Catalysis Communications 90 (2017) 47–50

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Efficient hydrothermal hydrodeoxygenation of triglycerides with *in situ* generated hydrogen for production of diesel-like hydrocarbons

Jun Mao, Dahao Jiang *, Zheng Fang, Xianyuan Wu, Jun Ni *, Xiaonian Li

State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Institute of Industrial Catalysis, Zhejiang University of Technology, Hangzhou 310014, China

ARTICLE INFO

Article history:
Received 22 July 2016
Received in revised form 4 November 2016
Accepted 17 November 2016
Available online 18 November 2016

Keywords:
Hydrothermal hydrodeoxygenation
Catalytic transfer hydrogenation (CTH)
Aqueous phase reforming (APR)
In situ hydrogen
Diesel-like hydrocarbons

ABSTRACT

An integrated catalytic transfer hydrogenation (CTH) and aqueous phase reforming (APR) process was applied for the hydrothermal hydrodeoxygenation of triglycerides to diesel-like hydrocarbons in the presence of water. Up to 71.91% yield of diesel-like hydrocarbons ($C_{17} + C_{18}$ products) could be achieved when using decalin as solvent at 523 K with autogenous pressure after 12 h of reaction time. The promotional effect on the hydrodeoxygenation of triglycerides was ascribed to the high reactivity of *in situ* generated H_2 from solvents.

1. Introduction

With the gradual depletion of fossil resources and further deterioration of the environment and its ecosystem, much effort has been devoted to explore renewable resources for the sustainable supply of chemicals and fuels. Various biomass have been identified as alternate source of energy fuels [1], among which microalgae are being considered as a promising renewable energy resource due to high cellular lipid contents (up to 60 wt%) [2] and high photosynthetic rates. Dry microalgae are usually used as feedstock for biofuels production, but the energy required for the dewatering process accounted for up to 90% of the total energy consumption [3,4]. Moreover, although the conversion of lipid by transesterification with alcohols into fatty acid alkyl esters (biodiesel) has been commercialized, biodiesel has the disadvantages such as poor chemical stability and low energy density because of its high oxygen content [5,6]. An alternative way to transform lipid is to remove oxygen *via* hydrodeoxygenation to produce diesel-like hydrocarbons [7,8], which are superior to biodiesel in terms of energy density and oxidation stability [9].

In the hydrodeoxygenation reaction, high pressure of molecular hydrogen is frequently required to achieve considerable feed conversions, which constrains its application for biofuels production because of its need for specialized equipment and potential safety issues. Thus, the use of *in situ* generated hydrogen as alternative to molecular hydrogen has been proposed in order to produce biofuels under mild reaction conditions. Hydrogen can be *in situ* generated by two catalytic routes, catalytic transfer hydrogenation (CTH) and aqueous phase reforming (APR). CTH is a process in which hydrogen is transferred from a hydrogen donor molecule to an acceptor. Reported hydrogen donors include formic acid [10], 2-propanol (2-PO) [11–13], methanol [13] and ethanol [12]. APR is a process in which hydrogen containing compounds (such as methanol, ethanol and glycerol) react with water to produce a hydrogen-rich gas stream. It is envisaged that a hydrodeoxygenation reaction using *in situ* generated hydrogen rather than molecular hydrogen generally has higher reaction rates. For example, a positive effect on the hydrodeoxygenation activity for conversion of triolein was observed over Pd/C aided by *in situ* hydrogen produced from glycerol reforming [14]. Similar promotional effect was also observed in conversion of stearic acid to hydrocarbons over Pt-Re/C with glycerol for *in situ* hydrogen production [15]. However, utilization of glycerol APR as the only source of *in situ* H_2 required either a high reaction temperature (573 K) or long reaction time (20 h) for the reaction to complete and sufficient amount of H_2 to form. Herein, we demonstrate that the conversion of triglycerides to hydrocarbon fuels could be efficiently catalyzed by Pd/C in the presence of water at 523 K within 12 h when an integrated CTH and APR process was employed.

2. Experimental

2.1. Catalyst preparation

The 5 wt% Pd/C was prepared by a wetness impregnation method as follows: Activated carbon was first impregnated with appropriate amount of aqueous solution of H_2PdCl_4. After impregnation for 2 h, excess water was then removed at 298 K in a rotary evaporator. The

---

* Corresponding authors.
E-mail addresses: dhjiang@zjut.edu.cn (D. Jiang), junni@zjut.edu.cn (J. Ni).

http://dx.doi.org/10.1016/j.catcom.2016.11.017

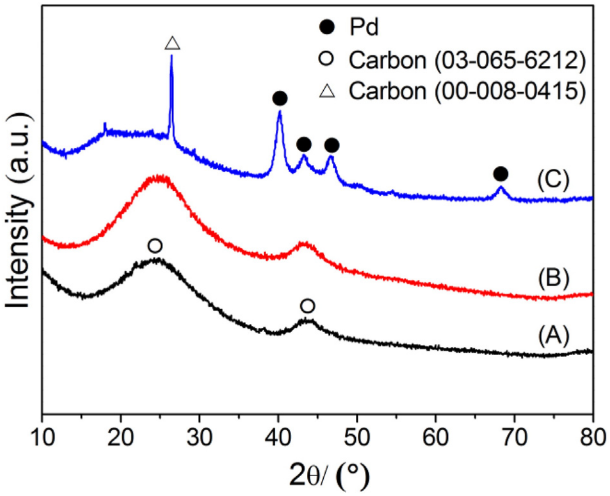

Fig. 1. XRD patterns of AC support (A) and reduced Pd/C catalysts before (B) and after (C) reaction.

resultant solid was dried in ambient air at 383 K for 4 h and subsequently reduced in H_2 flow at 523 K for 1 h in a tube furnace.

2.2. Catalyst characterization

BET surface areas of the samples were determined by N_2 adsorption using Quantachrome NOVA 1000e apparatus with liquid-N_2 at the temperature of 77 K. The samples were outgassed at 523 K for 4 h prior to analysis. X-ray diffraction (XRD) data were collected on an X'Pert PRO X-ray diffractometer with a vertical goniometer between $2\theta = 10^o$ and 80^o at 2^o min^{-1} employing a Cu-Kα radiation source ($\lambda = 0.15406$ nm). Transmission electron microscope (TEM) measurements were carried out using a HITACHI H600 microscope operated at an accelerating voltage of 120 kV. Before the catalyst characterization, all catalysts were reduced in H_2 flow at 523 K for 1 h.

2.3. Catalyst evaluation

One-pot catalytic hydrodeoxygenation reaction was performed in a tank reactor (300 mL capacity) with continuous stirring. Typically, triolein (4.25 g) was diluted in the mixture of solvent-water solution with solvent/water ratio of 0:100, 10:90, 30:70, 50:50, 70:30, and 90:10 (volume ratio with total volume set at 100 mL). The solvents were dodecane, toluene and decalin. The finial mixture was then charged into the reactor, together with Pd/C catalyst (1 g) pre-reduced at 523 K for 1 h. Before the reaction, the reactor was purged three times with N_2 to exchange the air inside. The reaction was performed at 523 K for 12 h with autogenous pressure at a stirring rate of 600 rpm. After the desired reaction time, the reactor was cooled rapidly to room temperature. The products in the organic phase and water phase were analyzed by GC–MS with a flame ionization detector (FID) and a HP-5 column (30 m, 0.25 mm inner diameter).

3. Results and discussion

3.1. Physicochemical properties of Pd/C catalysts

XRD patterns of activated carbon (AC) support and reduced Pd/C catalysts before and after reaction are shown in Fig. 1. TEM images of the reduced Pd/C catalysts before (A) and after (B) reaction are presented in Fig. 2. For the reduced Pd/C catalyst, no characteristic peaks assignable to metal Pd can be observed, suggesting a high Pd dispersion and small Pd particle size on the AC support. The average particle size of Pd metal nanoparticles calculated from TEM is 1.7 nm (Fig. 2A), which further confirms the XRD result. In addition, there is also no PdO crystalline phase, indicating that PdO was completely reduced by H_2 at 523 K for 1 h. In contrast, for the spent catalyst, intensive peaks characteristic of Pd metals are observed (Fig. 1C). Meanwhile, TEM shows Pd metal nanoparticles with average size of 5.7 nm are present over the spent catalyst (Fig. 2B). Both results indicate there was a growth of Pd metal nanoparticles during the reaction.

3.2. The catalytic performance of the Pd/C catalyst

Hydrothermal hydrodeoxygenation of triglycerides over the Pd/C catalyst was first performed with different dodecane/water ratios, and the reaction results are shown in Table 1. When *in situ* hydrogen generated solely from APR of glycerol was used in reaction, as the case of dodecane/water = 0/100, the major products in the organic phase were oleic acid and stearic acid while glycerol was the major product in the water phase. The presence of substantial amount of oleic acid and stearic acid at the complete conversion of triolein indicates the

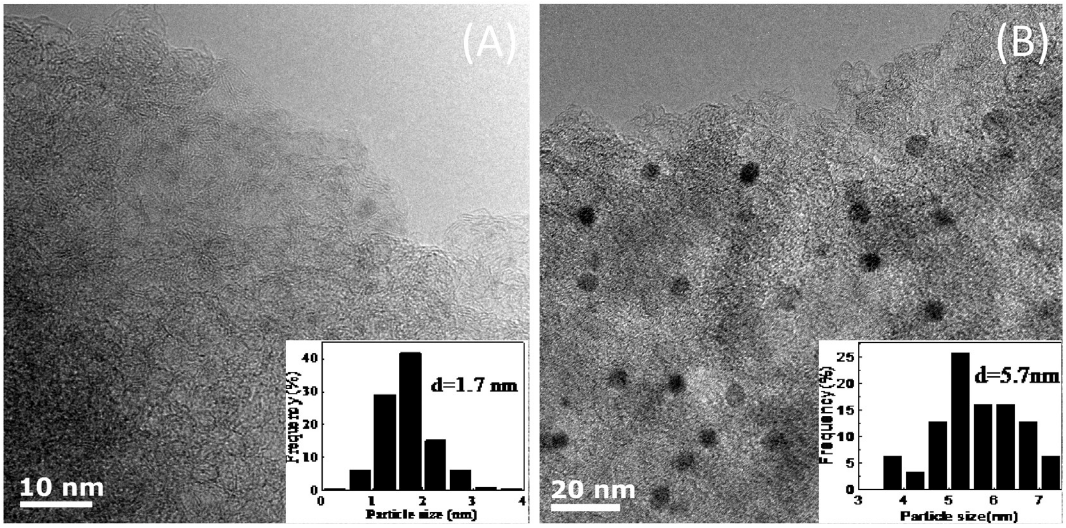

Fig. 2. TEM images of the reduced Pd/C catalysts before (A) and after (B) reaction.