Roles of monometallic catalysts in hydrodeoxygenation of palm oil to green diesel

Atthapon Srifa [a,b], Kajornsak Faungnawakij [a,*], Vorranutch Itthibenchapong [a], Suttichai Assabumrungrat [b]

[a] Nanomaterials for Energy and Catalysis Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Klong Laung, Pathumthani 12120, Thailand
[b] Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

HIGHLIGHTS

- Effective deoxygenation of palm oil to green diesel over supported metal catalysts.
- The order of catalytic activity is Co > Pd > Pt > Ni catalysts.
- DCO is selective over Ni, Pd, and Pt, while DCO, DCO_2, HDO are all selective over Co.
- Turnover frequency (TOF) over monometallic species supported on γ-Al_2O_3.
- Reaction network in hydrotreating of palm oil based on a model-compound study.

GRAPHICAL ABSTRACT
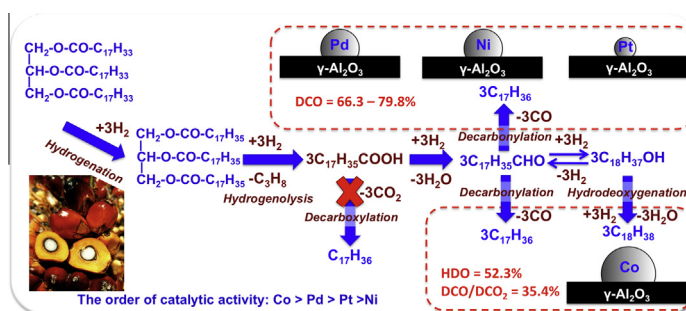
ABSTRACT

Diesel-like alkanes, so-called green diesel, produced from vegetable oil, have emerged as an important biofuel to replace petroleum diesel. In the present work, the deoxygenation of palm oil to green diesel was performed in a trickle-bed reactor over four γ-Al_2O_3-supported monometallic catalysts (Co, Ni, Pd, and Pt). The catalysts with various metal loadings (2–10 wt.%) were prepared by the incipient wetness impregnation method and were characterized by XRD, TPR, N_2 sorption, TEM, and CO pulse chemisorption. The results revealed that metallic sites of the catalysts were formed after pre-reduction in H_2 with differences in metal particle size and metal dispersion on γ-Al_2O_3. The reaction tests revealed that the catalytic activity was in the order of Co > Pd > Pt > Ni, whereas the turnover frequency (TOF) increased with increments of the metal particle size. The decarbonylation reaction was more dominant than the hydrodeoxygenation reaction when the reaction was catalyzed by Ni, Pd, and Pt catalysts. Meanwhile, the contribution of decarbonylation and/or decarboxylation was nearly comparable to that of the hydrodeoxygenation reaction over Co catalyst. By combining the reaction tests with a model compound, oleic acid, a reaction network for the deoxygenation of palm oil was suggested and discussed.

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1. Introduction

Currently, the development of renewable fuels from biomass is an important key to future energy due to the depletion of petroleum fuels. Triglycerides in vegetable oils and animal fats are generally composed of C_8–C_{24} fatty acids. They have been used as important renewable feedstocks for the production of renewable fuels because of their low degree of functionalization and simple structure compared with cellulosic biomass [1,2]. In particular, palm oil contains primarily C_{16} and C_{18} fatty acids, making it a promising feedstock for green diesel and biodiesel production.

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* Corresponding author. Tel.: +66 2 564 7100x6638; fax: +66 2 564 6981.
 E-mail address: kajornsak@nanotec.or.th (K. Faungnawakij).

There are two main catalytic reactions of triglycerides and/or organic acid using vegetable oil or animal fat for biofuel production for diesel engines: (1) a transesterification/esterification process to produce biodiesel, a mixture of esters, and (2) a catalytic deoxygenation process to produce renewable diesel, so-called bio-hydrogenated diesel (BHD) or green diesel, having a similar molecular structure to that of petroleum diesel. Typically produced by transesterification of triglycerides with methanol, fatty acid methyl esters (FAMEs) or biodiesel has been used as a component in diesel blending [3]. However, some disadvantages of biodiesel compared to petroleum diesel are the C=C bonds and C=O bonds remaining in the molecules of FAMEs, e.g., low thermal and oxidation stability because of its high oxygen content, high viscosity, and low heating value [4,5].

As a result, green diesel, which provides better diesel properties, such as high cetane number, zero oxygen containing [6], and high thermal and oxidation stability [7], has attracted significant attention. Green diesel can be produced by the catalytic deoxygenation of triglycerides through three major reaction pathways, including decarbonylation (DCO), decarboxylation (DCO_2), and hydrodeoxygenation (HDO) [2,8], under reaction conditions of 350–450 °C and 5–15 MPa H_2 [9,10]. Generally, the reaction first proceeds via hydrogenation of unsaturated triglycerides (C=C double bond) to form saturated triglycerides [11], followed by the hydrogenolysis of saturated triglycerides resulting in fatty acids and propane. Finally, the fatty acid undergoes the following reactions: (1) HDO, an exothermic reaction, to remove oxygen in the form of water and yield *n*-alkane with the same carbon number as the corresponding fatty acid, and (2) DCO and (3) DCO_2, endothermic reactions, to eliminate oxygen in form of CO and water or CO_2, respectively. The consequent *n*-alkane has one carbon atom loss compared to the original fatty acid [12].

The catalysts *most frequently* used in the deoxygenation of triglycerides, fatty acids, and esters are (1) bimetallic sulfide catalysts, e.g., $NiMoS_2$ [2,4,13,14], $CoMoS_2$ [14–18], and $NiWS_2$ [19,20]; (2) metal phosphide and carbide catalysts, e.g., Ni_2P [21,22], W_2C [23], and Mo_2C [23,24]; and (3) metal catalysts in a reduced state, such as Ni [1,11,25–27], Co [11,28], Pd [29–31], Pt [3], and Ru [32,33]. The conventional metal sulfide catalysts are less expensive catalysts [23] and show high activity in the deoxygenation of triglycerides and model compounds; however, sulfur leaching leads to catalyst deactivation and sulfur contamination in liquid products [28,34–36]. In addition, metal sulfide catalysts require the addition of sulfiding agents, e.g., CS_2 and DMDS, into the liquid feed to avoid catalyst deactivation during deoxygenation reactions [11,21]. The trace amount of water produced from DCO and HDO reactions would hasten the sulfur leaching and rigorously shorten the lifetime of the catalysts [37]. The metal phosphide and carbide catalysts also revealed high activity in oxygen removal and selectivity for diesel-range alkanes. Nevertheless, the preparation process of catalysts was complicated and transformation of their catalyst active phases was mostly observed during deoxygenation reactions, resulting in a short lifetime of these catalysts [28].

Alternatively, metal catalysts and sulfur-free catalysts have attracted great attention for deoxygenation reactions due to their high reactivity at mild temperature, no sulfur contamination in liquid products, and lower H_2 requirement [38]. Some metal catalysts, such as Ni, Pd, and Pt, are favorable in the DCO and DCO_2 pathways. The hydrogen consumption for the deoxygenation of triglycerides/fatty acids/esters were in the order of HDO > DCO > DCO_2 routes; thus, the DCO and DCO_2 routes may be more theoretically economical than the HDO route [34,35]. Several researchers have studied various metal catalysts for the deoxygenation of model compounds, such as palmitic acid [30,35], stearic acid [1,25,39–41], oleic acid [39], linoleic acid [39], methyl palmitate [27], methyl oleate [3], methyl heptanoate

[28], and methyl octanoate [42]. However, only a few studies investigated the deoxygenation of triglycerides, such as palm oil [43,44], jatropha oil [3,12], and sunflower oil [29]. In particular, Co species are good catalysts for hydrogenation/hydrogenolysis reactions [28]. However, to the best of our knowledge, the use of Co catalysts in the deoxygenation of triglycerides has never been reported in the literature. Consequently, four metal catalysts, namely Co, Ni, Pd, and Pt, are attractive for the deoxygenation of triglycerides.

In the present work, we prepared γ-Al_2O_3-supported monometallic catalysts (Co, Ni, Pd, and Pt) by the incipient wetness impregnation method. The physical and chemical properties were characterized by XRD, TPR, N_2 sorption, TEM, and CO pulse chemisorption, and their catalytic performances for the deoxygenation of palm oil were subsequently investigated in a continuous-flow trickle-bed reactor. To understand the roles of the four monometallic catalysts on the activity and selectivity in the deoxygenation of triglycerides to hydrocarbons, the contributions of HDO and DCO/DCO_2 were estimated based on the mole balance corresponding to fatty acids in the oil feed. The obtained data could be useful for the evaluation of the hydrogen consumption and heat balance in the deoxygenation process. Moreover, the reaction network of the deoxygenation of palm oil over four supported monometallic catalysts was also discussed based on a model compound study.

2. Experimental section

2.1. Chemicals

Cobalt (II) nitrate hexahydrate [(Co(NO_3)_2·6H_2O), purity $\geqslant 98\%$], nickel (II) nitrate hexahydrate [(Ni(NO_3)_2·6H_2O), purity 99.999%], *trans*-dinitrodiamminepalladium (II) [(2NO_2·Pd·2H_3N), purity 99.9%], and diamminedinitritoplatinum (II) [(Pt(NH_3)_2(NO_2)_2), 3.4 wt.% solution in dilute ammonium hydroxide] were obtained from Sigma–Aldrich Chemical Co. LLC., Germany. All chemicals were used without further purification. γ-Al_2O_3 (1.8 mm diameter, purity 99.9%) was obtained from Sasol Company, Germany.

2.2. Catalyst preparations

The γ-Al_2O_3 support was crushed and sieved to 0.18–0.5-mm diameter. The Co, Ni, Pd, and Pt supported on the γ-Al_2O_3 catalysts were prepared by the incipient wetness impregnation method using cobalt (II) nitrate hexahydrate, nickel (II) nitrate hexahydrate, *trans*-dinitrodiamminepalladium (II), and diamminedinitritoplatinum (II) as the corresponding metal salt precursors. After impregnation, the resultant samples were dried at 120 °C for 12 h and then calcined at 500 °C for 5 h. The metal catalysts with metal loadings of 2, 5, and 10 wt.% were labeled as 5CoAl, 10CoAl, 5NiAl, 10NiAl, 2PdAl, 5PdAl, 2PtAl, and 5PtAl, where the prefix numbers represent the %metal loadings.

2.3. Catalyst characterizations

Powder X-ray diffraction (XRD) patterns of the samples were collected on an X-ray diffractometer (D8 ADVANCE, Bruker, Ltd., Germany) using a Cu Kα radiation. The measurement was conducted at 40 kV and 40 mA, and in steps of 0.02° s^{-1} with a step time of 0.5 s over the range of 10° < 2θ < 80°.

Specific surface areas and total pore volumes were measured by a nitrogen sorption technique at −196 °C (Nova 2000e, Quantachrome Instruments, Germany). Prior to the measurement, the samples were degassed at 120 °C for 3 h. Pore size distributions of the samples were determined from the desorption branch of the isotherms using the Barrett–Joyner–Hallenda (BJH) method. The specific surface area was estimated based on the BET approach.