



Production of aviation fuel via catalytic hydrothermal decarboxylation of fatty acids in microalgae oil



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HIGHLIGHTS

- Alkanes can be produced via decarboxylation of fatty acids in microalgae oil.
- Pt/MWCNTs is capable for fatty acid decarboxylation with the selectivity up to 97%.
- Pt/MWCNTs and reactant loading amounts, reaction temperature and time are optimized.
- Rate constants and activation energy of stearic acid decarboxylation are obtained.

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ABSTRACT

A series of fatty acids in microalgae oil, such as stearic acid, palmitic acid, lauric acid, myristic acid, arachidic acid and behenic acid, were selected as the raw materials to produce aviation fuel via hydrothermal decarboxylation over a multi-wall carbon nanotube supported Pt catalyst (Pt/MWCNTs). It was found that Pt/MWCNTs catalysts exhibited higher activity for the hydrothermal decarboxylation of stearic acid with a 97% selectivity toward heptadecane compared to Pt/C and Ru/C under the same conditions. And Pt/MWCNTs is also capable for the decarboxylation of different fatty acids in microalgae oil. The reaction conditions, such as Pt/MWCNTs loading amount, reaction temperature and time were optimized. The activation energy of stearic acid decarboxylation over Pt/MWCNTs was calculated (114 kJ/mol).

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1. Introduction

The depletion of fossil resources necessitates the utilization of biomass, the only carbon resources except fossil resource, to produce fuels. In recent years, several kinds of fuels derived from biomass such as bio-ethanol and bio-diesel were developed and can be directly used or proportionately added into gasoline or diesel, to replace the traditional fossil fuels (Demirbas, 2007; Hahn-Hägerdal et al., 2006). Aviation fuel, consisted of C8–16 alkanes, alkenes and aromatic hydrocarbons, is a specific fuel requiring high heating value and energy density, and aviation fuels cannot be replaced by any industrial scale bio-fuel. Converting biomass to C8–16 alkanes, alkenes or aromatic hydrocarbons, is the only approach to obtain aviation fuel from biomass (Nygren et al., 2009; Rauch et al., 2006).

Currently, hydrodeoxygenation of plant or animal oils followed further cracking and isomerization, is the main approach to produce aviation fuel from biomass, which has been developed to a commercial scale (Darocha et al., 1993; Duan et al., 2013; Gusmão et al., 1989). However, the high cost of hydrogen in hydrodeoxygenation process and the use of refined plant and animal oil increased the price of produced aviation fuel. These aspects hinder the development and application of hydrodeoxygenation technology in large scale.

Finding a cheap raw material and replacing high cost hydrogen consumption is a challenge for scientists. Recently, direct decarboxylation of fatty acids or derivatives was reported as a new approach to produce aviation fuel due to the low cost of hydrogen (Santillan-Jimenez and Crocker, 2012). Nobel metals such as Pd and Pt were proved to be effective in catalyzing the decarboxylation reactions (Lestari et al., 2009, 2008; Rozmysłowicz et al., 2010; Simakova et al., 2010, 2009; Snåre et al., 2006), which attracts much attention. At the same time, microalgae are regarded as a promising low-cost raw material because of its rapid growth rate, few land requirement and high oil content (Arias-Penaranda

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et al., 2013; Chisti, 2007; Miao et al., 2004; Wang et al., 2013). But fresh microalgae contain a large amount of water (up to 80%), and drying microalgae to prepare feedstock for decarboxylation is a time and energy-cost process, which demands an alternative way to treat such a specific raw material. In order to solve these problems, a consecutive hydrolyze triglycerides to fatty acid, and followed decarboxylate the fatty acids to hydrocarbons in hydrothermal media was proposed by Fu et al. (2011a, 2010). This consecutive process does not require additional drying the microalgae before chemical conversion and separating the intermediate fatty acids between the two steps. The final products can be easily separated since organic compounds are not soluble in ambient water. Furthermore, no hydrogen is needed in neither hydrolysis nor decarboxylation process. It was reported that Pt/C was active for these hydrothermal decarboxylation reactions. However, the decarboxylation selectivity towards alkanes was affected by active carbon supports (Fu et al., 2011b) because those organic groups in active carbon catalyze side reactions.

Carbon nanotube is an allotrope of carbon with the distinct structure which gives high thermal conductivity, electrical and mechanical properties (Iijima, 1991; Smajda et al., 2007). Compared to active carbon, the relatively few organic groups in the carbon nanotube could decrease the possibility for occurrence of side reactions, making it a promising catalyst support for decarboxylation.

In this contribution, multi-wall carbon nanotube (MWCNTs) was selected as the support of Pt nanoparticles, and used in the production aviation fuel via hydrothermal decarboxylation of fatty acids in microalgae oil (stearic acid, lauric acid, myristic acid, palmitic acid, arachidic acid and behenic acid). The microalgae oil mainly consists of the C14–22 saturated and unsaturated fatty acid units (Sahu et al., 2013), so using C12–22 saturated fatty acid as model compounds would be a good start for the research on decarboxylation of microalgae oil.

2. Experimental section

2.1. Materials

Stearic acid (>99% purity), palmitic acid (>99% purity), lauric acid (>99% purity), myristic acid (>99% purity), arachidic acid (>99% purity), behenic acid (>99% purity) were all obtained from Sigma–Aldrich, USA. Acetone (analytic reagent grade) was obtained from Hangzhou Chemical Reagent Co., Ltd., China. Deionized water was purchased from Hangzhou Wahaha Co., Ltd., China. 5% Pt/C and 5% Ru/C was obtained from Sigma–Aldrich, USA. MWCNTs with a ranging diameter were obtained from Shenzhen Nanotech Port Co., Ltd., China. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (>99%) was obtained from Sigma–Aldrich, USA. $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (analytic reagent grade) was obtained from Tokyo Kasei Co., Ltd., Japan. All above chemicals and catalysts were used as received. 5% Pt/MWCNTs were synthesized in lab according to reference (Kim et al., 2006) (preparation method and characterization results were attached in [supplementary material](#)).

2.2. Experimental procedure

The decarboxylation of fatty acids were carried out in a micro batch reactor (1.67 cm³ volume), which was assembled from one 3/8-in. tube and two 3/8-in. caps purchased from Swagelok, USA. 0.176 mmol of reactant and 10 mg of 5% Pt/MWCNTs were added followed by loading certain amount of water in the reactor. In all experiments, the amount of water to be added was calculated by considering pure water vapor–liquid equilibrium at the reaction temperature, thus 95% of the reactor volume being occupied with

liquid water. Thereafter, the sealed reactor was placed in a fluidized sand bath (Techne SBL-2) set at the desired reaction temperature. After the desired reaction time had elapsed, the reactor was taken into water to quench the reaction. The sample in the cooled reactor was rinsed with acetone for further characterization.

2.3. Analysis method

Sample was rinsed from the reactor to a 10 mL flask with acetone. After filtered, the samples were analyzed with a gas chromatograph (GC, Agilent 7890A) equipped with a 30 m × 0.25 mm × 0.33 μm HP-5 capillary column and a flame ionization detector. 1 μL sample was injected into the GC with the split ratio of 10:1, and the carrier gas (nitrogen) flow rate was 11 mL/min. The temperature of the injector and detector were 280 and 300 °C, respectively. The oven temperature program consisted of a 4 min soak at 40 °C followed by a 10 °C/min ramp up to 280 °C, which was held for 5 min. The reaction products were identified by fragmentation patterns from an Agilent 5970 Mass Spectrometric (MS) detector and by matching gas chromatograph retention times with known standards. Quantitative analysis was performed using calibration curves for each compound of interest.

Reactant molar conversions were calculated as the number of moles of reactant consumed divided by the initial number of moles of reactant loaded into the reactor. Selectivities were calculated as the number of moles of product recovered divided by the number of moles of reactant that had reacted (i.e., yield/conversion). Uncertainties reported herein are standard deviations, which were determined by replicating experiments. Each data point represents the mean result from at least three independent experiments.

3. Results and discussion

3.1. Catalytic activity and maintenance

The catalytic hydrothermal decarboxylation of stearic acid over Pt/MWCNTs, Pt/C and Ru/C were carried out with 0.176 mmol of stearic acid and 10 mg of catalyst at 330 °C for 30 min. The conversions of stearic acid for stearic acid decarboxylation over Pt/MWCNTs, Pt/C and Ru/C were 52.4 ± 2.4%, 52.4 ± 2.5% and 42.3 ± 5.2%, respectively. Their corresponding selectivities to heptadecane were 97.0 ± 4.4%, 57.0 ± 2.7% and 42.9 ± 3.6%, respectively. The above standard deviations were determined from three replicate experiments. The conversions of stearic acid and selectivities to heptadecane over Pt catalysts were higher than those over Ru/C. Pt catalysts on different carbon support displayed similar conversion of stearic acid, but the selectivity to heptadecane over Pt/MWCNTs was higher than that over Pt/C. Large amount of by-products, such as tridecane, tetradecane, pentadecane, hexadecane, E-14-hexadecenal, 2-methyl-7-hexadecene, and eicosane were identified by GC–MS in the reaction mixtures of Pt/C catalyzed reactions. The side reactions to yield these by-products might be catalyzed by those organic groups existing in the active carbon (Fu et al., 2011b). On other hand, the high selectivity over Pt/MWCNTs was probably related to low amounts of organic group linked on MWCNTs. Furthermore, the activity maintenance of Pt/MWCNTs was evaluated at 330 °C (reaction time: 30 min, fresh/used catalyst: 10 mg, stearic acid: 0.176 mmol), shown in [Fig. 1](#). The conversions of stearic acid over fresh Pt/C (1st use), catalyst used once previously (2nd use), and catalyst used twice previously (3rd use) decreased as the recycle time increased. However, the selectivity kept stable in hydrothermal media. Even the selectivity to heptadecane over Pt/MWCNTs used twice previously (3rd use) was about 90%.

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