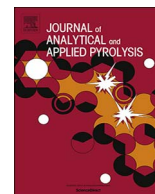




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# Pyrolytic-deoxygenation of triglycerides model compound and non-edible oil to hydrocarbons over SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiO-CaO catalysts

N. Asikin-Mijan<sup>a,b</sup>, H.V. Lee<sup>a,\*</sup>, T.S. Marliza<sup>b</sup>, Y.H. Taufiq-Yap<sup>b,\*</sup>

<sup>a</sup> Nanotechnology & Catalysis Research Centre (NanoCat), Institute of Postgraduate Studies, University Malaya, 50603 Kuala Lumpur, Malaysia

<sup>b</sup> Catalysis Science and Technology Research Centre (PutraCat), Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

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## ABSTRACT

Catalytic deoxygenation (DO) of triglycerides-based feeds to diesel-like fuel was investigated over NiO-CaO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and NiO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts using semi-batch reactor under partial vacuum and inert N<sub>2</sub> flow. The results showed that the bi-functional catalyst exhibited the highest DO activity with product selectivity toward diesel-like fuel *n*-(C<sub>13</sub>-C<sub>20</sub>). The catalytic process appeared to inhibit the occurrence of side reactions via neutralization of the strong acid sites. On the other hand, DO reaction under inert N<sub>2</sub> flow has improved the deoxygenated product, which demonstrate that N<sub>2</sub> flow condition has effectively removed the decarboxylation/decarbonylation gasses (CO<sub>2</sub>/CO) from poisoning the catalyst active sites. The high concentration of strong basic-acid 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 degree of unsaturated fatty acid in the feedstock has affected adversely the DO of triglycerides by accelerating the catalyst deactivation. The N<sub>2</sub> flow condition, degree of unsaturated fatty acid in the feedstocks, acidity and basicity of the catalysts are important factors to improve DO activity as well as product selectivity.

## 1. Introduction

The dwindling of global petroleum deposits and worsening environmental issues have triggered the global community to search for alternatives for fossil fuels. Over the past decades, mono alkyl esters of long-chain fatty acids (i.e., fatty acid methyl esters [FAME]) also known as biodiesel is widely used as alternative fuel, however, biodiesel is less than ideal fuel due to its oxygen content which could lead to low heating value, as well as high cloud and pour point [1]. Hydro-deoxygenation (HDO) and deoxygenation (DO) are among the well-known technologies that have been used extensively to remove oxygen from fatty acids [2] and resulted in production of hydrocarbon-based fuel that are capable of replacing petroleum derived fuel. Due to the considerable consumption of H<sub>2</sub> in HDO process which has become an obstacle to the widespread application of the HDO process. Therefore, catalytic DO through (decarboxylation (-CO) and decarbonylation (-CO<sub>2</sub>))(deCOx) of triglycerides and fatty acids are proposed to enhance the economic feasibility of HDO.

There was a numbers of solid acid catalyst involving metal sulfide-, noble metal-, metal phosphide-, and metal carbide-, metal, transition metals oxide- with supporting material reported in DO reaction. Sulfonated acidic catalyst shows high affinity toward the production of

hydrocarbon fractions, but suffers from sulfur leaching and affects the quality of oil [3]. Meanwhile, the high acidity noble metal catalyst is costly [4], which makes it unattractive. Medium acidity catalysts, such as metal phosphate and carbide, and mesoporous catalysts, such as SBA-15, MCM-41, and HMS catalysts, are generally selected for biofuel production as these catalysts pose low affinity toward the deactivation of the catalyst along with high DO activity [5,6]. However, the complexity of catalyst synthesis makes it unappealing [7]. Thus, the drawbacks of the abovementioned catalysts encouraged the exploration of non-sulfated, low-cost, and facile catalysts for high-quality renewable fuel production. The usage of metal oxides in DO reaction has been continuously reported and proven to be selective towards the formation of hydrocarbon fractions [8,9]. Common transition metal oxides that were used in DO process included Ni, Co, W [10], Mo, Cu, Fe and Zn [6]. 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 [11]. This finding is important because the cost of Ni is ~1750 and ~3450 times lower than Pd and Pt, respectively. Several studies indicated that Ni-promoted catalysts exhibited high DO activity via deCOx pathway during DO of triglyceride oil and model compounds (palmitic acid,

\* Corresponding authors.

E-mail addresses: [leehweivoon@um.edu.my](mailto:leehweivoon@um.edu.my) (H.V. Lee), [taufiq@upm.edu.my](mailto:taufiq@upm.edu.my) (Y.H. Taufiq-Yap).

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methyl stearate) to produce diesel-range hydrocarbons [1,8,12]. 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. It has been proven by Gomez et al. that the implementation of alkaline earth metal (Na) on zeolite (NaX1.4) has resulted in reduction of coke formation [13]. Meanwhile, Danuthai reported that the increase of Cs Lewis base sites from 2% to 20% has resulted in the reduction of coke formation from 4.4 wt.% to 3.5 wt.% [14]. Similar case was reported in our previous study [9] which has observed significant reduction of coke deposited from 14 wt.% to 8.2 wt.% when the basicity of the Co-CaO was improved by cobalt loading from 10% to 40%.

Recently, the present authors or researchers have reported on the optimization study of DO of triolein over SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalyst via response surface methodology (RSM) under partial vacuum condition [15]. It showed that the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalyst is effective for DO of triolein via deCO<sub>x</sub> pathway which produced 73% of C<sub>8</sub>-C<sub>20</sub> hydrocarbons and > 45% of deCO<sub>x</sub> 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<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalyst, the study of the effect of reaction atmospheres (i.e., partial vacuum and inert N<sub>2</sub> flow) and the role of CaO on DO reaction. The DO reaction under inert N<sub>2</sub> 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). In addition, the detail analysis on spent catalysts are further discussed.

## 2. Experimental

### 2.1. Material

Nickel (II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) with purity > 99% and calcium nitrate tetrahydrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) with purity > 99% were obtained from R&M Company. Silica-alumina (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) catalyst support grade 135 was purchased from Sigma-Aldrich. The standard solvent and chemicals for gas chromatography (GC) analysis: alkane (C<sub>8</sub>-C<sub>20</sub>), nonene standard solutions and internal standard (1-bromohexane) with purity > 98% were purchased from Sigma-Aldrich, and used without further purification. For GC solvent dilution, analytical grade *n*-hexane with purity > 98% was obtained from Merck. Triolein (65% purity) was obtained from Sigma-Aldrich, *Jatropha curcas* oil (JCO) was purchased from Bionas Sdn. Bhd., Malaysia, waste cooking oil (WCO) was collected at restaurant within the vicinity of Serdang and palm fatty acid distillate (PFAD) was supplied by Jomalina R&D, Sime Darby Sdn. Bhd., Malaysia. These feedstocks were used for DO reaction without further treatment and purification. The physico-chemical properties of the feedstocks were tabulated in Table 1.

### 2.2. Catalyst synthesis

SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiO-CaO catalyst was prepared using the wet impregnation method via weight percent determination (wt.%). Approximately 10 g of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powder was impregnated with an aqueous solution 10 wt.% of Ca and 10 wt.% of Ni concentration. Distillate water is used as a solvent for dissolving the metal salt and acted as a dispersion medium during impregnation process. Moreover, in order to maximize the metal impregnation on the support surface and avoid active metal leaching, the filtration process is avoided. Thus, the final mixtures were directly dried in the oven at a temperature of 100 °C for overnight. The dried samples were ground into fine powder before

**Table 1**

Analysis data of properties of the triolein, *Jatropha curcas* L. oil, waste cooking oil and palm fatty acid distillate.

Oil properties	Triolein	JCO	WCO	PFAD	Method
Density (g/cm <sup>3</sup> )	0.91	0.92	0.87	0.87	ASTM D1298
Moisture content (wt.%)	0.08	0.01	1-5	0.10	ASTM E203-08
Acid Value (mg KOH g <sup>-1</sup> )	5.0	30.8	36.8	172.6	AOCS Ca 5a-40
FFA Value (%)	2.5	15.4	18.4	86.3	AOCS Ca 5a-40
Fatty acid composition of Oil (%)					AOCS Ce1-62 & Ce-661
Myristic acid (C14:0)	1.2	-	1.6	1.9	
Palmitic acid (C16:0)	3.8	20.2	43.8	45.7	
Palmitoleic acid (C16:1)	4.3	-	-	-	
Stearic acid (C18:0)	1.9	7.2	4.1	4.3	
Oleic acid (C18:1)	83.3	39.8	39.4	40.2	
Linoleic acid (C18:2)	0.4	31.5	11.1	7.9	
Linolenic acid (C18:3)	0.3	-	-	-	
Others <sup>a</sup>	4.8	1.3	-	-	

<sup>a</sup> Other representing minor compound of myristoleic acid (C14:1), pentadecanoic acid (C15:0), arachidic acid (C20:1), gadoleic acid (C20:1) and behenic acid (C22:1).

being thermally activated at a temperature of 500 °C for 2 h under atmosphere condition. The catalyst was denoted as NiO-CaO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or NiO-10CaO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. 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<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, NiO-15CaO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and NiO-20CaO/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

### 2.3. Catalyst characterization

In this study, X-ray fluorescence (XRF) (Philips PW1404) equipped with scandium anode tube was used. The catalyst (2 g) was added to the sample cup (31 mm Double Open-Ended X-ray Cell with Collar) and transferred into the XRF chamber. The elemental composition of the catalyst was accurately quantified. X-ray powder diffraction (XRD) analysis was conducted to identify the dispersion states and chemical composition of modified SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported catalysts. XRD analysis was performed using Shimadzu diffractometer model XRD-6000. The specific surface area and pore distribution of the catalysts were determined by Brunauer-Emmett-Teller (BET) method with N<sub>2</sub> adsorption/desorption analyzer using Thermo-Finnigan Sorpomatic 1990 series. The catalyst was degassed overnight at 150 °C to remove moisture and foreign gases on the catalyst surfaces. The adsorption and desorption processes of N<sub>2</sub> on the catalyst surfaces were analyzed in a vacuum chamber at -196 °C. The basicity and acidity of the catalysts were investigated using temperature-programmed desorption with CO<sub>2</sub> and NH<sub>3</sub> as probe molecules (TPD-CO<sub>2</sub> and TPD-NH<sub>3</sub>, respectively). The analysis was performed using Thermo-Finnigan TPD/R/O 1100 instrument equipped with thermal conductivity detector (TCD). The catalyst (approximately 0.05 g) was pretreated with N<sub>2</sub> gas flow for 30 min at 250 °C and exposed to CO<sub>2</sub> gas for an hour at ambient temperature to allow the adsorption of CO<sub>2</sub> onto the surfaces. The excess CO<sub>2</sub> was subsequently flushed with N<sub>2</sub> gas flow at the rate of 20 mL/min for 30 min. The desorption of CO<sub>2</sub> from the basic sites of the catalyst was detected by TCD under helium gas flow (30 mL/min) from 50 °C to 900 °C and held for 30 min. The adsorption and desorption of NH<sub>3</sub> was similar to the TPD-CO<sub>2</sub> method. The morphological characteristics of the catalysts were investigated by field emission scanning electron microscopy (FESEM Rayny EDX-720). The FESEM images were observed through LEO 1455 VP electron microscope. The coking tendency of the catalyst was evaluated using thermogravimetric analysis (TGA) with simultaneous thermal analyzer (TGA, Mettler Toledo 990). The extent of coke/carbon deposition on the spent catalyst was

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