Applied Catalysis A: General 467 (2013) 261–269

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

A highly active nanocomposite silica-carbon supported palladium catalyst for decarboxylation of free fatty acids for green diesel production: Correlation of activity and catalyst properties

Elvan Sari[a], Manhoe Kim[b,c], Steven O. Salley[a,b], K.Y. Simon Ng[a,b,c,*]

[a] Department of Chemical Engineering and Material Science, Wayne State University, Detroit, MI 48202, USA
[b] National Biofuels Energy Laboratory, NextEnergy, Detroit, MI 48202, USA
[c] Alternative Energy Technology, Wayne State University, Detroit, MI 48202, USA

ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form 17 July 2013
Accepted 23 July 2013
Available online 1 August 2013

Keywords:
Decarboxylation
Green diesel
Fatty acid
Deoxygenation

ABSTRACT

A class of Pd catalyst supported on a silica-activated carbon nanocomposite for free fatty acid (FFA) decarboxylation was developed, and displayed excellent activity and operation stability selectively for the green diesel hydrocarbons formation in the absence of H_2 under mild reaction conditions. Six catalysts containing 5 wt% Pd were prepared by systematically varying the silica content in the support. In addition to the effect of particle size, the impact of catalyst preparation method on the activity and selectivity was elucidated. A 5 wt% Pd/Si-C-4 catalyst maintained stable activity for 16 days under reaction conditions of 1.5 MPa and 300 °C. Although a continuous supply of H_2 was not necessary, H_2 treatment was essential to restore the catalytic activity and the desired product selectivity. Characterization of the catalyst revealed that the highly active Pd/Si-C-4 catalyst has easily accessible and well-distributed metallic Pd nanoparticles inside the hybrid mesopores.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Environmental awareness and projected increases in the world's energy demand have been the motivation for seeking environmentally friendly, renewable alternative fuels. A large amount of waste cooking oil and grease is produced in the U.S. that can be exploited for liquid biofuel generation. In particular, brown grease, which contains mainly free fatty acids (FFAs), can be a potential inexpensive source for a process to obtain straight chain hydrocarbons in the diesel fuel boiling range (green diesel) via catalytic decarboxylation.

Recently, there has been considerable attention on the development of suitable catalysts for decarboxylation of free fatty acids (FFA) [1–6]. Most early studies focused on Pd-based catalysts, which exhibit high activity and selectivity for the formation of straight chain hydrocarbons with one carbon number less than the source FFA [7]. However, these supported palladium catalysts readily deactivate even in the presence of H_2. Although a 3 wt% Pd-SBA-15 catalyst was active at 300 °C under 17 bar of 5 vol% H_2 in argon for stearic acid decarboxylation for 5 h, deactivation was reported due to the formation of unsaturated heptadecene product [3]. A 1 wt% Pd supported on a synthetic mesoporous carbon catalyst showed 23% decrease in the BET specific surface area after decarboxylation of palmitic and stearic acids mixture at 300 °C and 17.5 bar H_2/Ar [1]. In all cases, the extensive catalyst deactivation was attributed to catalyst coking. Snare et al. related the catalyst deactivation to the amount of unsaturated products which further led to catalyst coking specifically for Ru/C and Rh/C catalysts after 6 h of stearic acid decarboxylation [7]. On the other hand, the Pd/C catalyst deactivation was attributed to the reaction atmosphere and degree of unsaturation of the FFA by some researchers [8–10] and to catalyst supports by others [4]. Recently, the Jones group showed that the deactivation of a mesoporous silica supported palladium catalyst occurred during FFA decarboxylation due to the loss in total surface area, porosity and accessible palladium surface area [5]. Unlike the previously reported literature claim of coke formation, it was claimed that strongly adsorbed reactants and products cause the deactivation. The Savage group [11] also investigated the stability of 5% Pd/C in fatty acid hydrothermal decarboxylation, and it was reported that the decarboxylation activity of the catalysts was maintained although metal dispersion was significantly reduced after catalyst reuse. The difference in catalytic behavior of the supported metal particles was attributed to the hydrothermal reaction where the catalyst was exposed to sub-critical water.

An ordered mesoporous silica-carbon catalyst support was synthesized as a novel hybrid material [12]. This nanocomposite

---

[*] Corresponding author at: Department of Chemical Engineering and Material Science, Wayne State University, Detroit, MI 48202, USA. Tel.: +1 313 577 3805; fax: +1 313 577 3810.
E-mail address: sng@wayne.edu (K.Y.S. Ng).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.07.053

support has gained increasing attention for catalysis applications in recent years due to several unique features such as high dispersion of palladium nanoparticles (about 3 nm), high surface area, large and tunable pore structure and excellent stability [13,14]. These silica-carbon nanocomposites were produced on the basis of a triblock copolymer templating approach which is a time consuming catalyst preparation technique.

The nature of the surface functional groups on the activated carbon support when modified by oxidative treatments was found to be very important for the catalytic activity of precious metals such as palladium [15,16]. After introducing such oxygen groups, the surface behavior of carbon changes; therefore their catalytic properties differ [17]. The components of activated carbon are disorganized polyaromatic sheets with reactive corner atoms and adsorbent surface atoms. The precursor that is selected for this study, TEOS, is expected to form the templates that contain —OH groups and bridged O atoms in a Si—O—Si structure on the amorphous silica walls, and these groups play a very important role for the incorporation of silica into activated carbon.

In the present work, a new, well-defined and highly efficient Pd/Si-C catalyst was developed for the decarboxylation of FFA. This new nanostructured hybrid catalyst has a well-defined mesoporous structure which allows a better understanding of structure–activity characteristics that are crucial in elucidating the FFA decarboxylation mechanism, unlike an activated carbon supported palladium catalyst. The decarboxylation reaction of oleic acid was investigated over these catalysts with the aim of producing green diesel in the absence of additional H_2 under mild reaction conditions, elucidating the effects of the nature of the functional groups on the activity and developing a procedure to maintain high catalytic activity.

2. Experimental

2.1. Materials

The following chemicals were used in this investigation: a commercial activated carbon (Charcoal Norit, Sigma–Aldrich), tetraethyl orthosilicate (TEOS, 99.999%, Sigma–Aldrich), palladium(II) chloride ($PdCl_2$, ≥99.9%, Sigma–Aldrich), oleic acid (technical grade 90%, Sigma–Aldrich, St. Louis, MO), dodecane (anhydrous, ≥99%, Sigma–Aldrich), carbon disulfide (HPLC grade ≥99.9%, Sigma–Aldrich), methyl arachidate (>99%, Nu-Chek Prep Inc., Elysian, MN), Ultra high purity grade argon (Ar), hydrogen (H_2) and nitrogen (N_2) were purchased from Cryogenic Gases (Detroit, MI).

2.2. Catalyst preparation

Activated carbon (AC) was immersed in liquid TEOS with varying mass ratios of TEOS to AC. The mixture was stirred vigorously for 2 h at 120 °C. Then, it was dried at 105 °C for 18 h. Prepared supports were designated as Si-AC-*x* where *x* represents the mass ratio of TEOS to AC. During the preparation of Si-AC-0.5 and Si-AC-1, ethanol was added to provide necessary wetness of AC. For comparison, only activated carbon and only silica supported catalysts were also prepared. A support containing only silica was prepared by calcination of the Si-AC-3 support at 550 °C for 5 h in air to remove activated carbon. In order to obtain 5 wt% Pd on the support, 1.1 wt% $PdCl_2$ solution was mixed with the support ($PdCl_2$/support = 0.088 wt/wt) at room temperature for 24 h. After each catalyst was dried at 100 °C for 5 h, the reduction was carried out under a flow of 10 vol% H_2–90 vol% N_2 at 200 °C for 3 h.

2.3. Material characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku MiniFlex 600 at a scan rate of 3°/min (40 kV, 15 mA). The Scherrer equation and Bragg's law were used to calculate the mean metal particle size and the lattice parameter, respectively.

A Brunauer–Emmett–Teller (BET) analysis was carried out using a Micromeritics TriStar II 3020 (V1.03) surface area analyzer. The samples were degassed in vacuum (P) at 200 °C for 6 h prior to analysis. The adsorption/desorption isotherms were acquired at 87.30 K in the relative pressure range of 0.01–0.99. The Barrett–Joyner–Halenda (BJH) model was used to derive the pore volumes, average pore diameters and pore size distributions from the desorption branches of the isotherms. A *t*-Plot was used to calculate the micropore surface areas and micropore volumes.

Catalyst acidity was determined with a Brinkmann/Metrohm 809 Titrando (Westbury, NY) potentiometric titrator. An acid–base technique [18] was performed to determine the total acid number of surface groups reacted in the catalyst slurry of 0.1 g catalyst and 75 mL titration solvent including a mixture of water, propan-2-ol and toluene. A solution containing 0.1 N KOH was used as titrant. The amount of titrant consumed to reach a potentiometric end point (EP) was used to calculate the amount of acidic groups.

Transmission electron microscopy (TEM) was conducted using a JEM-2010 microscope operating at 200 kV. The catalysts that were suspended in ethanol were placed on a carbon coated copper grid.

Fourier transform infrared (FTIR) spectra of powder catalysts were collected on a Spectra 400 spectrometer (Perkin-Elmer, Shelton, CT). Four scans were used to establish an acceptable signal to noise level for each spectrum.

2.4. Decarboxylation procedure

2.4.1. Batch reactions

The liquid-phase decarboxylation of oleic acid was investigated in a 100 mL Hanwoul (Geumjeong-dong, South Korea) stirred batch reactor. Gas flow rates were controlled by Brooks (Warren, MI) metal sealed mass flow controllers. In all experiments, the catalyst was soaked in dodecane (solvent) prior to the reduction of the catalyst under H_2 flow of 60 mL/min [10]. During the reduction step the agitation speed was kept at 250 ± 2 rpm, and the pressure was 0.5 MPa. As soon as the desired pressure was reached, the temperature was increased to 200 °C with a temperature ramp of 10 °C/min and kept under flowing H_2 for 1 h at 200 °C. After cooling the reactor under H_2 flow, excess H_2 was purged with inert gas and oleic acid was fed into the vessel through a one way valve.

For the activity test of each catalyst, 0.45 g catalyst, 2.0 g oleic acid and 30.0 g solvent were used. Throughout the reaction, the agitation speed was kept at 1000 ± 4 rpm. Ar gas was added into the vessel in order to obtain 1.5 MPa total pressure at 300 °C. After the reaction, the reactor was quenched in an ice bath and the final liquid product was analyzed. The standard deviation for conversion and product selectivities from a multiple run control experiment was ±2.4%.

2.4.2. Flow reactor

The continuous decarboxylation of brown grease was carried out in a fixed bed tubular reactor (40 mL BTRS-Jr, Autoclave Engineers, PA). Two grams of catalyst was placed between glass wool layers. The catalyst was first reduced at 200 °C and 0.5 MPa under H_2 flow. After reduction, the reactor was pressurized to 1.5 MPa under Ar gas and heated to 300 °C. Oleic acid (0.2 M in dodecane) was continuously fed through the catalyst bed at a volumetric flow of 0.04 mL/min.

Download English Version:

https://daneshyari.com/en/article/40058

Download Persian Version:

https://daneshyari.com/article/40058

Daneshyari.com