Catalysis Today xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of Cu promotion on cracking and methanation during the Ni-catalyzed deoxygenation of waste lipids and hemp seed oil to fuel-like hydrocarbons

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ARTICLE INFO

Article history:
Received 30 November 2016
Received in revised form 6 March 2017
Accepted 16 March 2017
Available online xxx

Keywords:
Hydrocarbons
Nickel
Copper
Decarboxylation
Cracking
Methanation

ABSTRACT

Deoxygenation of yellow grease and hemp seed oil was studied over 20% Ni/Al_2O_3 and 20% Ni-5% Cu/Al_2O_3 catalysts in the presence of H_2. In the deoxygenation of 25 wt% yellow grease (dissolved in dodecane) both catalysts afforded a liquid product consisting of mainly linear C10–C17 alkanes; however, the Cu-promoted catalyst showed improved selectivity to long chain (C15–C17) hydrocarbons as a result of its lower cracking activity. Analysis of the light hydrocarbon products (C10–C16) showed that cracking mainly occurred via the removal of terminal carbons (with methane formation), although a small amount of internal cracking also occurs based on the presence of C6–C11 in the product mixtures. Similar improvements were also observed in the deoxygenation of 25 wt% hemp seed oil, showing that Cu was able to curb cracking even when a highly unsaturated feed was employed. The Cu promotion effect was more pronounced in the deoxygenation of 75 wt% yellow grease in which the 20% Ni/Al_2O_3 catalyst did not yield any liquid products, whereas the 20% Ni-5% Cu/Al_2O_3 catalyst afforded liquid products consisting of >90% diesel-like hydrocarbons.

1. Introduction

A number of sustainability and environmental concerns have spurred interest in biofuels, which are renewable, carbon neutral and do not disrupt the food supply when produced from waste and inedible feedstocks [1,2]. Waste lipids can be converted via transesterification with methanol to a mixture of fatty acid methyl esters (FAMEs), commonly referred to as biodiesel. While biodiesel offers certain advantages over petroleum-derived fuels [3], the high oxygen content of FAMEs gives rise to several problems – including limited storage stability and engine compatibility issues – that render biodiesel a less than ideal fuel [4]. Thus, attention has shifted to deoxygenation processes capable of converting lipids to fuel-like hydrocarbons, such as hydrodeoxygenation (HDO) and decarboxylation/decarbonylation (deCO$_x$). HDO is a commercial process that is highly selective to diesel-like hydrocarbons, albeit there is a high hydrogen requirement associated with the removal of oxygen as H_2O [5]. Therefore, deCO$_x$ can be viewed as preferable not only because the hydrogen consumption is in principle lower than for HDO, but also because deCO$_x$ is catalyzed by simple supported metal catalysts as opposed to the sulfided metal catalysts used in HDO [5,6].

Although most deCO$_x$ work has focused on Pd and Pt catalysts, the high cost of these formulations is an impediment to their use in industrial applications. Consequently, inexpensive Ni catalysts have attracted interest for the deoxygenation of lipids to hydrocarbons via deCO$_x$ [7,8]. Admittedly, Ni catalysts face certain challenges that must be overcome if they are to become an industrially viable alternative for the conversion of lipids to diesel-like hydrocarbons. Indeed, the high cracking and methanation activity of Ni can favor the formation of short chain liquid hydrocarbons, methane and coke deposits, which reduces the selectivity to diesel, decreases the hydrogen efficiency and results in catalyst deactivation.

Recent results show that the aforementioned issues inherent to supported Ni catalysts can be assuaged to some degree by promoting Ni with Cu. Indeed, we have observed that Ni-Cu bimetallic

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http://dx.doi.org/10.1016/j.cattod.2017.03.025
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Please cite this article in press as: E. Santillan-Jimenez, et al., Effect of Cu promotion on cracking and methanation during the Ni-catalyzed deoxygenation of waste lipids and hemp seed oil to fuel-like hydrocarbons, Catal. Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.03.025

catalysts afford higher diesel yields as well as reduced coking and deactivation relative to Ni-only formulations in the deCO$_x$ of model lipid feeds such as stearic acid and tristearin [9]. Although the results from our previous study were promising, the study utilized mainly model compounds at low feed concentrations in semi-batch reaction conditions. The current study aimed to further elucidate the effect of Cu promotion under more industrially relevant conditions, namely, the use of a continuous flow fixed bed reactor and realistic, concentrated feedstocks. Previous reports have shown that cracking is more common with increased unsaturation in the feed [10]; therefore, two feedstocks with differing degrees of unsaturation were tested. Yellow grease (used cooking oil) was employed as a waste lipid feedstock composed primarily of triolein, a triglyceride with three 18-carbon acyl chains each containing a double bond between the 9th and 10th carbons. The second feed employed was hemp seed oil, a highly unsaturated feedstock composed mostly of trilinolein, a triglyceride with three 18-carbon acyl chains each containing two double bonds, one between the 9th and 10th carbons and another between the 12th and 13th carbons. The highly unsaturated nature of hemp seed oil provides a good test of the ability of Cu to mitigate the cracking activity of Ni.

2. Materials and methods

2.1. Feed lipid analysis

Fig. S1 shows the lipid profile of both the yellow grease and hemp seed oil used in this study. This was obtained by direct transesterification of the feed with methanol according to the method of Griffiths et al. [11]. The transesterified products were analyzed by an Agilent 6890A gas chromatograph equipped with a HP-88 column (30 m × 0.25 mm × 0.2 μm) and a flame ionization detector. Helium was used as the carrier gas, the flow rate was set to 1 ml/min and a split of 20:1 was employed. The temperatures of the inlet and the detector were 250 and 300 °C, respectively. The temperature program included an initial temperature of 50 °C followed by a ramp of 20 °C/min to 140 °C and a subsequent ramp of 3 °C/min to a final temperature of 240 °C. Calibrations were completed using a Supelco 37 FAME Mixture.

2.2. Catalyst preparation and characterization

20% Ni/Al$_2$O$_3$ and 20% Ni-5% Cu/Al$_2$O$_3$ catalysts were prepared by excess wetness impregnation using Ni(NO$_3$)$_2$·6H$_2$O (Alfa Aesar) and Cu(NO$_3$)$_2$·3H$_2$O (Sigma-Aldrich) as the metal precursors and γ-Al$_2$O$_3$ (Sasol; surface area of 216 m^2/g) as the support. Following impregnation, the materials were dried overnight at 60 °C under vacuum and then calcined at 500 °C for 3 h in static air. The catalysts and SiC diluent (Kramer Industries, Inc.) were pelletized to the desired particle size (150–300 μm) prior to use. The characterization of these catalysts has been described previously [9].

2.3. Deoxygenation experiments

Deoxygenation experiments were performed in a 1/2 in o.d. stainless steel fixed bed reactor equipped with a porous steel frit to support the catalyst bed. Prior to the deoxygenation experiments, the catalyst was reduced in situ for 3 h at 400 °C under H$_2$ (580 psi) with a continuous H$_2$ flow of 60 ml/min. The system was then taken to the reaction temperature while maintaining the H$_2$ flow, at which point the feed was introduced using an HPLC pump. Yellow grease (used cooking oil) deoxygenation experiments employed a feed obtained from the cafeteria of a local school and were performed using either 25 wt% yellow grease dissolved in dodecane (99+% Alfa Aesar) or 75 wt% yellow grease in dodecane. The 25 wt% yellow grease experiments were performed at 350 °C, using 0.5 g catalyst and a feed solution flow rate of 12 ml/h, equivalent to a WHSV of 4.7 h^{-1} (note that WHSV refers to only the feed to catalyst ratio, and excludes any amount of dodecane used). The 75 wt% yellow grease experiments were performed at 375 °C with a feed solution flow rate of either 2.76 ml/h or 1.5 ml/h (equivalent to a WHSV of 3.7 h^{-1} and 2.0 h^{-1}, respectively) over a thoroughly mixed catalyst bed containing 0.5 g of catalyst and 0.5 g of SiC as catalyst diluent. Blank experiments were conducted for the 75 wt% yellow grease experiments using 1 g of SiC and a feed flow rate of 1.5 ml/h. Hemp seed oil (Dr. Adorable, Inc.) deoxygenation experiments were performed with 25 wt% hemp seed oil (dissolved in dodecane) at 350 °C, with a feed solution flow rate of 12 ml/h and 0.5 g of catalyst (WHSV of 4.7 h^{-1}). In all experiments, the products were directed into a condenser held at 0 °C and liquid products were collected every hour. Incondensable gases were directed to a dry test meter before being collected in Tedlar® gas sample bags that were changed and analyzed hourly. Further details of the equipment and procedures employed have been described elsewhere [6]. Representative experiments were performed in duplicate to ensure reproducibility.

2.4. Methanation experiments

Methanation experiments were performed with the equipment and procedures employed for deoxygenation experiments (see Section 2.3) using a stream of ~5 vol% CO$_2$ in H$_2$ as the feed (63 ml/min).

2.5. Analysis of deoxygenation products and spent catalysts

Reaction feeds and product mixtures were analyzed using a combined Simulated Distillation-GC and GC–MS approach. An Agilent 7890B GC System equipped with an Agilent 5977A Extractor MSD and a flame ionization detector (FID) was used for these analyses. A 0.1 μl injection was employed and helium was used as the carrier gas. The multimode inlet, containing a helix liner, was run in split mode (split ratio 15:1; split flow 48 ml/min) using an initial temperature of 100 °C. Immediately upon injection, the inlet temperature was increased at a rate of 8 °C/min to a final temperature of 380 °C, which was maintained for the duration of the analysis. Similarly, the oven temperature (initially 40 °C) was increased immediately upon injection at a rate of 4 °C/min to 325 °C, followed by a ramp of 10 °C/min to a final temperature of 400 °C held for 12.5 min, the total run time being 91.25 min. An Agilent J&W VF-5ht column (30 m × 250 μm × 0.1 μm; 450 °C max.) was used as the primary column after which the eluents entered a Siltek MXT Connector which split the components into two fractions: one leading to the MSD (J&W Ultimetal Plus Tubing, 11m × 0.25 mm ID) and one leading to the FID (J&W Ultimetal Plus Tubing, 5m × 0.25 mm ID). MS zone temperatures – including those of the MS source (230 °C) and quadrupole (150 °C) – remained constant for the duration of the analysis. A 1.75 min solvent delay was implemented and the mass spectrometer scanned from 10 to 700 Da. The FID was set to 390 °C with the following flow rates: H$_2$ = 40 ml/min; air = 400 ml/min; makeup He = 25 ml/min. Chromatographic programming was performed using Agilent MassHunter Data Acquisition software. Data acquired using the above GC-FID method were converted – with the help of SimDis Expert 9 software purchased from Separation Systems, Inc. and a retention time-to-boiling point calibration curve built using a C5–C40 SimDis calibration sample purchased from Agilent Technologies – to a table of chromatogram integrated area percent versus boiling point temperature (using intervals of 0.1 °C), which was subsequently plotted to generate a boiling point distribution plot (BPDP). Reaction and GC solvents (i.e., dodecane and either chloroform or carbon disulfide) were subtracted and/or quenched from the chromatogram prior to any calculations. The accuracy and precision of this method were quan-

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