Triglycerides-based Feeds Deoxygenation over SiO_2-Al_2O_3 Supported NiO-CaO Catalysts for Production of Diesel-like Fuel

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Abstract: The deoxygenation (DO) of triglycerides-based feeds employing NiO-CaO/SiO_2-Al_2O_3 and NiO/SiO_2-Al_2O_3 catalysts was investigated using semi-batch reactor under partial vacuum and inert N_2 flow. It was found that bi-functional catalyst highly favorable toward DO activity primarily via decarboxylation/decarbonylation (deCOx) with product selectivity toward diesel-like fuel n-(C_{13}-C_{20}). The large existence of strong acid-base sites of the catalyst is the main reason for increased C-C cleavage pathway, while milder acidic sites responsible for C-O cleavage pathway. High amount of free fatty acid (FFA) in the feedstock has affected adversely the deoxygenation of triglycerides by accelerating the catalyst deactivation. The atmospheric condition, degree of unsaturated fatty acid in the feedstocks, acidity and basicity of the catalysts are main criteria's for promoting deoxygenation activity and deCOx selectivity.

Keywords: Deoxygenation, NiO-CaO Catalysts and Diesel-like Fuel

1.0 Introduction

Hydrodeoxygenation (HDO) and deoxygenation (DO) are among the well known technologies that have been used extensively to remove oxygen from fatty acids [1] and resulted in production of hydrocarbon-based fuel that are capable of replacing petroleum derived fuel. Due to the considerable consumption of H2 in HDO process which has become an obstacle to the widespread application of the HDO process. Therefore, catalytic DO through (decarboxylation (eCO) and decarbonylation (eCO2))(deCOx) of triglycerides and fatty acids are proposed to enhance the economic feasibility of HDO.

The usage of metal oxides in DO reaction has been continuously reported and proven to be selective towards the formation of hydrocarbon fractions [2,3]. Common transition metal oxides that were used in DO process included Ni, Co, W [4], Mo, Cu, Fe and Zn [5]. Among these metals, Ni showed the highest DO activity. It was consistent with Croker and coworkers who has reported that DO of tristearin over 20 wt.% Ni/C showed similar performance with those obtained over 5 wt.% Pd and 1 wt.% Pt-promoted catalyst [6]. Several studies indicated that Ni promoted catalysts exhibited high DO activity via deCOx pathway during DO of triglyceride oil and model compounds (palmitic acid, methyl stearate) to produce diesel-range hydrocarbons [7,3,8]. Although Ni-promoted catalyst is catalytically reactive, however, it is still plagued by coke formation problem. Coke formation can be prevented or reduced by integrating basic metal catalyst with acid metal catalyst.

SiO_2-Al_2O_3 supported catalyst is effective for DO of triolein via deCOx pathway which produced 73% of C8-C20 hydrocarbons and >45% of deCOx product, respectively. Additionally, the catalyst also exhibited low affinity toward coke formation with< 14 wt.% after being reused for consecutive four DO cycles by maintaining the hydrocarbon product yield at >65%. Therefore, the present study consists of detail study focused on the development of the SiO_2-Al_2O_3 supported catalyst, the study of the effect of reaction atmospheres (i.e., partial vacuum and inert N2 flow) and the role of CaO on DO reaction. The DO reactions under inert N2 flow were highlighted. Further studies on optimum set were evaluated and applied to the DO of realistic feeds, including waste cooking oil (WCO), jatropha curcas oil (JCO) and palm fatty acid distillate (PFAD).

2.0 Experimantal

SiO_2-Al_2O_3 supported NiO-CaO catalyst was prepared using the wet impregnation method via weight percent determination (wt.%). thermally activated at a temperature of 500 °C for 2 h under atmosphere condition. The catalyst was denoted as NiO-CaO/SiO_2-Al_2O_3 or NiO-10CaO/SiO_2-Al_2O_3. For further study, different content of Ca solution (5, 15 and 20 wt. %) were synthesized using a constant wt.% of Ni solution (10 wt.%) via similar method. The catalyst denoted as NiO-5CaO/SiO_2-Al_2O_3, NiO 15CaO/SiO_2-Al_2O_3 and NiO-20CaO/SiO_2-Al_2O_3.

In this study, X-ray fluorescence (XRF), X-ray powder diffraction (XRD) analysis and Brunauer–Emmett–Teller (BET) method was used. The basicity and acidity of the catalysts were investigated using temperature-programmed desorption with CO_2 and NH_3. The morphological characteristics were investigated by field emission scanning electron microscopy.

DO of triolein was performed in a 250 mL mechanically stirred semi-batch reactor under partial vacuum and N_2 flow. Two types of DO condition were studied: (i) the reaction was performed under partial vacuum condition at approximately of 10 mbar. (ii) DO process was performed under inert N2 flow at the flow rate of 20 cc/min, for reassure continues oxygen removal. Both DO reactions were performed at reaction temperature ≥300 °C, where decomposition of triglycerides via C-C cleavage generally occurred at early stage of reaction condition: >190 °C and >30 min. The liquid products were quantitatively analyzed using gas chromatograph (GC) (Shimadzu GC-14B) equipped with HP-5 capillary column coupled with flame ionization detector (FID).

3.0 Results and Discussion

In the present work, an effective DO reaction was disclosed by converting triglycerides-based feeds to diesel-like fuel over NiO/SiO_2-Al_2O_3 and NiO-CaO/SiO_2-Al_2O_3 catalysts. The improvement of DO activity over acid-base NiO-CaO/SiO_2-Al_2O_3 catalyst was due to the neutralization of the strong acidity catalyst. DO under inert N_2 flow are predominantly more reactive than partial vacuum condition due to the advantages of N_2 flow which is beneficial in maintaining a high catalytic activity by preventing generated CO_2/CO gases from poisoning the active catalyst surface. Cracking pathway was found to be enhanced with increase of CaO content due to the richness of the high-strength basic and acid sites of the NiO-CaO/SiO_2-Al_2O_3 catalyst. Among the CaO content (5–20 wt.%), the optimum content for deCOx activity 5 wt. % (NiO-CaO/SiO_2-Al_2O_3). The effects of reaction time, catalyst loading and temperature were further investigated with optimum DO condition of (hydrocarbon fraction = 92%, n-C15 + n-C17 = 61%) was achieved within 60 min, 7 wt.% catalyst loading at 350 °C under inert N_2 flow condition. The efficiency of NiO-5CaO/SiO_2-Al_2O_3 catalyst has been proven to be capable of deoxygenizing triglycerides-based feeds (JCO, WCO, PFAD) through selective deCOx pathways by rendering 54%, 74%, and 73% of n-C15 + n-C17 fractions and total hydrocarbon fraction of >74%.

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