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Decarboxylation of fatty acids over Pd supported on mesoporous carbon

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ABSTRACT

Fatty acid decarboxylation was studied in a semibatch reactor over 1 wt.% Pd/C (Sibunit) using five different fatty acids, C17–C20 and C22, as feeds. The same decarboxylation rates were obtained for pure fatty acids, whereas extensive catalyst poisoning and/or sintering and coking occurred with low purity fatty acids as reactants. One reason for catalyst poisoning using behenic acid (C22) as a feedstock was its high phosphorus content. The decarboxylation rate of fatty acids decreased also with increasing fatty acid to metal ratio.

1. Introduction

Biofuel production technologies have been recently studied very intensively, since the political decisions have been made to increase the use of biofuels, e.g. EU has put for 2020 the target level of 20% for the use of biofuels from the total sales of fuels. The first generation biofuels are fatty acid esters, which have certain drawbacks when used as traffic fuels in vehicles. The second generation biofuel technology is based on utilization of diesel-like hydrocarbons. This technology is currently used in industrial scale in Finland. The key reaction in this technology is catalytic deoxygenation through hydrotreating of fatty acids and their derivatives.

Catalytic deoxygenation of fatty acids in liquid phase by decarboxylation is performed preferably over carbon supported Pd and Pt catalysts [1–7]. In the previous studies the reaction conditions were optimized and kinetic models were developed describing well the kinetic data [5]. Furthermore, different feeds, such as saturated and unsaturated fatty acids and their esters and different reactor systems, namely semibatch and continuous [7] ones have been investigated in this reaction. In our recent publication the effect of metal dispersion using Pd supported on mesoporous synthetic carbon, Sibunit was studied [8]. There are no, however, systematic studies of the fatty acid chain length influence in the deoxygenation of fatty acids. In this work five different fatty acids have been used as raw materials in catalytic deoxygenation of fatty acids over a mesoporous Pd/C catalyst.

2. Experimental

Five different fatty acids ranging from C16 to C22 (heptadecanoic acid, Sigma, 98%, stearic acid, Merck, >97%, nonadecanoic acid, Fluka, >90%, arachidic acid, Sigma, 99%, behenic acid, Fluka, >80%) were used as raw materials in catalytic decarboxylation. The catalyst, 1 wt.% Pd/C (Sibunit) was prepared by depositing palladium hydroxide obtained by hydrolysis of palladium chloride at pH 8–10 [9]. The benefits using mesoporous synthetic carbon as a support material in catalytic deoxygenation of fatty acids is that this material is mechanically stable and due to its mesopores large organic compounds exhibit better accessibility to the active sites compared to the microporous support material [10].

The catalysts, both fresh and spent ones, were characterized by nitrogen adsorption, CO-chemisorption and TEM.

The pore size distribution and the pore volume were determined by nitrogen adsorption using Carlo Erba 1900 Instruments.

CO pulse chemisorption was performed using Autochem 2910 apparatus (Micromeritics). Prior to the measurements the catalysts were reduced similarly as prior to the reaction (see below). After reduction the catalyst was flushed with helium for 60 min at 300 °C to remove the adsorbed hydrogen. The CO-pulse chemisorption was performed at room temperature using 10 vol.% CO in helium (AGA). The Pd:CO stoichiometry was taken as unity.

HRTEM images were taken using JEM 2010 (JEOL, Japan) with a resolution 0.14 nm at accelerated voltage of 200 kV. The particle size distribution was calculated by 150,000-fold image upscaling.

Catalytic deoxygenation of fatty acids was performed in a semibatch reactor at 300 °C under 17 bar argon using dodecane as a solvent. Typically 1 g of catalyst was used together with 0.1 mol/l fatty acid solution in dodecane. The catalyst was reduced prior to the reaction using the following temperature programme: 10 °C/min – 60 °C, hold 1 h, 10 °C/min – 300 °C and then hold 10 min at 4.8 bar.

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The liquid phase samples were analyzed by silylating them with N,O-bis(trimethyl)-trifluoroacetamide (BSTFA) at 60 °C for 60 min after which they were analyzed in a gas chromatograph (HP 6890) equipped with DB-5 column (60 m × 0.32 mm × 0.5 μm) and FI detector. The following temperature programme was used for analysis: 130 °C, 169 °C (1 °C/min) hold for 5 min, 246 °C (5 °C/min), 250 °C (1 °C/min) hold for 1 min and 300 °C (10 °C/min) hold for 10 min. The initial pressure at 1.7 bar was kept for 30 min, thereafter the pressure was ramped with 2.4 bar/min until reaching the final pressure 2.2 bar and hold at this pressure for 64 min. The injector and detector temperature were 265 and 290 °C, respectively. The products were identified with a gas chromatograph–mass spectrometer (GC–MS). In order to make quantitative analysis eicosane was used as an internal standard.

Gas samples were taken during the reaction from the reactor and analyzed off-line with a gas chromatograph (FP 6890). The following temperature programme was used: 40 °C (7.5 min) – 25 °C/min – 80 °C (7 min) – 25 °C/min – 140 °C (5.5 min). The column was Porapack Q column (71 m, 500 μm, 50 μm). The gaseous compounds were quantified by using the following calibration gases: propene (393 ppm), propane (406 ppm), carbon monoxide (362 ppm), nitrogen (531 ppm), carbon dioxide (12 mol%) in helium (AGA) and CO 499 ppm, ethane 0.098%, methane 0.2126% in He (AGA).

Analysis of Cl^-, SO_4^{2-} and PO_4^{3-} in fatty acids was performed as follows: 0.1 g of fatty acid was immersed in 5 ml of concentrated HNO_3 (65%) and 1 ml H_2O_2 (30%). Later on, this solution was digested in a microwave oven (Anton Paar, Multiwave 3000) and diluted to 100 ml with deionized water. Two different techniques were applied in the digested sample, ICP-OES (Inductively coupled plasma optical emission spectrometry) and IC (Ion chromatography). The ICP-OES was performed in a PerkinElmer, Optima 5300 DV and the target was to see the presence of S and P. Moreover, IC was performed in Waters, HPLC 2690 with conductometric detector and suppressor, using a Dionex IonPac AS22 column.

3. Results

The BET specific surface areas of the support and the catalyst were determined by nitrogen adsorption. The mesoporous volume of the support ranging from 1.5 to 100 nm was 0.839 cm^3/g

Table 1
The relative volumes for the support material measured by nitrogen adsorption.

Pore size (nm)	Relative volume (%)
10–100	41
5–10	15
2–5	38
1–1.5	4
0–1	2

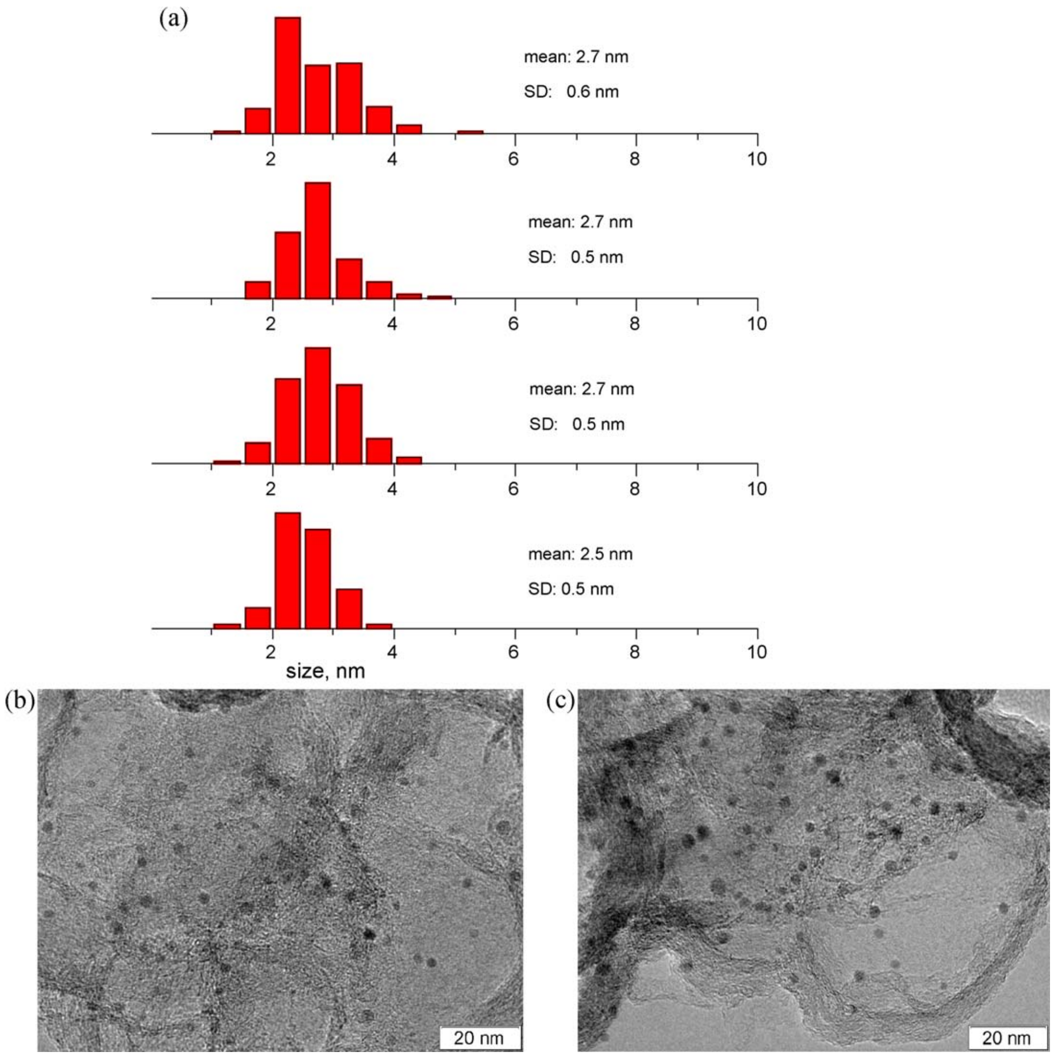

Fig. 1. (a) The metal particle size distributions of the catalysts being used in the decarboxylation of (1) C17, (2) C18, (3) C19 and C22 fatty acids. (b) and (c) TEM for spent catalysts used for decarboxylation of C19 and C20 fatty acids respectively.

corresponding to 85% of the total pore volume. Furthermore, the relative volumes for pores in different ranges are given in Table 1. The specific surface area and the metal dispersion of the fresh catalyst were 379 m^2/g and 38%, respectively. The average metal particle sizes for the fresh and spent catalysts (see below) were 2.5–2.7 nm according to TEM measurements indicating that the metal dispersion remained constant during the catalytic experiments (Fig. 1).

Decarboxylation of fatty acids was performed over 1 wt.% Pd/C (Sibunit) catalyst using five different fatty acids, C17, C18, C19, C20 and C22 as feedstocks at 300 °C in dodecane (Fluka) under argon atmosphere at 17 bar total pressure. Catalyst activity and stability during the deoxygenation of fatty acids is very much dependent on the acid-to-catalyst amount ratio [3]. In the current work catalytic deoxygenation of C18, C19, C20 and C22 (Entries 2, 3, 5 and 7 in Table 2) was performed using the same ratio of the initial acid concentration to catalyst mass and the results are presented in Fig. 2. Intuitively the initial rates for decarboxylation of fatty acids should be about the same over the same catalyst, since the hydrocarbon chain in fatty acid is inert towards catalyst surface, whereas the carboxylic group is adsorbed on the catalyst surface resulting in the formation of a hydrocarbon exhibiting one carbon atom shorter chain compared to the original carboxylic acid according to the following scheme:

$$\mathrm{RCOOH} \rightarrow \mathrm{RH} + \mathrm{CO_2}$$

Such experimental results confirming a possibility of neglecting a potential geometric effect were reported recently in case of palmitic and stearic acids decarboxylation [11].

The decarboxylation rates are not, however, the same for all acids in this study. The same initial decarboxylation rates for C18 and C20 were achieved (Fig. 2), whereas for nonadecanoic and behenic acids slow decarboxylation rates were obtained. The reason for the lower decarboxylation rates for C19 and C22 can be explained by the presence of impurities.

Table 2
Kinetic data from catalytic deoxygenation of fatty acids at 300 °C under 17 bar argon in dodecane.

Entry	Fatty acid	c_{FA} (mol/l)/$m_{cat.}$ (g)	Conversion after 150 min (%)
1	C17	0.05	91
2	C18	0.1	93
3	C19	0.1	19
4	C19	0.02	90
5	C20	0.1	83
6	C20	0.07	98
7	C22	0.1	23

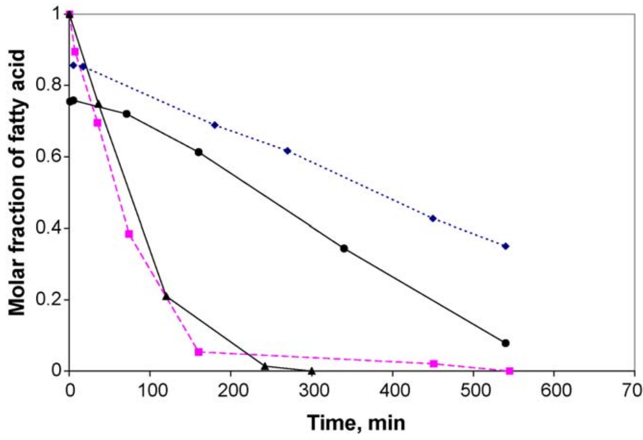

Fig. 2. Decarboxylation of stearic (■), nonadecanoic (◆), arachidic (▲) and behenic (●) acid at 300 °C in dodecane using 1.0 g 1 wt.% Pd/C (Sibunit) catalyst. The initial concentration of acid is 0.1 mol/l.

Table 3
Characterization of the spent 1 wt.% Pd/C (Sibunit) catalysts after using in decarboxylation of different fatty acids.

Spent catalyst (1 wt.% Pd/C) used in the decarboxylation of fatty acid	Metal dispersion[a] (%)	d Pd (nm)	BET specific surface area, (m^2/g)
Heptadecanoic acid	8	14	330
Stearic acid	4	27	331
Nonadecanoic acid	2	52	222
Arachidic acid	8	13	305
Behenic acid	3	40	242

[a] Measured by CO-chemisorption.

The amounts of Ca, Mg, Fe and P were investigated in nonadecanoic and behenic acids by ICP-techniques. Especially, in behenic acid the phosphorus content was relatively high being 266 mg/kg nonadecanoic acid. The ratio between the molar amount of phosphorus to molar amount of surface Pd was calculated by taking into account Pd dispersion and assuming that all phosphorus would adsorb on Pd. The P/Pd ratio was 0.42 indicating that about 40% of surface active Pd can be covered by phosphorus. This high phosphorus level is thus explaining the low decarboxylation activity achieved for behenic acid. Furthermore, the spent 1 wt.% Pd/C catalysts used in the decarboxylaiton of different fatty acids were characterized by determining the apparent Pd dispersion and the specific BET surface areas (Table 3). Very low values of apparent metal dispersion (note that HRTEM did not show any significant variations in the cluster size) and BET specific surface area were achieved for the catalysts used in behenic acid decarboxylation indicating both poisoning of Pd as well as coking. The other impurities in the behenic acid were according to GC–MS arachidic and palmitic acids, since the purity of behenic acid was 80%. These compounds should not, however, decrease the decarboxylation activity. On the other hand, their decarboxylation products were also obtained as products. In the case of nonadecanoic acid, which had the purity of 90%, the main impurities were behenic acid and palmitic acid. The amount of phosphorus in nonadecanoinc acid was only about 56% of the level found in behenic acid. Thus the low decarboxylation rate of nonadecanoic acid cannot be explained in exactly the same way as in case of behenic acid. One possible reason for low decarboxylation rate could be the presence of unsaturated fatty acids, which could undergo dimerization and Diels-Alder type of cyclisation [12]. Under lack of hydrogen Pd is also known to act as a dehydrogenation catalyst [13] and thus aromatic compounds could be formed. No unsaturated fatty acids were, however, found in GC–MS measurements in nonadecanoic acid. Coking was, however, indirectly confirmed by recording low BET specific surface area in the spent catalyst used for nonadecanoic acid decarboxylation (Table 3). Furthermore, the apparent metal dispersion measured by CO-chemisorption was very low for the catalysts used in nonadecanoic acid decarboxylation, which most probably can be explained by limited access to metal clusters due to pore blocking by coke rather than sintering.

The effect of the ratio between the initial concentration of fatty acid to mass of catalyst was also compared. With a lower ratio typically higher decarboxylation rates for fatty acids were achieved. Similar results were also achieved for nonadecanoic acid (Fig. 3) and for arachidic acid (Table 2). Decarboxylation of heptadecanoic acid was performed using the initial concentration to catalyst amount ratio of 0.05 (Table 2, Entry 1). For proper comparison the results obtained with different ratios substrate/catalyst should be plotted using a normalized abscissa, time multiplied by catalyst mass divided by the initial concentration of

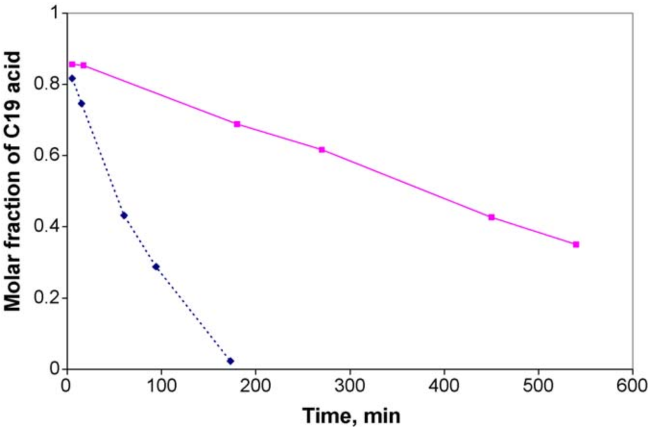

Fig. 3. Decarboxylation of nonadecanoic acid at 300 °C in dodecane using 1.0 g 1 wt.% Pd/C (Sibunit) catalyst. Symbols: the ratio between the initial acid concentration to the catalyst mass: (◆) 0.015 mol/l/$g_{cat.}$ and (■) 0.1 mol/l/g_{cat}.

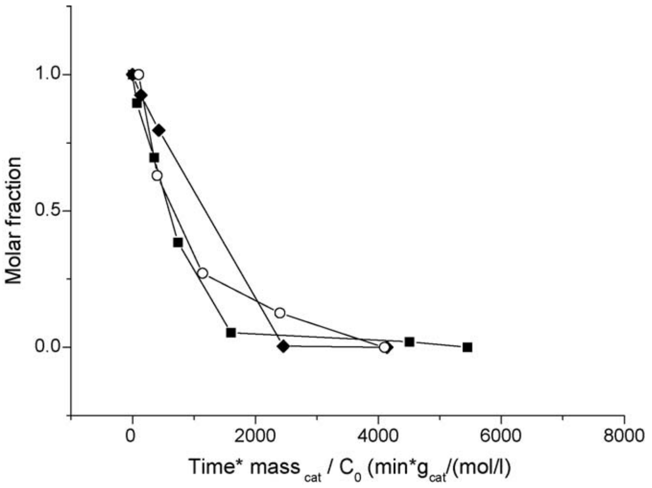

Fig. 4. Decarboxylation of heptadecanoic (○), stearic (■) and arachidic (◆) acid at 300 °C in dodecane using 1.0 g 1 wt.% Pd/C (Sibunit) catalyst as a function of a normalized abscissa, time multiplied by the catalyst mass and the initial concentration of fatty acid.

fatty acid. When drawing this plot (Fig. 4) it was observed that the kinetics for heptadecanoic acid decarboxylation coincided with that of arachidic and stearic acids additionally confirming that the reaction rate was independent on the fatty acid chain length. Furthermore, catalyst deactivation by coking was minor in case of stearic, heptadecanoic and arachidic acids judging only by surface area (Table 3). The apparent metal dispersions of the spent catalysts, measured by chemisorptions, were, however, lower than the initial ones even for these acids and the metal particle sizes calculated by CO-pulse chemisorptions were larger than those obtained by TEM. This result indicated that palladium was partially blocked by coke preventing access of CO during the chemisorption measurements of the spent catalysts.

4. Conclusions

Decarboxylation of fatty acids (C_{16}–C_{20}, C_{22}) was investigated in a semibatch reactor at 300 °C under argon using dodecane as a solvent. Over 1 wt.% Pd on mesoporous carbon, Sibunit, the same decarboxylation rates for pure carboxylic acids were obtained, whereas relatively low decarboxylation rates were recorded for nonadecanoic (C_{19}) and behenic (C_{22}) acids. The former acid contained phosphorus as the catalyst poison, whereas for nonadecanoic acid significant coking was noticed.

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