Catal Lett (2009) 130:48–51
DOI 10.1007/s10562-009-9889-y

Catalytic Deoxygenation of Stearic Acid and Palmitic Acid in Semibatch Mode

Siswati Lestari · Päivi Mäki-Arvela · Irina Simakova ·
Jorge Beltramini · G. Q. Max Lu · Dmitry Yu. Murzin

Received: 25 January 2009 / Accepted: 1 February 2009 / Published online: 24 February 2009

Abstract The deoxygenation experiments of different reactants, i.e., pure palmitic acid, stearic acid, and a technical grade stearic acid containing a mixture of 59% of palmitic and 40% of stearic acid were successfully performed over 4 wt% Pd/C mesoporous catalyst at 300 °C under 17 bar of 5% H_2 in argon. The main product in catalytic deoxygenation of saturated fatty acids, C16 and C18, were aliphatic chain length hydrocarbons containing one less carbon than the corresponding acid. Additionally it was found that the deoxygenation rates of different reactant were independent on carbon chain length of its fatty acids.

Keywords Green diesel · Deoxygenation · Stearic acid · Palmitic acid

1 Introduction

Over the recent decade, considerable efforts have been made to develop clean and renewable fuels technologies in order to secure the world energy reserves and gain environment benefits. Despite the ongoing debate on social and economic problems, biofuels remain the only alternative renewable fuels fit with current infrastructure with no or minor engine modification [1, 2]. The potential capacity of biofuels has been investigated and it was shown that they can cover only about 15% of total energy consumption which leads to a conclusion that although technologies for renewable energy production should be developed, they cannot alone solve the current energy demands [3].

Regarding biodiesel, several methods have been developed to produce fatty acid ester, e.g., transesterification of vegetable oils with alcohol can be performed over homogeneous acid and alkaline catalysts [4, 5], heterogeneous catalysts [5], or with enzymes [4]. The second generations of biodiesel, which consist of diesel-like hydrocarbons, have been generated with an emphasize to utilize a non-edible source [6, 7]. Unlike the first generation, this new generation of biodiesel is more favorable for industrial applications being compatible with the current engines, even avoiding need to be blended with petrol fuels and resulting in formation of less by-products, like glycerol from transesterification [8].

A novel technology to produce diesel-like hydrocarbon via catalytic deoxygenation reaction [7–13] has been intensively investigated during the recent years. This reaction has been successfully performed under an inert gas or hydrogen in a semibatch reactor in temperature and pressure ranges of 300–360 °C and 6–40 bar, respectively. The catalyst screening studies revealed that Pd and Pt supported on carbon catalysts are the most active and selective catalysts for this reaction [9, 14]. Typically, the reaction has been performed in the presence of a solvent, such as dodecane and mesitylene. The main liquid phase product was *n*-heptadecane with yield of 95% at the complete conversion of stearic acid. However, the previous investigation of the catalytic deoxygenation of technical grade stearic acid produced both *n*-heptadecane and *n*-

---

S. Lestari · J. Beltramini · G. Q. M. Lu
ARC Centre of Excellence for Functional Nanomaterials,
University of Queensland, Brisbane, QLD 4072, Australia

S. Lestari · P. Mäki-Arvela · D. Yu. Murzin (✉)
Laboratory of Industrial Chemistry, Åbo Akademi University,
20500 Turku, Finland
e-mail: dmurzin@abo.fi

I. Simakova
Boreskov Institute of Catalysis, Novosibirsk, Russia

pentadecane with the equal ratio [8]. This data is now revisited, since the careful GC–MS analysis and deoxygenation experiments with this raw material revealed that this feedstock contained not only stearic acid, but also palmitic acid [15]. Thus the erroneous mechanism involving both deoxygenation and cracking leading to *n*-pentadecane can now be attributed to deoxygenation of palmitic acid. As a comparison to the deoxygenation of technical grade stearic acid also palmitic and stearic acid deoxygenation was separately investigated in this work. As a result a mechanism involving the formation of one carbon less hydrocarbon, than the corresponding acid, i.e., the formation of *n*-pentadecane and *n*-heptadecane from palmitic and stearic acids, respectively, was reconfirmed.

2 Experimental Section

2.1 Materials

About 99% pure stearic acid (Sigma–Aldrich), 99% pure palmitic acid (Aldrich), and stearic acid (technical grade from Fluka), which contained 40% stearic and 59% palmitic acids, respectively, were used as feedstocks . Dodecane (Fluka) was applied as a solvent. *N*,*O*-bis(trimethyl)-trifluoroacetamide (BSTFA) was used as a silylation agent.

2.2 Catalyst Preparation Method

The catalyst containing Pd supported on mesoporous carbon subunit (surface area 358 m^2/g) with 4 wt% loading of Pd 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 [16]. The carbon subunit support was pre-oxidized by treating it with 5 wt% HNO_3 during 17 h, then washed by distilled water and dried. The Pd deposition was performed via sequential adsorption and hydrolysis of H_2PdCl_4 and Na_2CO_3. Thereafter the catalysts were washed with water and dried at 70 °C. The dry catalyst was reduced by molecular hydrogen at 150 °C for 1 h.

2.3 Materials Characterization

The impurities of sulfur, phosphor, and chlorine in three different reactants were measured by Inductively Couple Plasma Optical Emission Spectrometer (ICP-OES) PerkinElmer Optima 5300 DV. Approximately 0.2 g of sample was weighed, then HNO_3 (65%) and H_2O_2 (30%) were added to the sample for digestion treatment using microwave oven. Afterward, the samples were diluted to 100 mL in order to analyze in ICP-OES.

2.4 Experimental Setup

The catalytic deoxygenation of stearic acid and palmitic acid was performed in 300 mL semibatch reactor. The reaction mixture containing typically 0.05 M stearic acid and/or palmitic acid in dodecane was injected into the reactor containing 0.5 g of pre-reduced 4 wt% Pd/C catalyst. The liquid phase volume was 100 mL. The flow of carrier gas and reaction pressure inlet and outlet were controlled by a flow (Brooks 58505S) and pressure controller (Brook 5866), respectively. The stirring speed was maintained suitably high, at 1,100 rpm, to prevent external mass transfer limitation. The catalyst were reduced in-situ by hydrogen for 1 h prior to the catalytic tests at constant temperature and pressure, 60 °C and 4.8 bar, respectively. Before a reaction started, 30 mL/min of reaction atmosphere gas was passed through the reactor until reaching the reaction pressure. Thereafter, the reaction temperature was increased with heating ramp 10 °C/min to the desired reaction temperature and the reaction was started via turning on the stirrer. After the reaction, the spent catalysts were filtered and washed with acetone for further characterization.

2.5 Product 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 BSTFA in order to analyze 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 30 min. The internal standard eicosane, $C_{20}H_{42}$ was added for quantitative calculations. The samples were analyzed with a gas chromatograph (GC, HP 5890) equipped with a non-polar column (HP-1, 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 50:1, and the carrier gas (helium) flow rate was 137 mL/min. The injector and detector temperature were 280 and 290 °C, respectively. The following temperature program was used for analysis: 130, 169 °C (1 °C/min) hold for 15 min, 246 °C (5 °C/min) hold for 3 min, and 300 °C (10 °C/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).

3 Results and Discussions

The catalytic deoxygenation of three different types of fatty acids, i.e., pure 99% palmitic acid, pure 99% stearic acid, and a technical grade of stearic acid containing a mixture of 59% palmitic acid and 40% stearic acid, respectively, was studied. The reaction was performed at 300 °C and 17 bar, respectively, under 5% H_2 in argon.

The catalytic deoxygenation of different fatty acid resulted in formation of hydrocarbons with one carbon less than the corresponding acid, i.e., according to GC–MS chromatogram *n*-pentadecane was the main product in the deoxygenation of palmitic acid, while *n*-heptadecane was formed in the deoxygenation of stearic acid. In case of technical grade stearic acid (which in fact is a mixture of palmitic and stearic acid) both *n*-pentadecane and *n*-heptadecane were formed according to GC–MS. These results revise the previous study, which claimed that both *n*-heptadecane and *n*-pentadecane were formed in the deoxygenation of stearic acid [8]. This erroneous conclusion is revised in this work as follows: technical grade stearic acid contained besides stearic acid also significant amounts of palmitic acid and during the catalytic deoxygenation one carbon less hydrocarbon, i.e., *n*-heptadecane and *n*-pentadecane, respectively, were formed. Furthermore, the deoxygenation rates for different fatty acids were the same, being independent on the hydrocarbon chain length, as shown in Fig. 1 for deoxygenation of palmitic and stearic acid, which proceeds with the same rates. Analogous results have been recently reported [17] also for other fatty acids, such as stearic and arachidic acid. If fatty acids contain other impurities, the deoxygenation rates decreased [17]. In the current work the reactants did not contain large amounts of impurities according to the ICP-OES analysis (Table 1). Other potential impurities were all below the detection limits. Due to the pure feedstocks, generally, over 94% of conversion after 180 min reaction time was achieved for all three feedstocks. The selectivity to the desired hydrocarbons was very high (>99%).

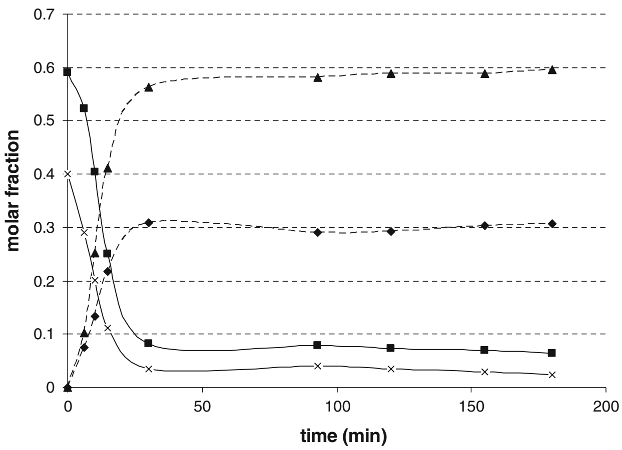

Fig. 1 Kinetics of stearic acid (technical grade, Fluka) deoxygenation. Reaction conditions: 300 °C under 17 bar in 5% H_2 in argon over 4 wt% Pd/C subunit catalyst (■ palmitic acid, × stearic acid, ▲ *n*-pentadecane, ◆ *n*-heptadecane)

Table 1 ICP-OES analysis of reactant

Reactant	S (%)	P (%)	Cl (mg/kg)
I	<0.02	<0.04	<200
II	<0.03	<0.03	<200
III	<0.03	<0.03	<200

The notation for the different reactants is given in Table 2

Table 2 Conversions of different fatty acids during their deoxygenation over 4 wt% Pd/C subunit

Reactant	Conversion (%)
99% palmitic acid (I)	98
99% stearic acid (II)	95
Technical grade stearic acid (a mixture of stearic and palmitic acid) (III)	94

Total conversion after 180 min

4 Conclusion

The deoxygenation experiments with different reactants, i.e., pure palmitic acid, stearic acid and a technical grade stearic acid containing 59% of palmitic and 40% of stearic acid, respectively, were performed over 4 wt% Pd on mesoporous carbon at 300 °C under 17 bar of 5% H_2 in argon. The main products in catalytic deoxygenaiton of saturated fatty acids, C16 and C18, were aliphatic straight chain hydrocarbons containing one carbon less than the corresponding acids. Moreover, the reaction rates of different fatty acids were independent of the fatty acid chain length.

Acknowledgments This work is part of the activities at the Åbo Akademi University Process Chemistry Centre within the Finnish Centre of Excellence Program (2000–2011) appointed by the Academy of Finland. S. L. would like to acknowledge also the travel grant support by ARC Centre of Excellence for Functional Nanomaterials, University of Queensland, Australia and Johan Gadolin Scholarship Process Chemistry Centre Åbo Akademi University. The authors are grateful to Mr. S. Lindholm from Process Chemistry Centre, Åbo Akademi for performing ICP-OES measurements.

References

1. Ramadhas AS, Jayaraj S, Muraleedharan C (2004) Renew Energy 29:727
2. Gerpen JV (2005) Fuel Process Technol 86:1097
3. Addison K (2008) Oil yields and characteristic. Journey to forever http://journeytoforever.org/biodiesel_yield.html accessed 9 Jan 2009

4. Ma F, Hanna MA (1999) Bioresource Technol 70:1
5. Xie W, Peng H, Chen L (2006) App Catal A: Gen 300:67
6. Ghadge SV, Raheman H (2005) Biomass and Bioenergy 28:601
7. Kubickova I, Snåre M, Eränen K, Mäki-Arvela P, Murzin DYu (2005) Catal Today 106:197
8. Lestari S, Simakova I, Tokarev A, Mäki-Arvela P, Eränen K, Murzin DYu (2008) Catal Lett 122:247
9. Snåre M, Murzin DYu (2006) Ind Eng Chem Res 45:6875
10. Mäki-Arvela P, Kubickova I, Eränen K, Snåre M, Murzin DYu (2007) Energy Fuels 21:30
11. Snåre M, Kubickova I, Mäki-Arvela P, Eränen K, Wärnå J, Murzin DYu (2007) Chem Eng J 134:29
12. Snåre M, Kubickova I, Mäki-Arvela P, Chichova D, Eränen K, Murzin DYu (2008) Fuel 87:933
13. Murzin DYu, Kubickova I, Snåre M, Mäki-Arvela P, Myllyoja J (2006) PCT International application WO2006-FI50031 20060116, p 21
14. Snåre M, Kubickova I, Mäki-Arvela P, Eränen K, Murzin DYu (2006) Ind Eng Chem Res 45:5708
15. Simakova I, Simakova O, Mäki-Arvela P, Simakov A, Estrada M, Murzin DYu (2009) Appl Catal A: Gen (accepted)
16. Simonov P, Troitskii S, Likholobov V (2000) Kinet Catal 41:255
17. Simakova I, Simakova O, Mäki-Arvela P, Murzin DYu (2008) Proceedings of the 3rd International symposium on carbon for catalysis, CarboCat III, Berlin, p 105