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Synthesis of Biodiesel via Deoxygenation of Stearic Acid over Supported Pd/C Catalyst

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Abstract High catalytic activity was achieved in the deoxygenation of stearic acid in dodecane in a temperature range of 270–300 °C under 17 bar helium over palladium on nanocomposite carbon Sibunit. Besides *n*-heptadecane, which was obtained previously in this reaction with palladium on activated carbon, *n*-pentadecane was also formed in significant amounts.

Keywords Deoxygenation · Fatty acid

1 Introduction

The potential capacity of bio-oil for replacing the use of oil-based energy demand has been evaluated as follows: If all the farming land would be used for oil and fat production, its hypothetical yield would be 1.5×10^{12} kg per harvest being equal to 52×10^{18} J per harvest. The energy obtained per harvest is then 34.7 MJ/kg, which is about 80% of the diesel energy value (43.3 MJ/kg) covering only 15% of the total annual energy consumption [1, 2]. These considerations lead to the conclusion that although technologies for renewable energy production should be developed but they cannot alone covers the current energy demand. Additionally it should be pointed out that ethically more sustainable method would be to use as a raw material for biodiesel production non-edible oil-yielding plants, such as mahua, karanja and jatropha [3–5].

Biodiesel has been traditionally defined as fatty acid (methyl) esters. The second generation of biodiesel consists of diesel-like hydrocarbons, which are industrially produced [6]. Synthesis of biodiesel has been under intensive research efforts in the recent years [7–12], since the annual energy consumption is expected to grow. There exist several other technologies to prepare biodiesel, like pyrolysis [13] and transesterification [14]. A novel technology to prepare biodiesel is to use metal supported catalysts and deoxygenate fatty acids and their derivatives [7]. The main advantage of this technology compared to the transesterification method is that less by-products, like glycerol, are formed.

Catalytic deoxygenation of fatty acids, esters and triglycerides has been studied intensively during the recent years [7–12]. Catalytic deoxygenation has been successfully performed under inert gas or hydrogen in a semibatch reactor in temperature and pressure ranges of 300–360 °C and from 6 to 40 bar, respectively [8–10]. Since the main gaseous products are carbon dioxide and carbon monoxide the use of semibatch reactor helps to maintain the catalytic activity high due to purging out the formed product gases. The catalyst screening study revealed that Pd and Pt supported on carbon catalysts are the most active and selective for this reaction. Typically the reaction has been studied in the presence of a solvent, dodecane and the main liquid phase product has been *n*-heptadecane. Furthermore a minor amount of unsaturated C17 compounds has been formed and the yield of the main product has been 95% at the complete conversion of stearic acid [9]. Besides applicability of a

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semibatch reactor also continuous deoxygenation of fatty acids and their esters has been successfully demonstrated.

The aim of this work was to study the effect of carbon support material in catalytic deoxygenation of stearic acid over palladium, since only a limited number of different carbons were tested previously. In this work Pd catalyst supported on synthetic carbon was prepared and applied in stearic acid deoxygenation.

2 Experimental

2.1 Catalyst Preparation and Characterization Methods

About 4 wt.% Pd/C catalyst was synthesized by using Sibunit as the support material. The catalyst was prepared by hydrolysis of H_2PdCl_4 at pH 5–6 to yield so-called polynuclear hydroxocomplexes of palladium followed by their adsorption on carbon and increasing of pH slurry up to Na/Pd ratio 1:2 [15]. Prior to the catalyst preparation the carbon was pre-oxidized by treating it by 5 wt.% HNO_3 during 17 h, then washed by distilled water and dried.

The metal dispersion was determined by CO pulse chemisorption using Autochem 1900 (Micromeritics). The catalyst was reduced with flowing hydrogen in situ at 60 °C for 1 h and heated up under inert gas to the reaction conditions and cooled down to ambient temperature prior to the adsorption of CO for 30 min. A gas mixture containing 10 vol.% CO in helium was used for adsorption. The stoichiometric relationship between CO and Pd was assumed to be unity [16].

SEM-EDXA was used to determine the surface composition of the catalysts. SEM-EDXA was carried out with a LEO 1530 scanning system equipped with a secondary and backscattered electron detector for all the reduced catalysts.

Catalyst acidity was determined by measuring pH of the catalyst slurry containing 50 mg of catalyst and using deionized water. The pH electrode was from Mettler Toledo. The titration of acidic groups was performed using an acid–base technique with NaOH, determining the number of surface groups reacted in the pH interval from 3 to 7.5, following the procedure developed in [17].

2.2 Reaction

The catalytic deoxygenation of stearic acid (Fluka) was performed in 300 mL semi-batch reactor coupled to condenser and heating jacket with liquid phase volume of 100 mL. The reaction temperature was kept constant during reaction in the range of temperature 270–330 °C. The reaction pressure was 17 bar. The flow of carrier gas and reaction pressure inlet and outlet were controlled by a flow (Brooks 58505 S) and a pressure controller (Brooks 5866), respectively. The stirring speed was maintained suitably high, at 1,100 rpm, to prevent external mass transfer limitation. The catalysts were reduced in situ by hydrogen (AGA, 99.999%) for 1h prior to the catalytic test at constant temperature and pressure, 60 °C and 4.8 bar, respectively. In a typical reaction, the catalyst and feed amount were used as follows: 0.5 g of catalyst (below 63 μm to suppress internal diffusion; 0.05 M feed (1.4 g of stearic acid in 100 mL dodecane (Acros Organic, 99%)). The reactor was then flushed thoroughly with helium (AGA, 99.996%) using a gas flow rate of 25 mL/min. Thereafter the reaction pressure was increased to 17 bar and temperature was adjusted with the heating ramp of 10 °C/min to the desired reaction temperature. At this point (zero reaction time) stirring started. After the reaction, the catalyst particles were filtered and washed with dodecane for further characterization.

2.3 Analysis

2.3.1 Liquid Phase Analysis

Liquid phase samples were withdrawn from the reactor vessel via a sampling valve during the experiment. Typically, the samples had to be dissolved in pyridine and silylated with N,O-bis(trimethyl)-trifluoroacetamide, BSTFA in order to be analyzed by GC. Generally 100 wt.% excess of BSTFA were added to the sample. After addition of the silylation agent, the samples were kept in an oven at 60 °C for 1 h. The internal standard eicosane, $C_{20}H_{42}$ was added for quantitative calculations. The samples were analyzed with a gas chromatograph (GC, HP 6890) equipped with non-polar column (DB-5, with dimension of 60 m × 0.32 mm × 0.5 μm) and a flame ionization detector. 1 μL sample was injected into the GC with split ratio of 50:1, and the carrier gas (helium) flow rate was 137 mL/min. The injector and detector temperature were 265 and 290 °C, respectively. The following temperature program was used for analysis: 130, 169 °C (1 °C/min) hold for 5 min, 246 (5 °C/min), 250 °C (1 °C/min) hold for 1 min and 300 °C (10 °C/min) hold for 10 min. The chromatographic pressure program was well-adjusted to achieve satisfactory separation of desired product. The initial pressure at 1.7 bar was kept for 30 min, after which the pressure was ramped with 2.4 bar/min until reaching the final pressure 2.21 bar and hold at this pressure for 64 min. The gas chromatographic method was calibrated using the following chemicals: *n*-pentadecane (Acros, 99%), *n*-heptadecane (Acros, 99%). The product identification was validated with a gas chromatograph–mass spectrometer (GC–MS).

2.3.2 Gas Phase Analysis

In some experiments the gas phase was analyzed by using a GC (FP 6890) with the following temperature programme: 40 °C (7.5 min)−25 °C/min−80 °C (7 min)−25 °C/min−140 °C (5.5 min) using 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).

3 Results and Discussion

3.1 Catalyst Characterization Results

BET specific surface area of the used support and the metal dispersion were 450 m^2/g_{cat} and 37%, respectively. The relatively high metal dispersion was achieved for the catalyst, in which carbon support was oxidized prior to metal deposition. It is known that well-dispersed Pd catalysts can be prepared when using an oxidized carbon material as a catalyst support [18]. The pH of the catalyst slurry was before and after reduction 6.9 and 5.9, respectively. A SEM image of the catalyst is shown in Fig. 1. The synthetic carbon has a smooth surface. Pd is relatively well dispersed, since also very small white spots are clearly visible.

3.2 Catalytic Results

The effect of the reaction temperature for stearic acid deoxygenation was studied at temperatures 270, 300 and 330 °C (Table 1; Fig. 2a). The initial reaction rates increased with increasing temperature, as expected. The time needed for achieving complete conversion for stearic acid increased with decreasing reaction temperature. Interestingly it can be seen from Fig. 2a, that there is an induction time for a fast deoxygenation reaction at 270 °C

Table 1 Kinetic data in the deoxygenation of stearic acid over 4 wt.% Pd/C (Sibunit) in the range of 270–330 °C under 17 bar He

Temperature (°C)	Initial reaction rate (mmol/min/g_{cat})	Time needed for 100% conversion (min)
270	0.12	248
300	0.94	47
330	1.54	20

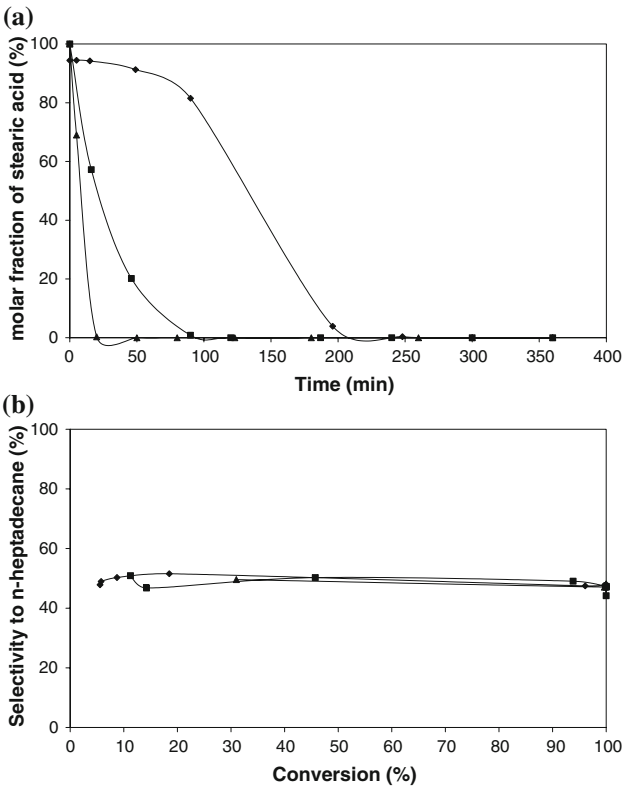

Fig. 2 (**a**) Concentration curves for stearic acid deoxygenation and (**b**) selectivity to *n*-heptadecane as a function of conversion over 4 wt.% Pd/C (Sibunit). Symbols: (◆) 270 °C, (■) 300 °C and (▲) 330 °C under total pressure of 17 bar in helium

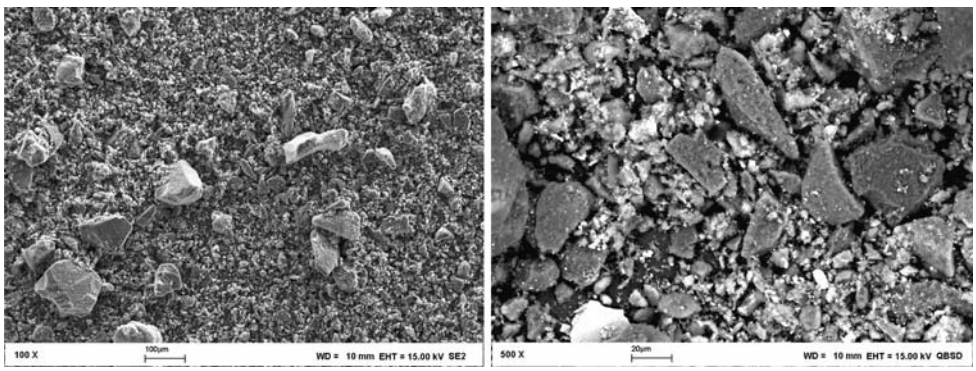

Fig. 1 A SEM picture of 4 wt.% Sibunit catalyst with two different magnifications (100 and 500)

within first 60 min thereafter the reaction started to proceed faster.

The catalytic deoxygenation of stearic acid resulted in the parallel formation of *n*-pentadecane and *n*-heptadecane. The selectivities to *n*-heptadecane are shown in Fig. 2b. Analogous selectivities were obtained for *n*-pentadecane indicating that these products are formed parallelly. Moreover, the product distribution was independent on conversion. Formation of *n*-pentadecane was not previously reported over several Pd/C catalysts, like 5 wt.% Pd/C (Aldrich) and 1 wt.% Pd/C (Alfa) (Fig. 3a) [8–10], over which mainly heptadecane was achieved as products in stearic acid deoxygenation at 300 °C and 6 bar helium [10]. The presence of *n*-pentadecane was confirmed by GC–MS and in GC chromatogram (Fig. 3b). Additionally formation of *n*-pentadecane follows indirectly from analyzing the gaseous compounds generated during stearic acid deoxygenation over 4 wt.% Pd/C (Sibunit) at 300 °C (Fig. 4). The main products in the gas mixture after 300 min of reaction time were carbon dioxide, carbon monoxide, methane, propane and heavy compounds. The initial molar ratio between C1 and C3 compounds was 2.7

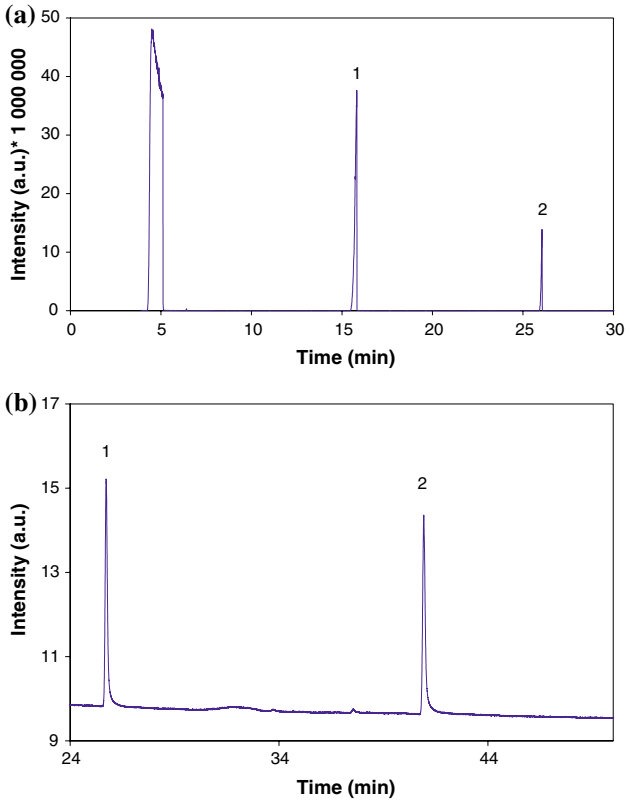

Fig. 3 GC–MS of stearic acid deoxygenation (**a**) over 5 wt.% Pd/C (Aldrich) at 300 °C at 7 bar He: 1. *n*-heptadecane, 2. stearic acid and (**b**) over 4 wt.% Pd/C (Sibunit) at 300 °C at 17 bar He over 5 wt.% Pd/C (Sibunit): 1. *n*-pentadecane and 2. *n*-heptadecane, other peaks are originating from the silylation agents

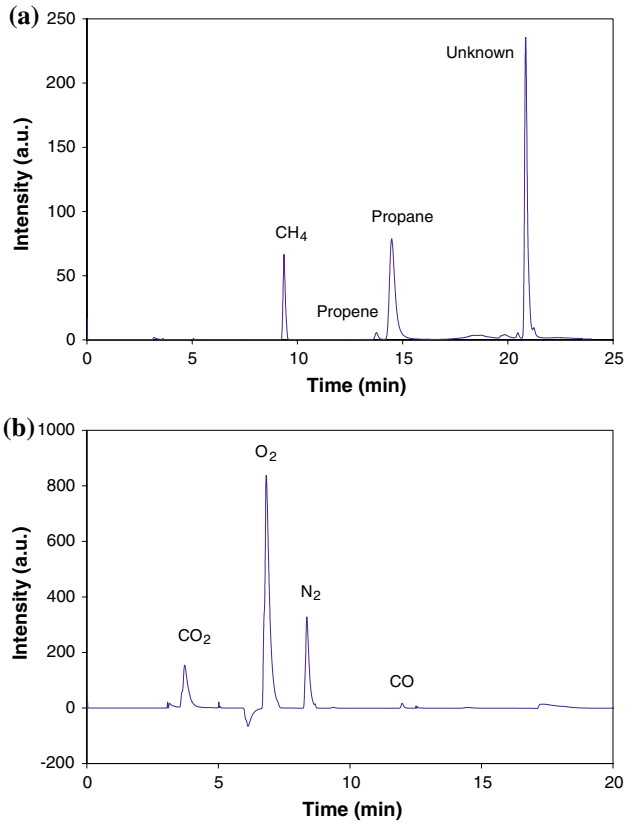

Fig. 4 The gas phase analysis of stearic acid deoxygenation after 300 min of reaction time over 4 wt.% Pd/C (Sibunit) at 300 °C in helium atmosphere at 17 bar: (**a**) FI detector, (**b**) TC detector. The peaks were confirmed with two standard gases containing (1) CO, methane and ethane in helium and (2) CO_2, CH_4, propene, propane and nitrogen in helium

indicating the excess of C1. Since equal amounts of *n*-pentadecane and *n*-heptadecane were obtained in the liquid phase analysis, the analogous ratio in C1-to-C3 would be expected. There were, however, after 2 min of reaction time also heavy compounds present in the gas mixture. They could be dimers of C3, since traces of propene were also present in the gas mixture, which is expected to be active for dimerisation at these temperatures. Furthermore the presence of oxygenated compounds, like propanal cannot be excluded.

The main result of the current work is that the product distribution in catalytic deoxygenation of stearic acid is dependent on the type of the support and the nature of the surface groups in carbon material. It should be pointed out here, that a mild reduction procedure, 60 °C for 1 h, was applied for the catalysts in this work, thereafter the catalysts were heated up to the reaction temperature under the reaction atmosphere. This procedure might also partially explain the product distribution, since more acidic groups remain on the catalyst surface when the catalysts were treated at low temperatures. The titration of acidic groups

showed that amount of them is almost two-fold higher for Pd/C (Sibunit) than for the commercial catalyst Pd/C (Aldrich), e.g. 0.63 mmol/g_{cat} for the former and 0.35 mmol/g_{cat} for the latter. Additional difference between Sibunit, which is a porous carbon–carbon composite materials, and active carbons, is that Sibunit composites are characterized by a high mesopore volume and a controllable narrow pore size distribution. A system of wide pores with the size 50–80 nm and volume 0.2 cm^3/g provides efficient transport of the reactants to and from palladium particles, which are situated on a well-developed surface with the pores of the size 2–6 nm.

When *n*-pentadecane is formed as a main product in addition to *n*-heptadecane, the cetane number is slightly lower, since the cetane numbers for *n*-heptadecane and *n*-pentadecane are 105 and 96, respectively [19]. The overall process economy also suffers, since C3 hydrocarbons are formed as well thus lowering the yield of C17 paraffins.

4 Conclusions

The deoxygenation of stearic acid was studied over a palladium catalyst supported on synthetic carbon (Sibunit). The reaction was performed in dodecane as a solvent in a temperature range of 270–330 °C under 17 bar helium. The relatively high metal dispersion was achieved for 4 wt.% Pd/C (Sibunit), which was oxidized prior to catalyst preparation. The formation of oxidized surface groups facilitated the formation of highly dispersed Pd.

The initial reaction rate in stearic acid deoxygenation increased with increasing reaction temperature. At the same time the time needed form full conversion of stearic acid decreased with increasing reaction temperature. The two main liquid phase products were *n*-heptadecane and *n*-pentadecane, which were formed parallelly from the very beginning of the reaction. The selectivity values of both paraffins were independent on stearic acid conversion. The presence of *n*-heptadecane and *n*-pentadecane was confirmed by GC–MS as well as by the gas phase analysis. In the gas phase the main product in addition to carbon dioxide and carbon monoxide was propane. Our previous studies reported mainly formation of *n*-heptadecane in the liquid phase. As a conclusion it can be therefore stated that the selection of the carbon support is crucial, especially for the beneficial production of longer chain paraffins from stearic acid.

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