



Hydrothermal deoxygenation of triglycerides over carbon-supported bimetallic PtRe catalysts without an external hydrogen source

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ARTICLE INFO

Keywords:

Hydrothermal deoxygenation
Triglyceride
PtRe
Bimetal
Carbon supports

ABSTRACT

Hydrothermal deoxygenation is a promising route for producing oxygen-free hydrocarbons from triglycerides even without an external H₂ source. In this study, PtRe catalysts supported on various carbons were investigated for this reaction. The PtRe catalysts showed enhanced rates of glycerol reforming for in situ H₂ production and higher deoxygenation activities, as compared to Pt catalysts. Consequently, the PtRe catalysts showed superior hydrothermal deoxygenation performances. Carbon supports with low oxygen content (e.g., CNT) were beneficial for supporting highly dispersed and well alloyed PtRe particles, which were prerequisites for high catalytic activity. Oxygen-rich carbon surfaces caused the segregation of Re, causing low catalytic activity. PtRe/CNT showed the best performance, yielding 72 wt% *n*-paraffin (theoretical yield: 79 wt%) from palm oil. The catalyst could be recycled for 5 times without significant loss of activity.

1. Introduction

Triglycerides (e.g., microalgal oil, vegetable oil, and waste cooking oil) are a promising feedstock for producing bio-derived fuels. They are esters combining one glycerol and three long-chain fatty acids (generally C₁₄–C₂₂) which contain relatively low oxygen contents and high energy densities compared to other biomass feedstock [1–3]. The synthesis of biodiesel (e.g., fatty acid methyl ester) from triglycerides via transesterification is a major commercially applied process [3,4]. However, the presence of oxygen in biodiesel diminishes its energy density, storage stability, and cold flow properties [5–7]. To overcome the limitations of biodiesel, catalytic upgrading of triglycerides to oxygen-free fuels through hydroprocessing has been developed [8–17]. In these processes, triglycerides are hydrotreated over MoS₂-based catalysts [9,10] or supported metal catalysts [11,9–17] under high-pressure H₂. Under such conditions, triglycerides containing unsaturated fatty acid units are first hydrogenated and cleaved into three saturated fatty acids by hydrogenolysis (Scheme 1a). The resulting fatty acids are then deoxygenated via decarboxylation/decarbonylation (DCO) and hydrodeoxygenation (HDO) pathways. DCO produces *n*-paraffins with one less carbon atom than the initial fatty acids, whereas HDO produces *n*-paraffins having the same carbon number. With the production of long-chain paraffins, light gaseous hydrocarbons (C₁–C₃) are also coproduced due to the glycerol hydrogenolysis and the CO

methanation. These side reactions all consume significant amounts of H₂. Although the produced liquid paraffins have significantly improved fuel quality, the large consumption of H₂ in these processes is disadvantageous for overall economics and sustainability. It should be noted that H₂ is currently primarily produced from natural gas.

Hydrothermal deoxygenation of triglycerides in subcritical water (523–653 K) can provide an alternative pathway for producing oxygen-free hydrocarbons [18–23]. Savage and colleagues first reported that the high-temperature hydrothermal treatment of model fatty acids over Pt/C and Pd/C catalysts could produce saturated paraffins even in the absence of an external H₂ source [18,19]. The result indicated that hydrogen could be supplied in situ during the reaction. Considering that a significant amount of heavy oligomers were also formed, hydrogen transfer might be involved under those reaction conditions. More recently, other researchers investigated the hydrothermal deoxygenation of natural triglycerides or the mixtures of fatty acids and glycerol [20–23]. The main difference between these studies and the earlier works by Savage is that glycerol in the reactants can be readily transformed to H₂ in situ via aqueous phase reforming (APR) (Scheme 1b). In principle, one glycerol can generate seven H₂ molecules at maximum through APR [24–32], which is sufficient for the saturation and the deoxygenation of fatty acids. Under this novel reaction scheme, glycerol acts as a source for H₂ production rather than a consumer of H₂ (the case of conventional hydroprocessing). This can enable essentially net-

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<https://doi.org/10.1016/j.mcat.2019.110419>

Received 19 March 2019; Received in revised form 19 May 2019; Accepted 20 May 2019

Available online 30 May 2019

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