Fuel 89 (2010) 2033–2039

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Deoxygenation of dodecanoic acid under inert atmosphere

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ARTICLE INFO

Article history:
Received 14 April 2009
Received in revised form 20 October 2009
Accepted 5 November 2009
Available online 24 November 2009

Keywords:
Deoxygenation
Decarboxylation
Fatty acid
Palladium
Carbon

ABSTRACT

A laboratory-scale fixed bed reactor (down-flow) was developed for the deoxygenation of dodecanoic (lauric) acid under inert atmosphere. This reaction can be utilized to produce renewable diesel components. The main products were undecane (decarboxylation) and undecene (decarbonylation). The catalysts were a palladium catalyst supported on mesoporous carbon, Sibunit (egg-shell type with spherical granules of 1.6–2.0 mm in diameter), and a commercial Pd/C catalyst. The challenge was to obtain a high activity and selectivity to undecane, as pure dodecanoic acid without any solvents was used. Moreover, the complete reactor system consisting of a reactant feed vessel, a pump, lines, a sampling valve, and a collector of the residue had to be heated, since saturated fatty acids with more than nine carbon atoms have a melting point exceeding 20 °C. The influence of reaction conditions, such as reaction temperature (300–360 °C), pressure (5–20 bar), gas flow rate, reactant concentrations, was studied. The reactant conversion increased when an inert gas (argon) flow was applied co-currently with the reactant flow. The argon pressure did not have any significant impact on the performance. The reason for the catalyst deactivation was determined to be coking.

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1. Introduction

Within process development, many factors have to be taken into account to achieve an optimal design. For catalytic reactions, the catalyst has a key role and factors, such as selectivity, activity, lifetime, regeneration ability, mechanical and thermal stability, morphology, and production costs are all of crucial importance [1,2]. Besides the catalyst, the selection of the reactor equipment is the most important factor in process development [1]. The reaction conditions, the size and shape of the reactor, as well as the operating mode have to be selected and optimized.

Societies all over the world are encouraged to utilize renewable energies such as solar, wind, hydroelectricity, and biomass. One of the major driving forces to use renewable energy is to secure the access of energy at an affordable price, since the world demand for energy is constantly growing due to the increase of the world population and mobility as well as an improved standard of living. Another driving force for renewable energy sources is the threat of climate change that would result from the anthropogenic emission of CO_2 into the atmosphere [3]. The power sector can use a variety of renewable sources, while the transportation sector is limited to biomass, since it is the only renewable resource of liquid fuels [3]. In the next 25 years, the global need for liquid fuels is expected to increase more rapidly in the transportation sector than in any other end-use sector [4]. Examples of alternative transportation fuels are bioethanol, fatty acid methyl esters, and n-paraffinic compounds. The renewable diesel NExBTL of Neste Oil consists of n-paraffinic compounds obtained through hydrotreating of vegetable oils and animal fats [5]. NExBTL has a very high cetane number, is free from aromatics and sulfur and has been commercially available since 2007. The current production technology, where alkanes are produced through hydrotreating, requires large volumes of hydrogen. To avoid the use of hydrogen and consequently ensuring a higher safety and reducing the production costs, the feed stock can be deoxygenated under inert atmosphere (alternatively inert gas with 1–5% of hydrogen).

The deoxygenation (decarboxylation and decarbonylation) of saturated and unsaturated fatty acids and fatty acid derivatives under inert atmosphere (Ar, N_2, and He) and in the presence of hydrogen has previously been studied and published by our laboratory during the period of 2005–2008 [6–12]. Several catalysts, such as supported Ni, Ru, Pd, Pt, Ir, Os, and Rh, were evaluated in the deoxygenation of stearic acid (dissolved in dodecane) in a pressurized semi-batch reactor and it was concluded that the most promising catalyst was a carbon-supported palladium catalyst [6]. Already

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0016-2361/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2009.11.006

in 1936, Bertram [13] published results of the decarboxylation of stearic acid to heptadecane using a homogeneous selenium catalyst. Later on in 1979, Foglia and Barr [14] used homogeneous palladium and rhodium complexes in the conversion of fatty acids to alkenes. Prior to 21st century, heterogeneous catalyzed decarboxylation of vegetable-based feeds was scarcely studied (with except of pyrolysis). The decarboxylation of aliphatic and aromatic carboxylic acids has been carried out in gas phase over Pd/SiO_2 and Ni/Al_2O_3 [15]. Moreover, in a patent [16] the production of straight chain olefins from saturated fatty acids and fatty acid esters over nickel-based catalysts promoted with either tin, germanium or lead has been described.

The deoxygenation of fatty acids and their derivatives has not only been studied in semi-batch but also in continuous mode [10–12]. Mäki-Arvela et al. [11] investigated the deoxygenation of dodecanoic acid in a fixed bed reactor operated in up-flow mode. The reactant dodecanoic acid was dissolved in dodecane at a concentration of 0.22–0.44 mol/l (pure dodecanoic acid has a concentration of 4.4 mol/l). A 5% Pd/C powder catalyst was used and the effect of the catalyst mass, the initial concentration of dodecanoic acid, and the solvent was studied. Due to deactivation, the conversion of dodecanoic acid declined from around 100% to 5–20%, depending on the conditions used, within 10–20 min of time-on-stream. Catalyst reactivation with hydrogen did not restore the catalyst activity.

Deoxygenation of fatty acids is a challenging task, mainly because of the low reaction rate and the rapid catalyst deactivation. Moreover, saturated fatty acids (with more than nine carbon atoms) have a high melting point, which makes the operation in continuous mode particularly challenging, since the complete reactor system must be heated. Laboratory-scale reactor systems that fulfill all the requirements do not exist on the commercial market and especially laboratory high-pressure pumps that can be heated are, to our knowledge, not available. Therefore, there was a need to develop a new reactor system. The reactor is a laboratory-scale fixed bed reactor and all parts of the reactor set-up, namely reactant feed vessel, pump, lines, sampling valve, and collector of the residue, were heated. A detailed description of the new reactor system along with the results from the deoxygenation of dodecanoic acid is presented in this paper.

Since carbon-supported palladium catalysts were superior to the other catalysts screened in the deoxygenation of fatty acids in slurry reactors [6,7], the synthetic mesoporous carbon Sibunit [17,18] was selected as the support material in the present work. Sibunit is the name of a class of porous carbon–carbon composite materials combining the advantages of graphite (chemical stability and electric conductivity) and active carbon (high specific surface area and adsorption capacity) [17,18]. Sibunit is produced in the form of powders with particle sizes of 5–200 μm, spherical granules of 0.2–4 mm diameter, and extrudes in the shape of cylinders, tubes, trefoils, and quatrefoils, as well as blocks of honeycomb structure.

For fixed bed applications, the catalyst particles should be large enough to avoid a significant pressure drop, but at the same time, internal diffusion can become be significant for large organic molecules. A 1.6–2.0 mm spherical egg-shell Pd/Sibunit catalyst was synthesized for the dodecanoic acid deoxygenation in the fixed bed reactor. The egg-shell catalyst structure was preferred since the large organic molecules (dodecanoic acid and the products) have low values of diffusion coefficients and thus the internal mass transfer limitation on a conventional catalyst pellets is severe.

In this study, a laboratory-scale fixed bed reactor (down-flow) was developed for the deoxygenation of dodecanoic acid under inert atmosphere. As pure dodecanoic acid without solvent was used (the melting point was 45 °C), the complete reactor system had to be heated. The aim was to develop a continuous reactor system and to study the catalyst deactivation, which has been the main challenge in previous studies [11]. The fresh and used catalyst were characterized by transmission electron microscopy (metal particle size, sintering) and nitrogen physisorption (catalyst surface area, coking).

2. Experimental

2.1. Catalyst preparation

Samples of the egg-shell Pd/Sibunit catalyst with a Pd content of 1.0 wt% were prepared by an incipient wetness impregnation method, which includes spraying the solutions H_2PdCl_4 and Na_2CO_3 onto the carbon granules agitated in a rotating cylinder. The aqueous solution of H_2PdCl_4 and Na_2CO_3 with the molar ratio 1:21 was ripened for 18 min to form polynuclear palladium (II) hydroxocomplexes. After the metal impregnation and drying at room temperature and subsequently in vacuum at 70 °C, the catalyst was reduced in the flow of hydrogen at 250 °C (temperature ramp 10 °C/min). Washing with water was continued until no Cl^- ions were detected in the wash water, after which the catalyst was dried at 70 °C. Profiling analysis has previously demonstrated that palladium was predominantly located within a distance of 18 μm from the outer surface [19].

2.2. Catalyst characterization

The catalyst was characterized by transmission electron microscopy (TEM) and nitrogen physisorption. Electron microphotographs of the samples were taken by a LEO 912 OMEGA energy-filtered transmission electron microscope by using 120 kV acceleration voltage. Histograms of particle size distribution were obtained by counting at least 100 particles on the micrographs for each sample.

The specific surface areas of fresh and used (washed with hot ethanol) catalysts were measured with a combined physisorption-chemisorption apparatus (Sorptometer 1900, Carlo Erba Instruments). The catalysts were outgassed at 150 °C for 2 h prior to the analysis. The BET method was used for the calculation of the surface areas.

2.3. Reactor set-up

The first step in developing the fixed bed reactor system for the deoxygenation of fatty acids was to construct a small fixed bed reactor (for diluted fatty acid). The reactor length was 150 mm and the inner diameter was 5.6 mm. The reactant dissolved in the solvent was pumped from a glass bottle. The pump (Eldex pump 1 SMP, flow interval 0.003–5.0 ml/min) was connected with the upper part of the reactor via stainless steel tubing. The samples were withdrawn at the bottom of the reactor and the residue was led to a collector. The reactor allowed operation in the pressure range of 0–40 bar, the temperature interval of 25–500 °C and a flow rate of the inert gas (Argon) of 0–300 ml/min. The pressure and mass flow controllers were manufactured by Brooks Instruments. A thermocouple was placed in the bottom of the reactor and the temperature in the catalyst bed was monitored. In the first reactor set-up, only the fixed bed itself was heated, which implies that only reactants being in liquid phase at room temperature could be used.

The following step of the reactor development was to modify the pump, the lines, the reactant feed vessel, and the collector to be able to heat the complete reactor system (see schematic picture in Fig. 1). The heated system allowed us to use reactants having a melting point exceeding room temperature without diluting them

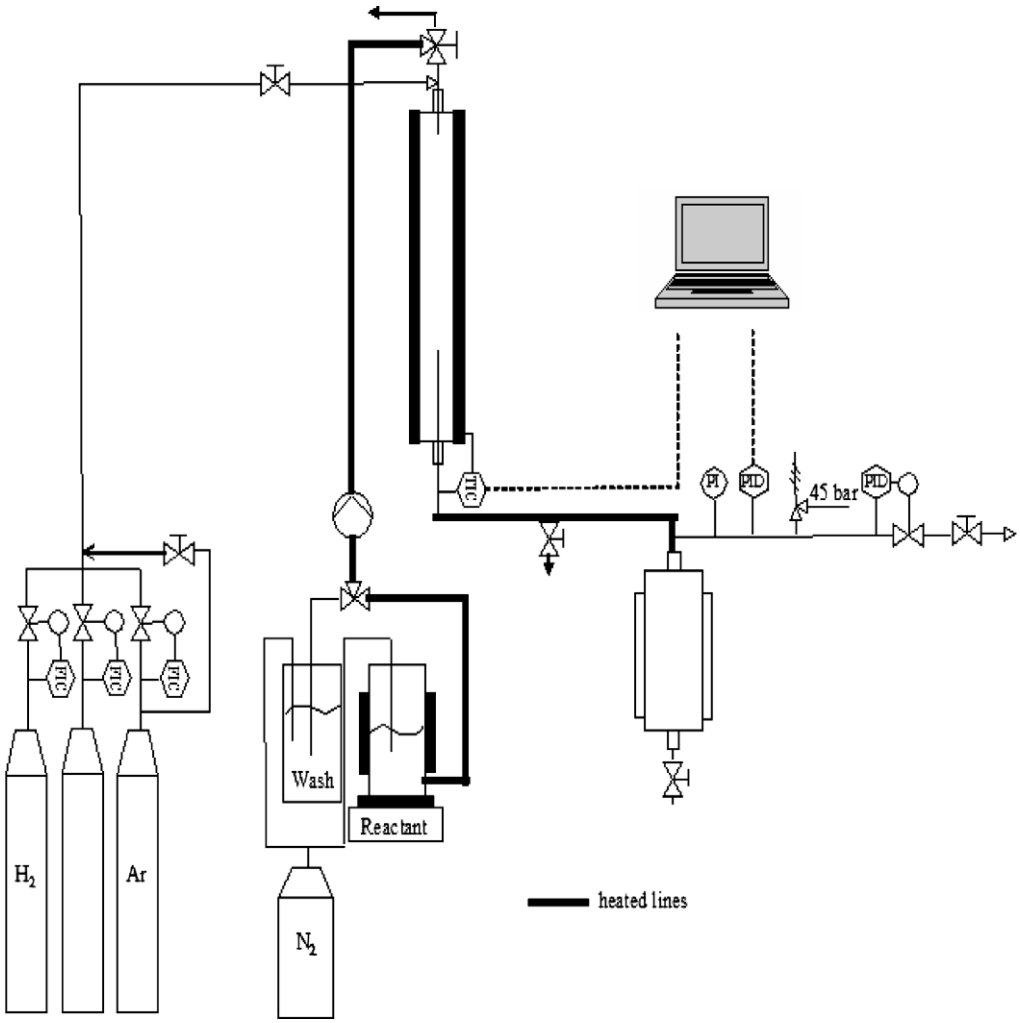

Fig. 1. Schematic picture of the reactor system.

with a solvent. A larger fixed bed reactor with the inner diameter 15.9 mm (the reactor length was 150 mm, the same as the small reactor) was built to allow larger catalyst amounts to be used with a concentrated reactant feed. The reactant feed vessel was made of stainless steel and surrounded by a heating jacket and placed on a hot plate. The pump was modified by using a heater block around the pump head and heated with a heating cartridge. A heating cord was twisted around the line from the pump to the inlet at the top of the reactor and insulation (Armacell HT/Armaflex) was put around the line to avoid cold spots. The reactor was a stainless steel tube surrounded by heated aluminium blocks. All lines and valves were heated by heating cords. The collector was heated by a heating jacket. The temperature controllers were supplied by Bernd Kletti GmbH. Since the small and large reactors were of the same length (only the diameter was different), the possibility to change between the smaller and larger fixed bed reactor made the system more flexible. In this work, the experiments with 2 g of the catalyst were carried out in the smaller reactor, while the rest of the experiments were made in the larger reactor.

2.4. Experimental procedure

The inlet tube for the liquid feed was placed in the upper part of the fixed bed and the thermocouple was located in the bottom of the bed. Quartz wool with a layer of quartz sand on top of it was used to keep the catalyst in place. The smaller reactor was filled with the catalyst and a layer of quartz sand was placed at the top of catalyst bed to distribute the liquid phase over the reactor cross-section. As the larger reactor was used, quartz sand was not only put as layers, but also mixed into the catalyst bed to dilute the catalyst. Prior to the experiment, the catalyst was reduced at 200 °C for 2 h in 100 ml/min hydrogen flow (heating rate 10 °C/min). After the reduction, the hydrogen flow was replaced by argon and the reactor was pressurized to the desired pressure and heated to the reaction temperature. As the reaction pressure and temperature were attained, the feeding of reactant, dodecanoic acid (lauric acid, Aldrich, 98%) with or without solvent dodecane (Fluka, 98%), was started and the reaction time was set to zero.

Samples from the reactor outlet were withdrawn at different time intervals. The samples were diluted with dodecane and the internal standard n-pentadecane (Acros, 99%) was added to a small volume of a diluted sample. From this mixture, an aliquot of 40 μl was inserted into a vial and 200 μl of the silylation agent N,O-bis(trimethylsilyl)trifluoro-acetamide (BSTFA, Acros, 98%) was added. The samples were placed in an oven at 70 °C for 30 min and analyzed by a gas chromatograph (GC, HP 6890). The GC was equipped with a DB-5 column (length 60 m, inner diameter 0.32 mm, film thickness 0.5 μm) and a flame ionisation detector (FID) operating at 300 °C. An aliquot of 1 μl of the silylated samples was injected with an autosampler. The injection temperature was 260 °C and the split ratio was 1:10. Helium served as the carrier gas. The initial temperature of the column was 80 °C (for

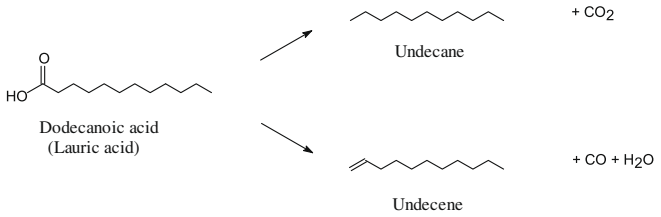

Fig. 2. Reaction scheme for the deoxygenation of dodecanoic acid to undecane and undecene.

0.5 min) and the temperature increased with a rate of 10 °C/min to 150 °C and with 5 °C/min to 290 °C (for 10 min). The peaks in the chromatogram were identified by analysis with combined gas chromatography-mass spectrometry (GC-MS) analysis. The quantification of the results was made using the internal standard and normalization of the results from the analysis of the liquid samples (the sum of mass fractions of all liquid components found in the sample was equal to 1).

3. Results and discussion

The reaction scheme for deoxygenation is displayed in Fig. 2. The main reaction is the decarboxylation of dodecanoic (lauric) acid to undecane and the side reaction is the decarbonylation to undecene (different isomers). Other reactions, such as cracking to form shorter carbon chains, aromatization as well as oligomerization and polymerization, can also take place. As solvent free dodecanoic acid was used, small amounts of aromatic compounds (e.g. pentylbenzene, 1-methylbutylbenzene, 1-methyl-4-(1-methylpropyl)-benzene) were also formed during the reaction. These products were detected by GC-MS in the liquid samples. However, even though the amount of aromatic compounds was only about 10%–20% of the amount of undecane and undecene, the aromatic compounds can still have a significant effect on the catalyst deactivation.

The carbon balance was assessed based on the analysis of the liquid phase. Calibration with an internal standard was performed for the reactant and the product, giving the response factors, which were then used in quantitative analysis of the products. The combined molar yield of undecane and undecene (as well as of aromatic compounds) corresponded well to the consumption of lauric acid within the precision of calibration and GC analysis.

The influence of concentration and gas flow on the deoxygenation (for a commercial Pd/C catalyst) is shown in Fig. 3. The conversion of dodecanoic acid was between 90 and 100% as the concentration of dodecanoic acid was 0.22 mol/l and the argon flow through the reactor was 10 ml/min (co-current with the liquid

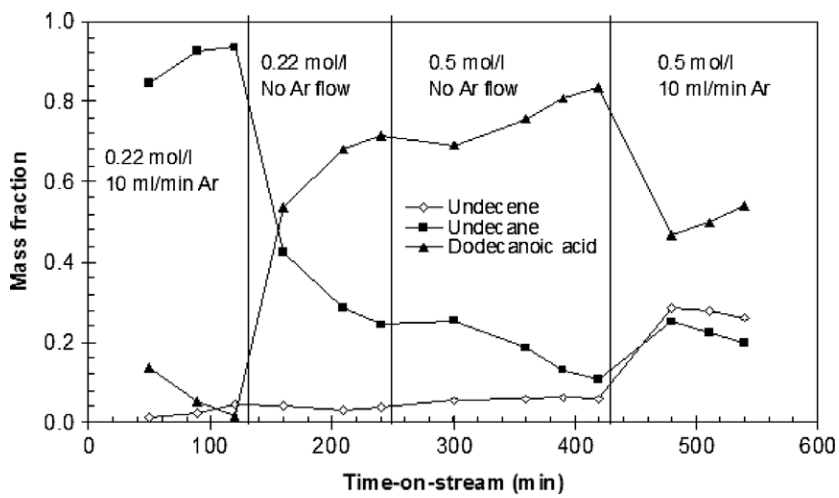

Fig. 3. Deoxygenation of dodecanoic acid as a function of time-on-stream. Operating conditions: 2 g of commercial Pd/C catalyst, 0.075 ml/min reactant flow rate (WHSV 1.7 h^{-1}), 15 bar argon pressure, 300 °C.

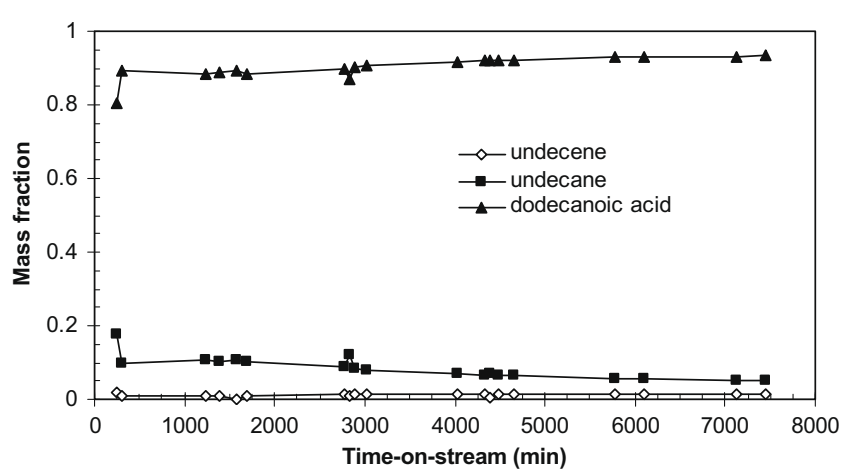

Fig. 4. Deoxygenation of dodecanoic acid as a function of time-on-stream. Operating conditions: 2 g 1% Pd/Sibunit, 0.075 ml/min reactant flow rate (WHSV 1.7 h^{-1}), 15 bar argon pressure, 300 °C, no gas flow through the reactor, 0.5 mol/l dodecanoic acid in dodecane.

flow). As the gas flow was stopped, the conversion dropped to approximately 30%. Subsequently the concentration of dodecanoic acid was increased to 0.5 mol/l (no gas flow). During a period of three hours with the higher concentration and no gas flow, the conversion slowly decreased. Thereafter, the argon flow was switched on again, and the conversion increased from 20% to 50%. Applying an inert gas flow through the reactor could remove the product gases such as CO_2 and CO from the catalyst surface and from the reactor, thus improving the conversion. The deoxygenation of diluted dodecanoic acid in an up-flow fixed bed reactor was studied in reference [11]. No inert gas flow was applied and the catalyst deactivated rapidly; within 30 min of time-on-stream the conversion went from close to 100% to less than 5% [11].

The results for the 1% Pd/Sibunit catalyst are given in Fig. 4. At a low concentration domain, e.g. as 0.5 mol/l dodecanoic acid in dodecane and 2 g of catalyst was used (WHSV 1.7 h^{-1}), the catalyst was deactivating slowly and was rather stable at around 10% conversion.

The influence of the inert gas (argon) pressure (5–20 bar) and temperature (300 and 360 °C) was studied using diluted dodecanoic acid and 1% Pd/Sibunit. The argon pressure did not have any influence on the reaction rate, while the influence of the temperature was significant, as shown by Fig. 5. As the temperature was increased from 300 to 360 °C, the conversion increased from 10% to 60%.

Experiments with lauric acid (not shown here) as well as data obtained for stearic acid [20] performed using different catalyst batches under identical conditions demonstrated very good reproducibility of catalytic activity within 5%–10%. The precision of GC analysis was within 5%.

The larger fixed bed reactor (the heated reactor system) was used at higher concentrations of dodecanoic acid. Dodecanoic acid diluted with dodecane was used in the beginning of the experiment, after which the concentration was gradually increased until solvent-free conditions were reached. The results presented in Fig. 6 show that an almost complete conversion was achieved as the reactant concentration was 0.8 mol/l (at the beginning of the experiment) and the temperature 360 °C. Then the concentration was increased to 1.4 mol/l and eventually solvent-free conditions (4.4 mol/l) were applied and the conversion started to decrease rather rapidly until reaching a value of ca. 30%.

The results from the deoxygenation at solvent-free conditions and 300 °C are shown in Fig. 7. It can be seen that the catalyst deactivated within 28 h: the conversion level dropped 85% to merely 3%. However, the catalyst activity can be improved by increasing the temperature. The reasons for the catalyst deactivation can in

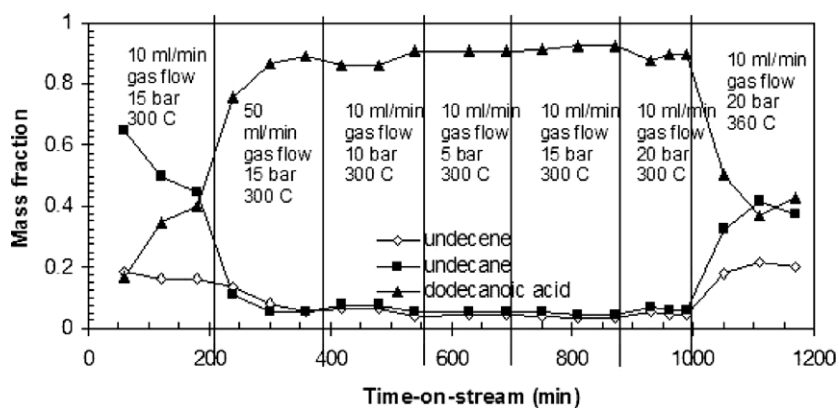

Fig. 5. Deoxygenation of dodecanoic acid as a function of time-on-stream. Operating conditions: 2 g 1% Pd/Sibunit, 0.075 ml/min reactant flow rate (WHSV 1.7 h^{-1}), 0.5 mol/l dodecanoic acid in dodecane.

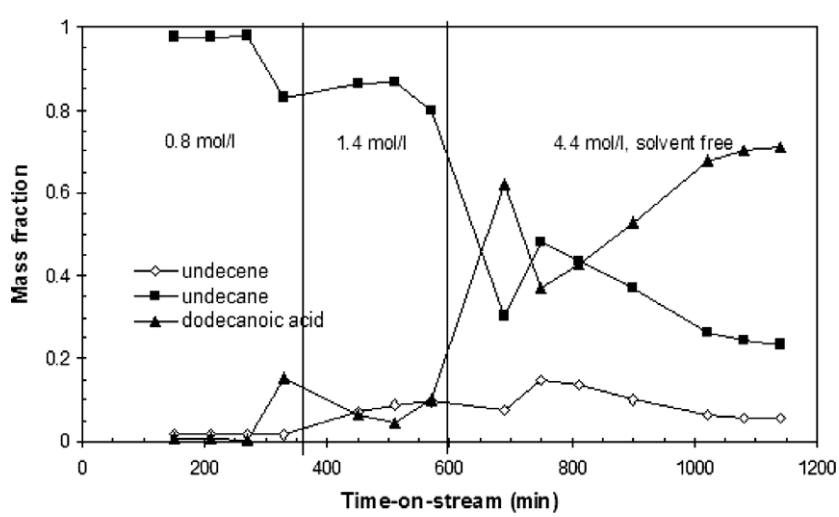

Fig. 6. Deoxygenation of dodecanoic acid as a function of time-on-stream. Operating conditions: 5 g 1% Pd/Sibunit, 0.075 ml/min reactant flow rate (WHSV 0.8 h^{-1} at solvent-free conditions, 4.4 mol/l), 360 °C, 20 bar argon pressure, 10 ml/min argon flow.

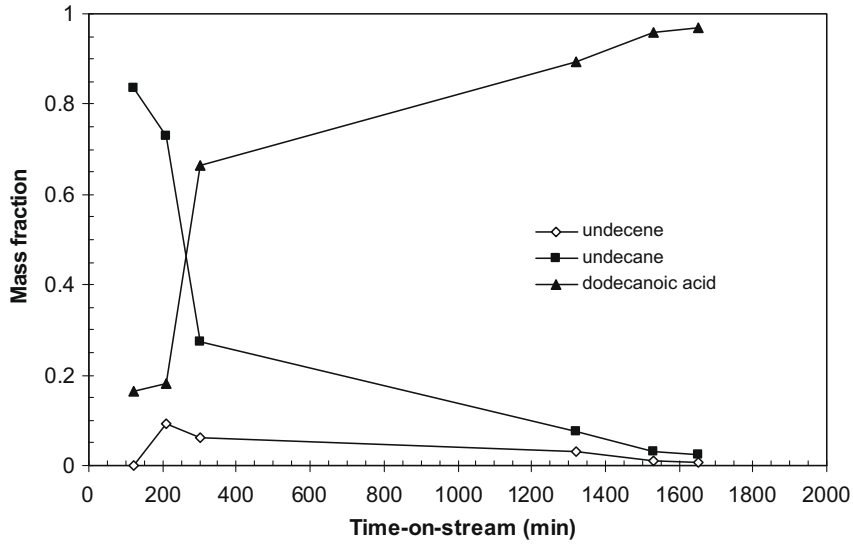

Fig. 7. Deoxygenation of dodecanoic acid as a function of time-on-stream. Operating conditions: 12 g 1% Pd/Sibunit, 0.075 ml/min reactant flow rate (WHSV 0.33 h^{-1}), 300 °C, 15 bar argon pressure, 10 ml/min argon flow, 4.4 mol/l (solvent-free conditions).

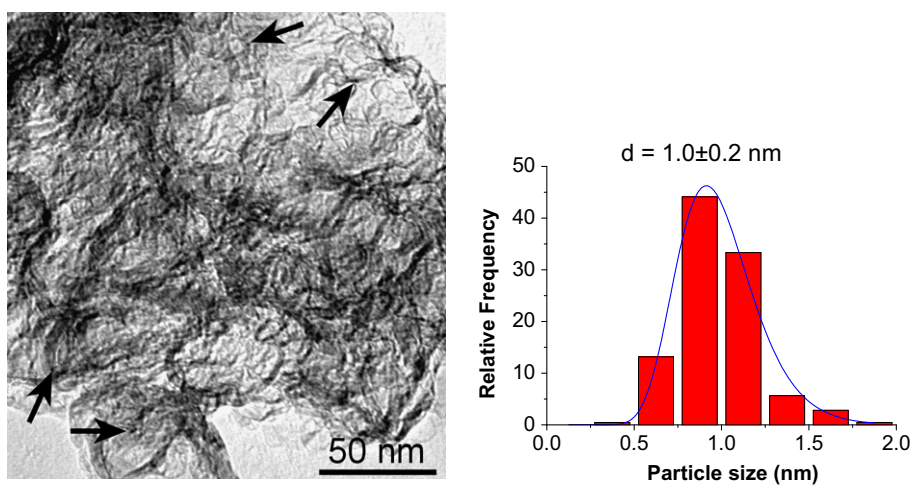

Fig. 8. Transmission electron microgram (TEM) and histogram of the fresh 1% catalyst Pd/Sibunit.

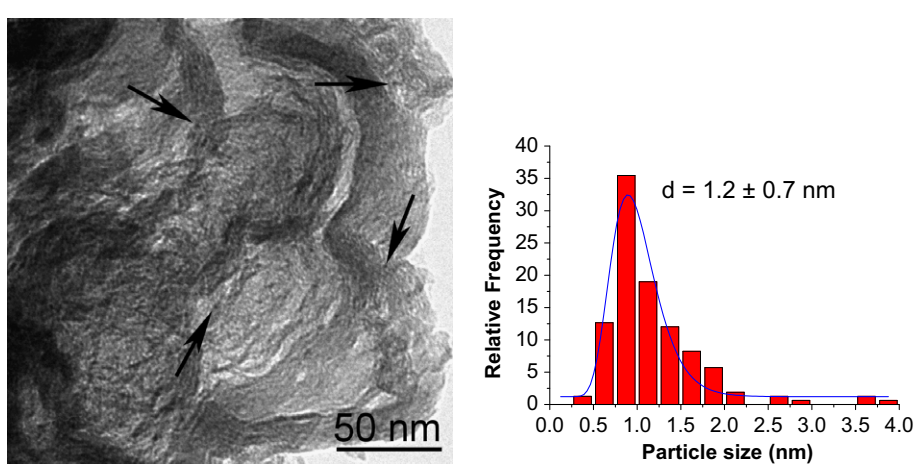

Fig. 9. Transmission electron microgram (TEM) and histogram of the spent 1% catalyst Pd/Sibunit (taken at the end of the experiment in Fig. 7).

Table 1
Surface area of the fresh and the used catalysts.

Catalyst	BET surface area (m^2/g)
1% Pd/Sibunit, fresh	390
1% Pd/Sibunit, used[a]	310

[a] The catalyst was used in the experiment in Fig. 7.

principle be metal sintering, metal leaching, poisoning and/or fouling.

In this case, the deactivation cannot be due to leaching of palladium as no palladium was detected in the product. The metal particle size of the fresh and the used catalyst was determined using transmission electron microscopy (TEM). The microgram and histogram of the fresh catalysts are presented in Fig. 8; the mean diameter of the palladium particles was 1 nm. Minor sintering could be visible, as the mean diameter of the metal particles was 1.2 nm after the reaction (Fig. 9) and a small fraction of particles in the range 3.5–4 nm was noticeable. In practice, the metal particle size did not change during the reaction and sintering cannot be an explanation for deactivation.

The surface area of the fresh and the used catalyst was determined by nitrogen adsorption (Table 1, catalyst used in the experiment in Fig. 7). The surface area of 1% Pd/Sibunit decreased with 20% during the reaction, which suggests coking to take place. From this result it can be concluded that the most probable reason for catalyst deactivation is coking of the catalyst.

4. Conclusions

The deoxygenation of dodecanoic (lauric) acid to undecane (decarboxylation) and undecene (decarbonylation) was carried out under inert atmosphere in a laboratory-scale down-flow fixed bed reactor. A mesoporous 1% Pd/C catalyst (egg-shell, 1.6–2.0 mm spherical particles) was used. The deoxygenation of fatty acids is a challenging task, mainly because of the low activity, the rapid catalyst deactivation, the high melting point of the reactant (for saturated fatty acids with more than nine carbon atoms), which require that the entire reactor system must be heated when operated under solvent-free conditions. A reactor system that fulfills all the requirements was constructed and used in studying the deoxygenation of dodecanoic acid.

The influence of the reactant concentration (0.22–4.4 mol/l, where 4.4 mol/l corresponds to solvent-free conditions), gas flow, pressure (5–20 bar), and temperature (300–360 °C) was studied. The activity can be increased by increasing the reaction temperature and the gas flow rate, while the pressure did not have any significant impact on the performance. Coking is the most probable reason for catalyst deactivation, as the surface area decreased during the reaction and no leaching or sintering took place.

Acknowledgements

This work is part of the activities at the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Programmes (2000–2011) by the Academy of Finland. Krisztian Kordas is acknowledging the Academy of Finland for funding (120853, 124357, 128626).

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