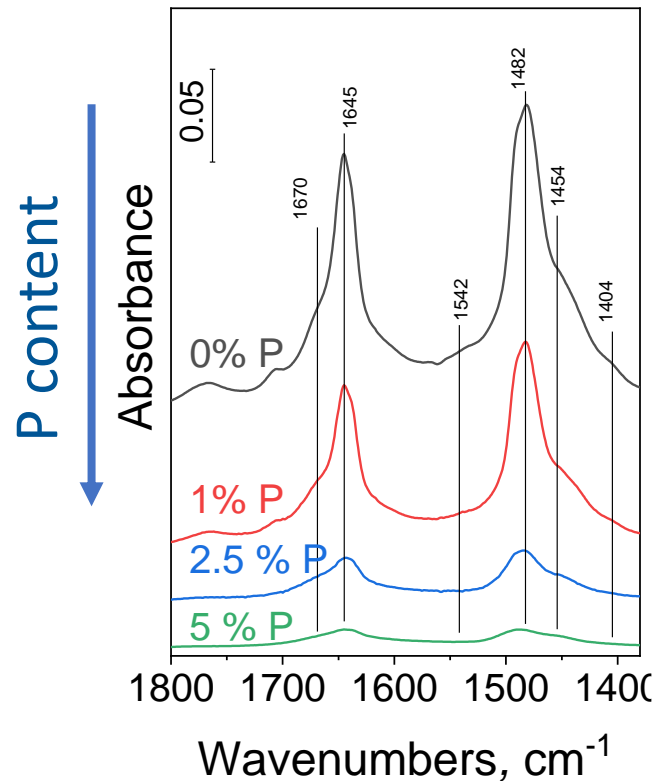
Catalyst	Pd/Al ₂ O ₃	Pd/Al ₂ O ₃ -1P	Pd/Al ₂ O ₃ -2.5P	Pd/Al ₂ O ₃ -5P
Specific surface area, m ² g ⁻¹	212	183	167	132
Pd dispersion %	86	70	74	74

Acidic and basic properties of catalyst supports

Pyridine adsorption



CO₂ adsorption



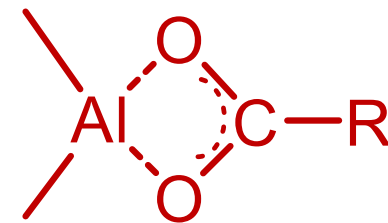
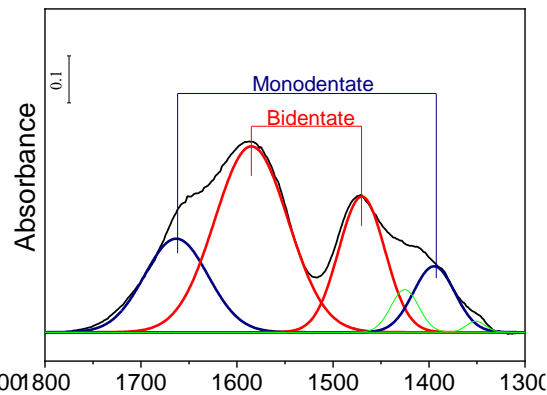
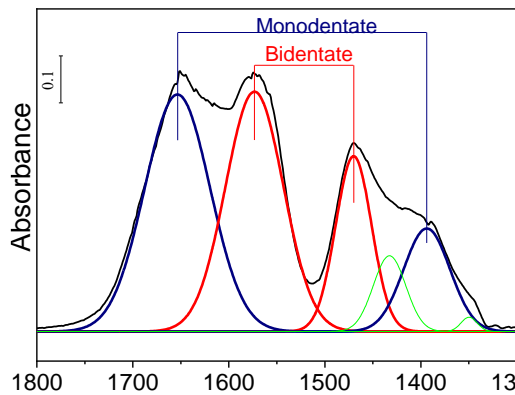
- The intensity of the characteristic absorption bands of the carbonate species as well as the coordinatively bound pyridine species are **inversely proportional to the phosphate loading**.
- The formation of surface phosphate **decreased the concentration of both basic and Lewis acid sites**.

Quasi-operando DRIFT spectroscopy of valeric acid hydroconversion

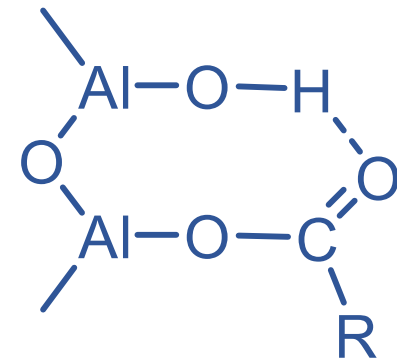
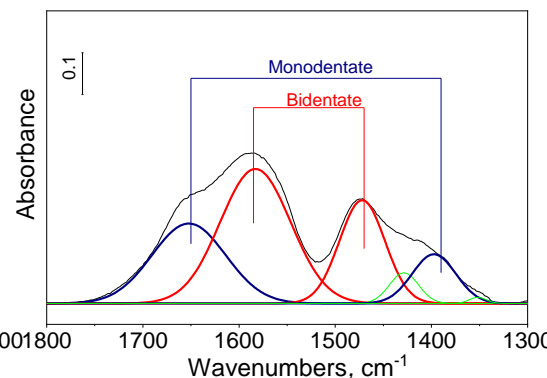
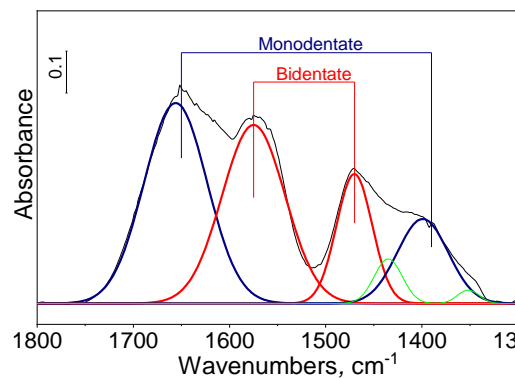
Pd/Al₂O₃

Pd/Al₂O₃-5P

in He



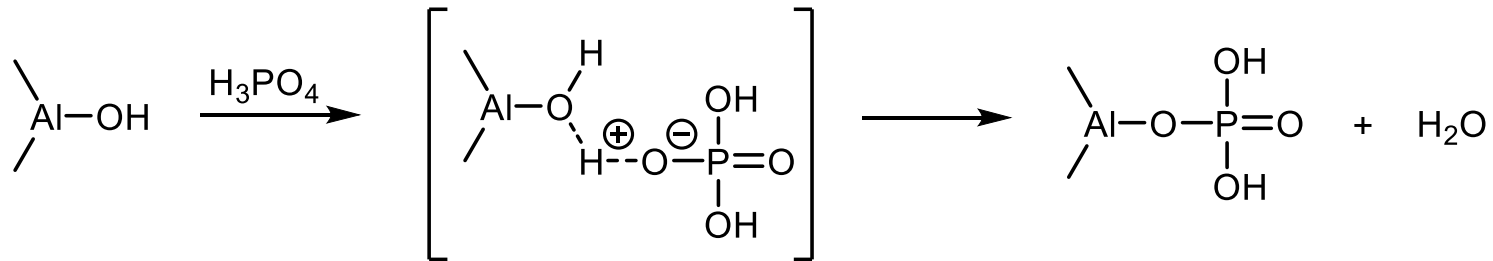
in H₂



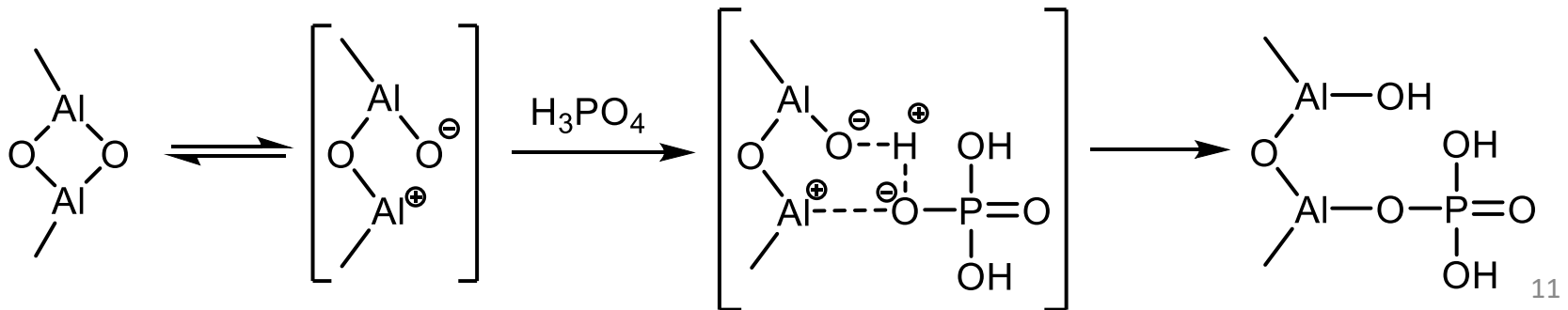
- Phosphatization significantly decrease the concentration of **monodentate** species.
- **Bidentate** carboxylate species are more reactive with H₂ than the **monodentate** species.
- **Bidentate** species, formed in reaction with less basic hydroxyls, are more ready to react.

Effect of surface phosphatization

1. Consumes surface Al–OH groups

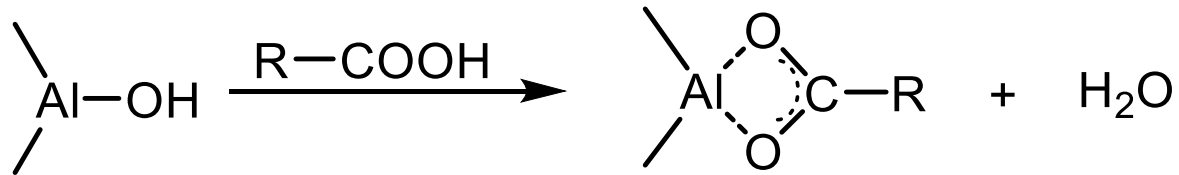


2. Reduces the concentration of Lewis acid sites and consequently the concentration of the Lewis acid–Lewis base pair sites (accompanied by the formation of non-reactive terminal Al^{IV}-OH groups)

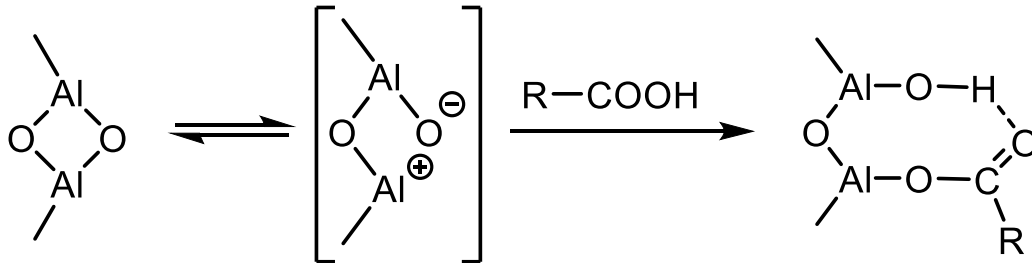


Formation of carboxylate species on surface

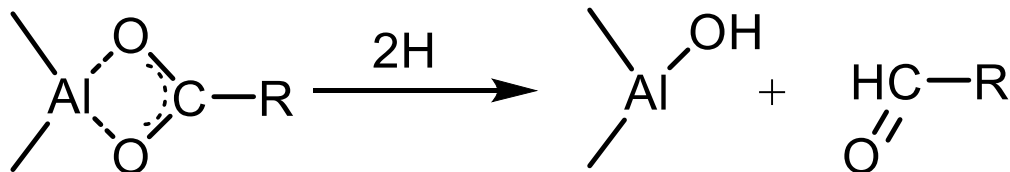
Bidentate carboxylate species were formed via acid-base reaction between fatty acid and a surface hydroxyl groups.



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

- The Pd/ γ -Al₂O₃ 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 γ -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.

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