



The selective catalytic deoxygenation of stearic acid using Pd/Al₂O₃ in the absence of H₂; decarboxylation versus decarbonylation pathways

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Introduction

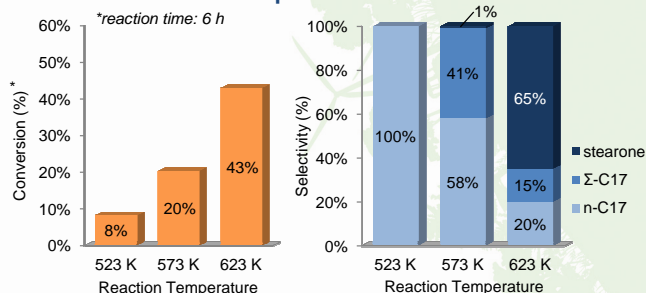
- Currently 2nd generation biodiesel is obtained by hydrodeoxygenation of (unsaturated) vegetable oils at elevated H₂ pressures and temperatures, yielding mainly saturated hydrocarbons
- The need for large amounts of (non-renewable) hydrogen and concomitant reduction of the double bond functionalities present in unsaturated oils or fatty acids remains a challenge to overcome in current research
- Obtaining more insight in the deoxygenation reaction pathways is expected to be essential to improve catalyst performance

General reaction procedure

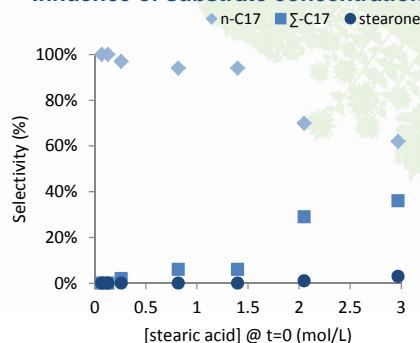
- Activation:** 5 wt% Pd/γ-Al₂O₃, dried and reduced in static H₂ atmosphere (523 K, 2 h, flushed with N₂ at 523 K after reduction)
- Reaction conditions** (unless stated otherwise): Batch reactor
Feedstock: stearic acid (0.14 mol L⁻¹) T = 523 K
Solvent: dodecane p = 7 bar N₂
Internal standard: tetradecane t = 24 h
- Characterization:** Conversions & selectivities based on GC analysis after methylation of filtered reaction mixture

Results

Influence of reaction temperature

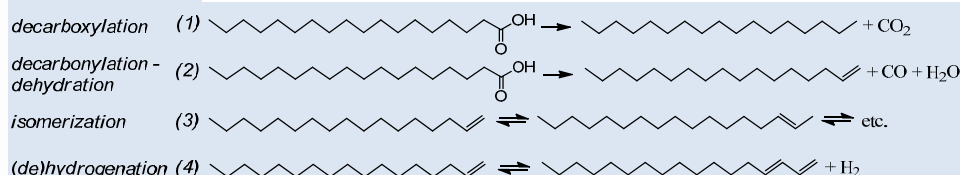


Influence of substrate concentration

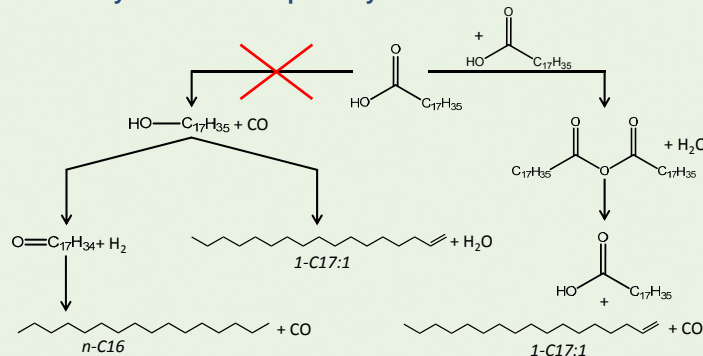


- Stearone is only formed at high temperature or high stearic acid concentration
- Selective decarboxylation to heptadecane occurs at 523 K
- At higher stearic acid concentration also decarbonylation products are formed, even at 523 K

liquid phase reactions



Decarbonylation reaction pathways from stearic acid



- Experiments with octadecanol, octadecanal and stearic anhydride performed to verify decarbonylation pathways

Conversion and selectivity after catalytic experiments with stearic acid and various possible intermediate (or closely related) products

Reactant	Conversion (%)	Deoxygenation selectivity (%)		
		n-C17	C17:1	n-C18
Stearic acid	20	100	0	0
Stearic acid	10 [a]	89	11	0
Octadecanol	100	86	0	14
Octadecanal	100	100	0	0
Stearic anhydride	100 [b]	28	26	0

[a] stearic acid concentration 10 times as high (=1.4 mol L⁻¹)

[b] 46% conversion to stearic acid

- Heptadecanol as intermediate product would yield significant amounts of hexadecane, which is not observed
→ Heptadecanol is not an intermediate product during stearic acid decarbonylation
- Reaction pathway via stearic acid anhydride is verified
→ Explains occurrence of decarbonylation at high substrate concentration
→ Fast conversion of stearic anhydride implies anhydride formation to be the rate limiting step in the decarbonylation pathway

Conclusions

- The catalyst is highly selective towards heptadecane at 523 K at low stearic acid concentration
- Stearic anhydride is proposed as intermediate product in the decarbonylation reaction
- Rate limiting step in the decarbonylation pathway is suggested to be the formation of stearic anhydride

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