



Selective decarboxylation of stearic acid over Pd/Al₂O₃

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Introduction

- Currently 2nd generation biodiesel is obtained by hydrodeoxygenation of (unsaturated) vegetable oils at elevated H₂ pressures and temperatures, yielding mainly saturated hydrocarbons
- Especially the need for large amounts of (non-renewable) hydrogen remains a challenge to overcome in current research
- Furthermore, the use of hydrogen results in reduction of the double bond functionalities present in unsaturated oils or fatty acids

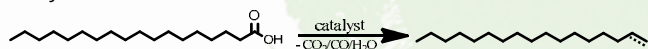
Objectives

Aim: Develop a new, low temperature catalytic decarboxylation procedure for the production of 2nd generation biodiesel, based on vegetable oil, without the need for additional hydrogen

- Formation of biodiesel with superior fuel properties
- Generate new feedstocks for high value chemicals production

Focus

- Oxidic materials are used as supports, which offer the advantage of thermal regeneration
- Stearic acid is used as model compound to minimize coking
- Later on more realistic feedstocks will be used
- In this part of the research the focus will be on Pd/γ-Al₂O₃ catalysts



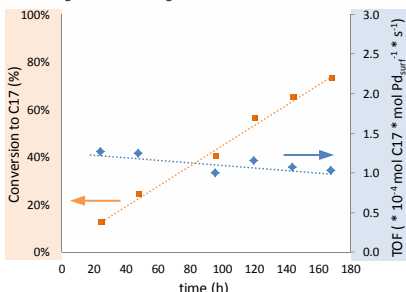
General reaction procedure

- **Activation:** 5 wt% Pd/γ-Al₂O₃ is dried and reduced in static H₂ atmosphere @ 250 °C for 2 h
- **Catalytic reaction:** in Parr autoclave system using dodecane as solvent
- **Characterization:** GC analysis after methylation of filtered reaction mixture



Results

Catalyst activity over time

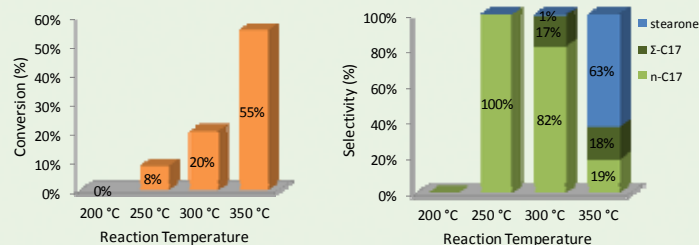


- Catalyst remains active over 170h, only slight decrease in TOF

Reaction parameters

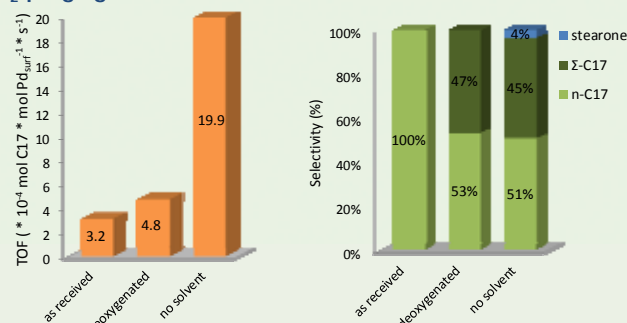
- T = 250°C, p = 7bar N₂, t = 5 h unless stated otherwise
- mass ratio of metal, substrate and solvent is 1:40:1440
 - tetradecane is used as internal standard
- conversions & selectivities are based on GC analysis

Influence of reaction temperature



- A clear effect of temperature on conversion & selectivity is observed
- At 250°C heptadecane (n-C17) is formed as the only product
- At higher T also unsaturated C17 hydrocarbons (Σ-C17) and stearone (symmetrical ketonized product of stearic acid) are formed

N₂-purging / exclusion of solvent



- TOF increases with 50% when using N₂-purged dodecane
- 6-fold increase in TOF in solvent-free conditions, selectivity remains high, only minor stearone production

Conclusions

- Selective decarboxylation of stearic acid to heptadecane was accomplished over Pd/γ-Al₂O₃ at 250 °C in the absence of H₂
- Reaction is tuned towards higher stearic acid conversion with excellent selectivity to C17 hydrocarbons

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