Electronic Supplementary Information (ESI)

for

Selective deoxygenation of stearic acid via an anhydride pathway

Stefan A.W. Hollak, Johannes H. Bitter, Jacco van Haveren, Krijn P. de Jong and Daan S. van Es

CATALYST CHARACTERIZATION

Pd/γ-Al_2O_3 (4.5 wt% Pd) was obtained from BASF. Room temperature XRD measurements were carried out using a Bruker-AXS D2 Phaser powder X-ray diffractometer, in Bragg-Brentano mode, equipped with a Lynxeye detector. The radiation used is Cobalt $K_{\alpha 1,2,}$ l = 1.79026 Å, operated at 30 kV, 10 mÅ. The system is theta-theta coupled with a goniometer radius of 217.5 mm. The XRD diffractogram of the catalyst can be found in figure S2.

Nitrogen physisorption was performed at 77 K using a Micromeritics Tristar 3000 V, 6.04 Å. The obtained data were used to calculate the BET surface area. Prior to the physisorption measurements, the samples were dried at 473 K for about 14 h under nitrogen flow. Micropore volumes and external surface areas were determined using t-plot analysis and are shown in table S1.

Imaging of the sample was obtained through Transition electron microscopy (TEM), performed on a FEI Tecnai20F Transmission Electron Microscope operated at 200 kV. The instrument is provided with a Schotkky Field Emission Gun and a Twin Objective lens. The magnification range is 25 x – 700 kx, the point to point resolution is 0.27 nm and the lattice image resolution of 0.14 nm. The images are made with a Megaview II digital camera. Furthermore the microscope is provided with an Energy Dispersive X-ray micro analysis system (EDAX) to provide elemental information, and a Scanning Transmission Electron Microscope (STEM) to obtain images with a High Angle Annular Dark Field (HAADF) and Secondary Electron (SE) detector. The samples were suspended in ethanol using an ultrasonic treatment and brought onto a holey carbon film on a copper grid. TEM images of the catalyst are shown in figure S3.

Palladium dispersion was determined by hydrogen chemisorption measurements using a Micromeritics ASAP 2020 apparatus. The samples were dried at 393 K in a He flow for 30 min and subsequently reduced in a 50 % H_2 / He flow at 523 K for 2 h (5 K min^{-1}). The H_2 adsorption isotherms were measured at 423 K, and calculations for the percentage Pd dispersions were performed assuming a complete Pd reduction with the stoichiometry of one hydrogen atom adsorbed per Pd surface atom (table S1).

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) measurements were performed on an optima 7000 DV/ Perkin Elmer spectrometer to measure the Palladium content of the catalyst. The analyses were performed in duplicate and have an accuracy of ± 0.3 %. The metal loading of the Pd/γ-Al_2O_3 was measured to be 4.5 ± 0.3 wt% Pd.

REACTION PROCEDURE

The catalyst (typically 0.5 g) was activated prior to catalytic reactions in a plug flow reactor where the catalyst was heated to 523 K (5 K min^{-1}) in nitrogen (3.0, Linde, 200 mL min^{-1}) atmosphere and subsequently reduced at 523 K for 2 hours in 10 % hydrogen (9.86 vol% in nitrogen, Praxair). After reduction, the catalyst was flushed with nitrogen at 523 K to remove all hydrogen from the reactor and catalyst surface and cooled to room temperature in nitrogen (200 mL min^{-1}). The plug flow reactor was subsequently transferred to a glovebox to add solvent, reactant and internal standard prior to catalytic reactions.

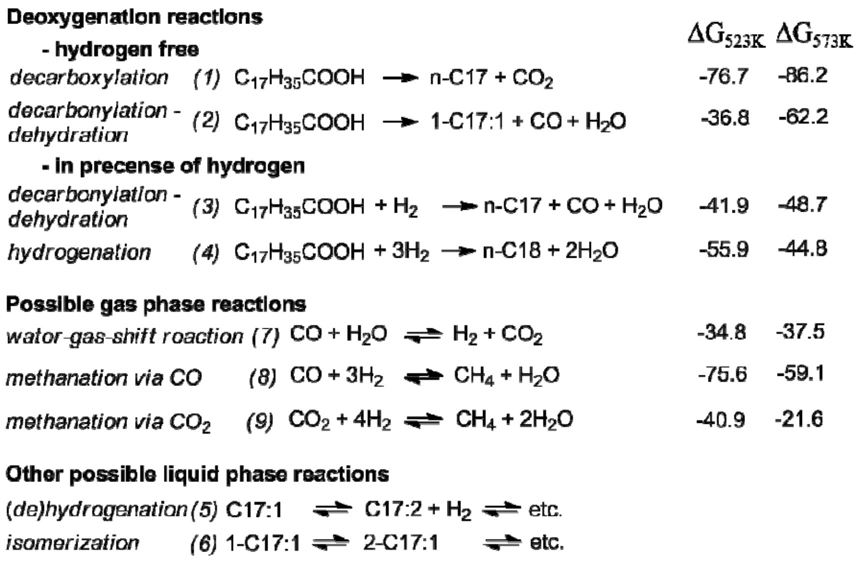
Catalytic experiments at temperatures up to 523 K were performed in a multiple reactor system (Parr, model MRS 5000) containing six 75 mL vessels with magnetic stirring. Pressure and temperature were monitored continuously during catalytic tests using this setup. The catalyst used was a fine powder with d50 of 70 µm and was stirred (1100 rpm) to avoid external mass transfer limitations. It was determined that pore diffusion limitations are negligible for all reaction conditions according to the Weisz-Prater Criterium (the liquid phase effective diffusivities were estimated according to Wilke and Chang[25]).

In a typical reaction 1 g feed was used and 18 g dodecane (25 mL, 99+%, Fluka) as solvent. 0.5 g Tetradecane (2.5 mmol, puriss., olefin free, ≥99%, Aldrich) was used as internal standard for quantitative analysis by GC. A 600 mL single bench top autoclave reactor system (Parr, model 4563) with mechanical stirrer was used for reactions at reaction temperatures up to 623 K. Analogous ratios of catalyst, reactant and feed was used as in the multiple reactor system. When feed concentration was varied, the total volume was kept constant to retain the same proportion of dead volume in the reactor.

PRODUCT ANALYSIS

The reaction mixtures were dissolved in chloroform and hot filtration at 313 K was performed to collect the spent catalyst. Part of the filtered samples were mixed with trimethyl sulfonium hydroxide (TMSH, purum, ≈ 0.25 M in methanol, Aldrich) as *in-situ* esterification reagent to derivatise carboxylic acids for accurate quantification of these products. Other part of the filtered samples were mixed with diethylamine (>99.5%, Aldrich) to convert residual stearic anhydride to octadecanamide and stearic acid in order to facilitate quantification. Product analysis of low molecular weight (approx. 350 g mol^{-1}) products was performed on a Hewlett-Packard 5890 Series II Gas Chromatograph (GC) equipped with an automatic injection system (HP7673 GC/SFC Injector and Controller). Injection volume 1µl. Split ratio 1:20. Column pressure 150 kPa Helium. GC column: Varian CP-FFAP (free fatty acids), 25 m x 0.32 mm x 0.30 µm. Detector: FID at 553 K. Injection port temperature 523 K. GC program: Hold 1 min at 323 K, ramp 7 K min-1 to 423 K, then ramp 4 K min-1 to 523 K and hold at 523 K for 20 minutes. Product analysis of stearone and other relatively large molecules was performed on a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with an automatic injection system (HP7673 GC/SFC Injector and Controller). Injection volume 1µl. Split ratio 1:20. Column pressure 150 kPa Helium. GC column: Varian Select Biodiesel for Glycerides, 15m x 0.32mm x 0.45µm. Detector: FID at 553 K. Injection port temperature 653 K. GC program: Hold 1 min at 323 K, ramp 15 K/min to 453 K, then ramp 7 K/min to 503 K, then ramp 30 K/min to 653 K and hold 7 min at 653 K. GC-MS analyses were performed on an Interscience TraceGC Ultra GC with AS3000 II autosampler. He carrier gas, flow 1 mL min^{-1}, split flow 20 mL min^{-1}; Restek GC column Rxi-5ms 30 m x 0.25 mm x 0.25 µm; GC program hold 1 min at 323 K, ramp 7 K min^{-1} to 423 K, then ramp 4 K min^{-1} to 613 K and hold at 613 K for 20 minutes. The GC column is connected to an Interscience TraceDSQ II XL quadrupole mass selective detector (EI, mass range 35 - 500 Dalton, 150 ms sample speed).

TABLES AND FIGURES



Deoxygenation reactions			ΔG_{523K}	ΔG_{573K}
- hydrogen free				
decarboxylation	*(1)*	$C_{17}H_{35}COOH \rightarrow n\text{-}C17 + CO_2$	-76.7	-86.2
decarbonylation - dehydration	*(2)*	$C_{17}H_{35}COOH \rightarrow 1\text{-}C17{:}1 + CO + H_2O$	-36.8	-62.2
- In precense of hydrogen				
decarbonylation - dehydration	*(3)*	$C_{17}H_{35}COOH + H_2 \rightarrow n\text{-}C17 + CO + H_2O$	-41.9	-48.7
hydrogenation	*(4)*	$C_{17}H_{35}COOH + 3H_2 \rightarrow n\text{-}C18 + 2H_2O$	-55.9	-44.8
Possible gas phase reactions				
water-gas-shift reaction	*(7)*	$CO + H_2O \rightleftharpoons H_2 + CO_2$	-34.8	-37.5
methanation via CO	*(8)*	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-75.6	-59.1
methanation via CO_2	*(9)*	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	-40.9	-21.6
Other possible liquid phase reactions				
(de)hydrogenation	*(5)*	$C17{:}1 \rightleftharpoons C17{:}2 + H_2 \rightleftharpoons$ etc.		
isomerization	*(6)*	$1\text{-}C17{:}1 \rightleftharpoons 2\text{-}C17{:}1 \rightleftharpoons$ etc.		

Figure S1. Overview of possible deoxygenation reactions, gas phase reactions and other liquid phase reactions which could occur during catalytic reactions with or without hydrogen. Thermodynamic data are included (ΔG in kJ mol^{-1} at 1 bar).[23]

Table S1. Physical properties of the Pd/Al_2O_3 catalyst before and after catalytic reaction.

	BET specific surface area[a] [m^2 g^{-1}]	Particle Size[b] [nm]	Dispersion[c] [%]
Before reaction	111	6.7	17
After reaction [d]	116	7.0	16

Obtained by [a] N_2 physisorption, [b] H_2-chemisorption, [c] Dispersion calculated from particle size as described by Scholten et al.[26] [d] Reaction conditions: 573 K, 24h, 7 bar N_2

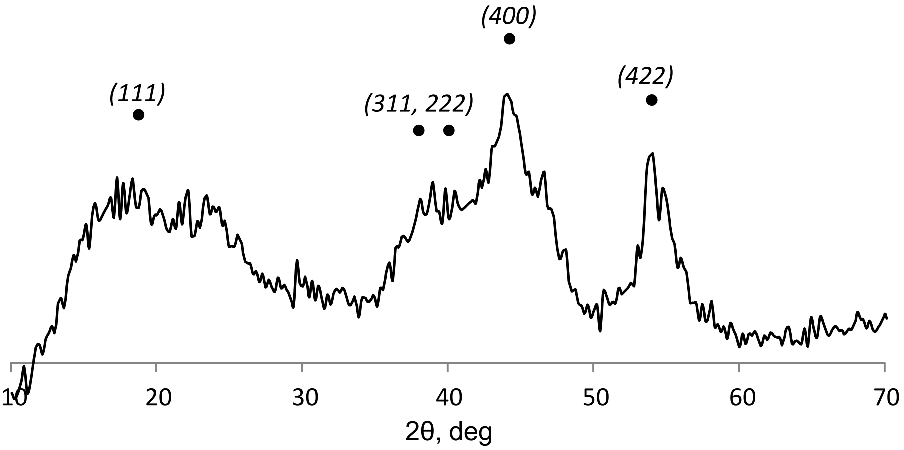


Figure S2. XRD pattern of fresh Pd/Al_2O_3 catalyst. γ-Al_2O_3 diffractions marked with a dot. Palladium diffractions (at 2θ = 46.6° and 54.2°) not detected due to overlap with γ-Al_2O_3 diffractions.

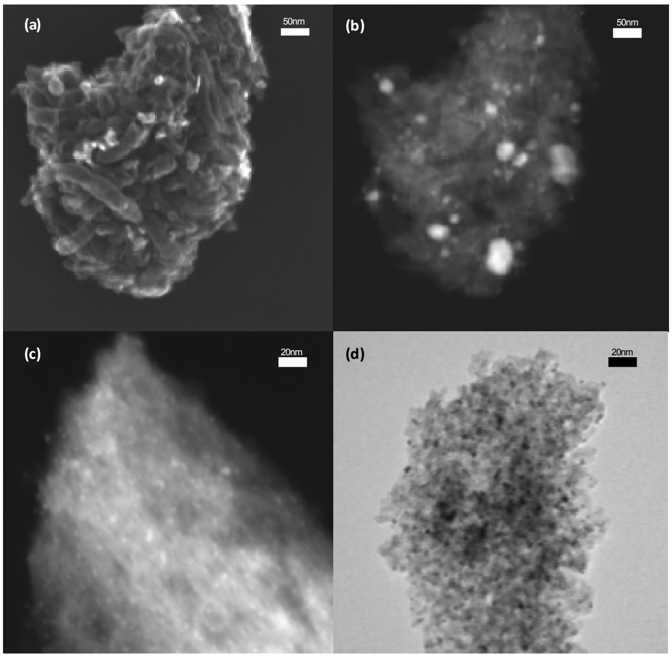


Figure S3. Electron microscopy images of Pd/Al_2O_3 catalyst. a) SEM image displaying relatively large (10-50 nm) palladium particles on surface. b) Dark field image displaying same position as (a). c) TEM dark field image and d) TEM bright field image with small, finely dispersed (3.8 ± 1.4 nm) palladium particles.

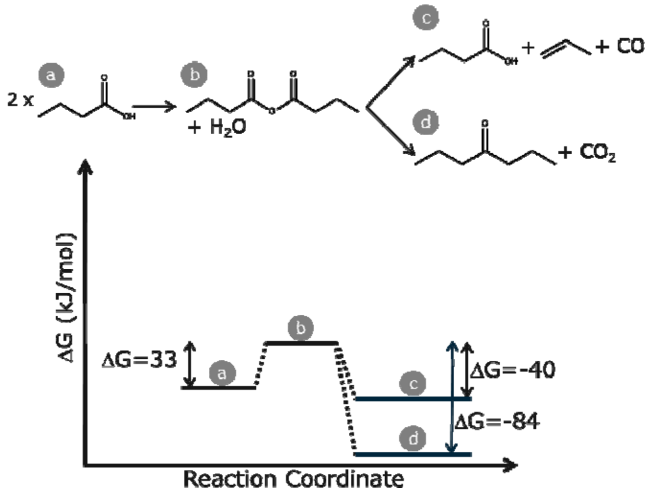


Figure S4. Gibbs free energy of decarbonylation and ketonization reaction pathways from butyric acid via a butyric anhydride intermediate. Calculations for 523 K at 1 bar; data calculated with HSC Chemistry.[23]

25 C. R. Wilke and P. Chang, *AIChE J.*, 1955, **1**, 264-270.

26 J. J. F. Scholten, A. P. Pijpers and M. L. Hustings, *Catal. Rev. Sci. Eng.*, 1985, **27**, 151-206.