

Deoxygenation of oleic acid under an inert atmosphere using molybdenum oxide-based catalysts



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ARTICLE INFO

Keywords:

Deoxygenation
Dehydrogenation
MoO₃
DFT
Green diesel

ABSTRACT

In this study, the deoxygenation of oleic acid under a N₂ atmosphere over metal oxide catalysts is investigated for the production of green diesel hydrocarbons. The molybdenum oxide catalysts with promoters (Ni, Co, and Cu) and varying catalyst loadings (19–34 wt%) on γ -Al₂O₃ support are prepared by an incipient wetness impregnation method and characterized by XRD, FE-SEM/EDX, TEM, XPS, and N₂ sorption. The catalytic testing is carried out in a batch reactor with various reaction times (3–9 h) and temperatures (300–350 °C) under N₂ pressure (10 and 40 bar). The NiMo oxide/ γ -Al₂O₃ exhibits the highest performance with over 80% conversion and good selectivity toward C17 hydrocarbon products. The catalytic performance of the NiMo oxide/ γ -Al₂O₃ remains stable during 4 reaction cycles. Decarboxylation (DCO₂) and decarbonylation (DCO) are observed to be the reaction pathways of the deoxygenation and these reactions are enhanced by increasing reaction temperature and time. Stearic acid and other hydrogenated compounds were produced via the *in situ* hydrogenation which was proposed as a competitive reaction in the deoxygenation of oleic acid under the N₂ pressure. The DFT calculations confirm that the dehydrogenation and hydrogenation reactions could occur on the MoO₃ surface. These processes are responsible for the *in situ* formation of hydrogen species, leading to the formation of hydrogenated products. Hydroxyl groups on the terminal oxygen sites created by dehydrogenation could contribute to the surface vacancy and further promote the DCO₂ or DCO pathway. The molybdenum oxide-based catalysts show a great potential for green diesel production without the use of H₂ feed.

1. Introduction

Due to the depletion of fossil fuel, biofuel technology has been employed worldwide as an alternative and renewable energy source. In recent years, biofuel production from triglyceride in fats and oils, mainly obtained from animal and plant, has gained a lot of interests because triglyceride molecules consist of fatty acids and glycerol with suitable chain length and low number of functional groups. While there are concerns about insufficient non-food grade triglyceride feedstocks to supply the global energy demand, biofuel technology is still a viable method for fuel production as the triglyceride feedstock can be co-processed with unrefined streams in a crude oil refinery. The fatty acid methyl ester (FAME), so-called biodiesel, is typically produced via transesterification of triglycerides and methanol [1–3]. Although addition of FAME into fossil diesel yields high cetane number, it contains high oxygen and unsaturated units. Hence, many drawbacks arise from the high ratio of biodiesel blending i.e. B10 or greater, such as higher

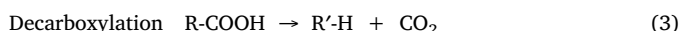
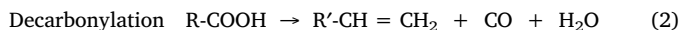
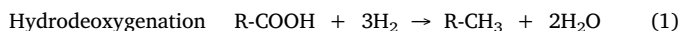
viscosity and cloud point, and lower thermal resistant properties. Alternative processes such as deoxygenation or hydrotreating could be preferable than the conventional transesterification reaction because they can remove oxygenated component in triglycerides and produce a proper long-chain paraffin in a diesel-like biofuel. This renewable diesel, or so-called green diesel, contains similar chemical structure as found in fossil diesel and provides better fuel properties with much higher blending ability than FAME [4].

Generally, deoxygenation of fatty acids proceeds via three main reaction pathways to yield green diesel products [2,5–8]. Hydrodeoxygenation (HDO) produces a straight-chain alkane which retains hydrocarbon chain length of the original fatty acid and a water by-product, as shown in Eq. (1). Decarbonylation (DCO) and decarboxylation (DCO₂) yield straight chain alkanes with shorter hydrocarbon chains than that of the original fatty acid and the by-products for those two reactions are CO and water (Eq. (2)) and CO₂ (Eq. (3)), respectively. Although, all reactions can produce diesel hydrocarbons, the

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HDO reaction consumes the highest amount of H₂ in comparison to the others. The use of high pressure H₂ gas in the green diesel production over conventional catalysts, e.g., CoMoS₂, NiMoS₂, leads to the high cost and serious concerns for equipment, safety, operations, and industrial up-scaling; hence, preventing the widespread utilization of this technology. Moreover, the water by-product in HDO could lead to catalyst deactivation. The DCO and DCO₂ reactions might be more practical as they can be operated under mild conditions with low amount of H₂, even accounting for the unintentional CO₂/CO hydrogenation (methanation reaction) which could occur under the conventional conditions of deoxygenation [9,10]. The liquid fuel products from both DCO and DCO₂ also contain low water content, which would extend the catalyst lifetime.



R, R' = saturated alkyl group

In literature, metal catalysts such as Ni, Pt, Pd [6,9,11–18], and metal sulfide catalysts such as MoS₂, NiMoS₂, CoMoS₂ [10,19–23] have been typically applied to the deoxygenation of triglycerides and biomass-derived oxygenated compounds. The transition metal catalysts that have been reported to be selective for DCO₂ and DCO [11,24,25] often suffer from fast deactivation due to their susceptibility to CO poisoning and coke formation [5,26,27]. The metal sulfide catalysts that are selective toward HDO suffer from sulfur leaching which could contaminate the product under the extreme operating conditions i.e. high H₂ pressure over 40 bar at a reaction temperature range of 300–350 °C [28,29]. Metal oxide catalysts including molybdenum oxides have gained attentions as alternative deoxygenation catalysts under the H₂ pressure [30,31]. Recently, MoO₃ catalysts have been reported to be active in removing oxygen atoms from lignin-derived oxygenates and producing aromatic hydrocarbons via HDO under a low hydrogen pressure [31,32]. In addition, the MoO₃ catalyst demonstrated the highest activity in deoxygenation of small oxygenates among other metal oxide catalysts i.e. La₂O₃, V₂O₅, Fe₂O₃, CuO, and WO₃ [33,34]. Importantly, the oxygen vacancies on MoO₃ surface, which can be generated by reacting with H₂ molecules and consequently producing H₂O as a by-product, play an important role as active sites for the C–O bond breaking. Nonetheless, the C–C bond cleavage pathway in DCO and DCO₂ over metal oxide catalysts in a H₂-free condition has not been reported. Previously, there are several studies on the deoxygenation of fatty acid under the inert atmosphere such as the deoxygenation of dodecanoic acid on a Pd/C catalyst under inert atmosphere [35] and the conversion of coconut oil (lauric acid as a main component) to lauryl alcohol in methanol without an extraneous hydrogen on a hydrothermally prepared Cu/SiO₂ catalyst [36].

In our work, the deoxygenation of oleic acid, the main components in palm oil, sunflower oil, and jatropha oil, was investigated under a N₂ atmosphere over MoO₃-based catalysts. To the best of our knowledge, a catalytic reaction of oleic acid under an inert atmosphere using metal oxide catalysts has never been reported. Our results show that adding another transition metal promoter (Ni, Co, Cu) to the MoO₃ without a catalyst reduction process could promote the green biofuel production route without H₂ feed via DCO₂ and/or DCO pathways.

2. Experimental

2.1. Catalyst preparation

Bimetal NiMo oxide catalysts were prepared by impregnating a commercial γ -Al₂O₃ (Sasol company, Germany) with (NH₄)₆Mo₇O₂₄·4H₂O (Carlo Erba) and Ni(NO₃)₂·6H₂O (Ajax Finechem) solution containing 0.3 atomic ratio of Ni/(Ni + Mo). Next, the samples

were dried at 65 °C for 12 h and then calcined at 500 °C for 4 h in air. The catalysts with metal loading on alumina (wt%) of 19%, 27%, and 34% were denoted as 19NiMo-Al, 27NiMo-Al, and 34NiMo-Al, respectively. Additionally, the 19NiMo-Al was reduced at 500 °C for 3 h in a H₂ flow and collected in a N₂ atmosphere, denoted as 19NiMo-Al (Red.), to compare the active phase and catalytic activity with the non-reduced catalysts. Also, the monometal Mo oxide and other bimetal CuMo and CoMo oxides on the alumina were prepared in the same manner with 19NiMo-Al using (NH₄)₆Mo₇O₂₄·4H₂O (Carlo Erba), Cu(NO₃)₂·4H₂O (Carlo Erba) and Co(NO₃)₂·6H₂O (Carlo Erba) as Ni, Cu, and Co precursors. These catalysts were denoted as 19Mo-Al, 19CuMo-Al, and 19CoMo-Al, respectively.

2.2. Catalyst characterization

The phase identity of the as-synthesized catalysts was investigated by X-ray diffraction (XRD, Bruker D8 Advance) using Cu K α source at 40 kV and 40 mA, 2theta scan ranges from 10° to 80° with a step of 0.02° s⁻¹. Surface area and porosity were determined by N₂-adsorption-desorption technique at -196 °C on a Quantachrome Instruments Nova 2000e surface area analyzer. The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) equation and pore size and pore diameter were calculated by the Barrett-Joyner-Hallenda (BJH) method. Morphology, elemental distribution, and crystallization of the catalysts were examined by a field emission scanning electron microscope/energy dispersive X-ray spectroscopy (FE-SEM/EDX, Hitachi SU8030) and a transmission electron microscopy (TEM, JEOL 2100). The surface species of the as-synthesized catalyst were determined by X-ray photoelectron spectroscopy (XPS) using a PHI5000 Versa Probe II XPS system (ULVAC-PHI, Japan) at the SUT-NANOTEC-SLRI Joint Research Facility, Synchrotron Light Research Institute (SLRI), Thailand. Binding energies were calibrated by C1s peak at 284.9 eV.

2.3. Catalytic deoxygenation testing and product analysis

Deoxygenation reactions were carried out in a 300 mL Parr 4568 batch reactor. An oleic acid (Aldrich, technical grade, 90% purity) was used as a model compound of palm oil without further purification. The catalyst loading was 20% w/w of reactant, i.e. 6 g of catalyst and 30 g of oleic acid. The reaction testing was performed under these conditions: N₂ pressurizing at room temperature (10–40 bar), stirring rate of 450 rpm, reaction temperature of 300–350 °C, and reaction time of 3–9 h. Mass transfer limitation could be neglected because of the small catalyst particle size and high stirring speed. The stability testing of NiMo oxide catalyst was observed during 4 cycles of deoxygenation at 330 °C for 6 h under the N₂ pressure of 40 bar. The spent catalyst in each cycle was filtered and washed with hexane several times, then dried at 80 °C in air for 12 h. Lastly, the catalyst was calcined at 500 °C for 4 h in a static air before use in the next cycle.

Liquid products, which mainly consisted of *n*-paraffin, oxygenated intermediates (long chain aldehydes, ketones, and alcohols), stearic acid, and oleic acid, were analyzed by a gas chromatography mass spectrometry (GC-MS, Agilent Technologies, 7890A) and a GC-FID (GC-2014, Shimadzu) equipped with DB-1HT columns (30 m × 0.32 mm × 0.1 μ m). A diluted sample was injected into the GC with the split ratio of 100. An injection temperature of 340 °C, a detector temperature of 370 °C, and a column temperature ramping from 40 to 270 °C were used for the analysis. The gas products were analyzed by a GC-TCD-FID (Shimadzu, GC-2010plus) equipped with molecular sieve 13X and Porapak Q columns. The oleic acid conversion and liquid product distribution were calculated by using the following equations:

$$\% \text{conversion} = \frac{\text{oleic acid in feed (mol)} - \text{oleic acid in products (mol)}}{\text{oleic acid in feed (mol)}} \times 100\% \quad (4)$$

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