Ni_2P as catalyst in oleic acid HDO: Influence of different carbon based supports

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Introduction

- Biomass is a potential source for making liquid fuel;
- Vegetable oils have C-chains similar in length to diesel;
- Oxygen content in vegetable oil too high for direct use as diesel
- Deoxygenation is needed;
- Metal phosphides are promising catalysts for deoxygenation;
- Carbon supports are stable under the relevant deoxygenation conditions;
- Role of the type of carbon support is unknown.

Objective

Investigate the role of the carbon support (Activated carbon, carbon nanofibers, carbon covered alumina) in carbon supported Ni-phosphide catalysts for the deoxygenation of oleic acid.

Methods

Catalysts were synthesized via TPR from room temperature to 650 °C under H_2 flow (heating rate 1 °C min^{-1}).
Reactions were carried out in a trickle bed reactor at 350 °C and 30 bar H_2 with dodecane as solvent and tetradecane as standard pattern.
Catalysts were diluted in SiC in a ratio of 1:1 (wt/wt).

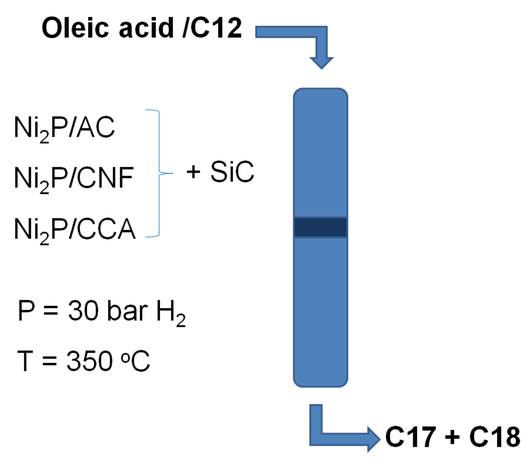

Figure 1. Scheme of reaction.

Catalytic activity

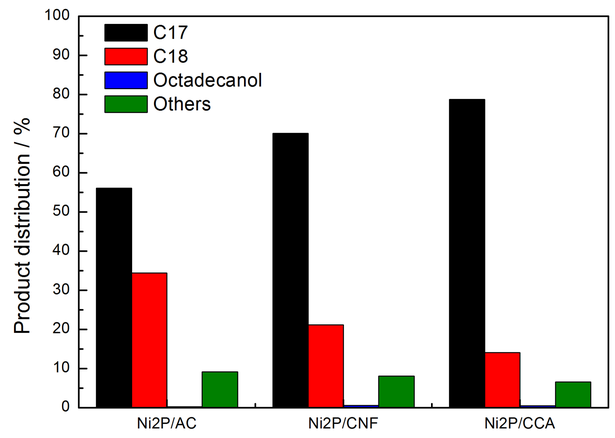

Figure 2. Product distribution of deoxygenation of oleic acid at 350 °C and 30 bar H_2 over Ni_2P/AC, Ni_2P/CNF and Ni_2P/CCA

- At conversion > 90% the C17/C18 product ratio increased in the order Ni_2P/AC < Ni_2P/CNF < Ni_2P/CCA;
- Over Ni_2P/CCA the decarbonylation and decarboxylation prevails;
- Over Ni_2P/AC hydrodeoxygenation is more significant (higher C18 yield).

TPD to visualize electronic effects

- Ni_2P/CCA binds CO more strongly than Ni_2P/CNF and Ni_2P/AC;
- The stronger CO binds to the catalyst the higher the C17 yield.

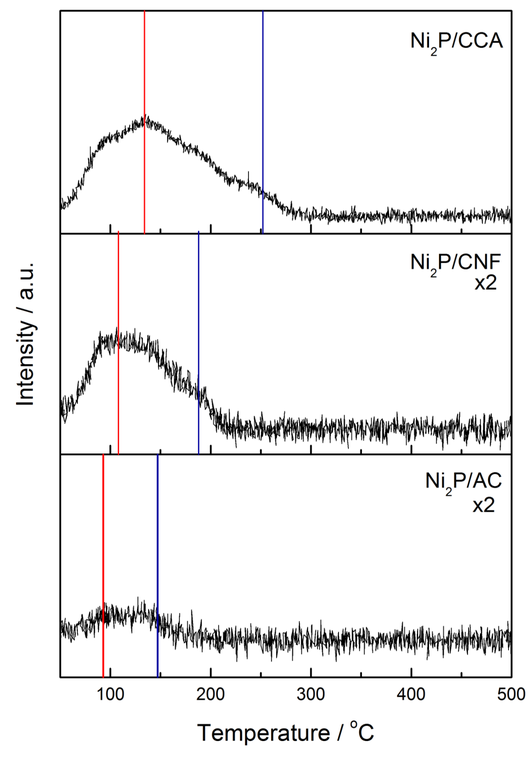

Figure 3. CO TPD profile for catalysts Ni_2P/AC, Ni_2P/CNF and Ni_2P/CCA.

Catalyst properties

Support	$S_{B.E.T.}$ (m^2 g^{-1})
Activated carbon (AC)	823
Carbon covered alumina (CCA)	193
Carbon nanofibers (CNF)	180

Catalyst	Crystallite diameter (nm)
Ni_2P/AC	32
Ni_2P/CCA	32
Ni_2P/CNF	19

- Metal loading, 30 wt% in all cases;
- Lower density of Ni sites for Ni_2P/AC compared to Ni_2P/CNF and Ni_2P/CCA (same loading and different surface area of supports).

Conclusions/summary

- Support influences reaction pathway;
- Stronger interaction between CO and catalyst enables higher C17 yield – decarbonylation and decarboxylation pathway (Ni_2P/CCA);
- Lower density of Ni sites enables higher C18 yield – hydrodeoxygenation pathway (Ni_2P/AC).

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