Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over Ni–Al layered double hydroxide

Eduardo Santillan-Jimenez *, Tonya Morgan, Jaime Shoup, Anne E. Harman-Ware, Mark Crocker [1]

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington 40511, KY, USA

ABSTRACT

The conversion of fatty acids and triglycerides to fuel-like hydrocarbons was investigated over a Ni–Al layered double hydroxide catalyst and over 20% Ni/Al_2O_3 for comparison purposes. Both catalytic performance and the extent of catalyst fouling were found to show a marked dependence on the hydrogen partial pressure used during reaction and on the Ni-specific surface area of the catalyst employed. The amenability of a representative spent catalyst to regeneration *via* calcination in air was also demonstrated. The regenerated catalyst was observed to outperform the fresh formulation when tested for activity in the conversion of lipids to fuel-like hydrocarbons. This is attributed to the formation of strong basic sites – which are capable of catalyzing the deoxygenation of lipids – during the regeneration process. The fact that inexpensive Ni-based catalysts capable of affording good yields of fuel-like hydrocarbons can be regenerated by treatment in hot air makes these formulations interesting from an industrial standpoint. Results suggest that the conversion of triglycerides to fuel-like hydrocarbons is intermediated by fatty acids and that the conversion of fatty acids – either as the reaction feed or as reaction intermediates – to hydrocarbons proceeds via aldehyde and/or fatty acid ester intermediates.

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1. Introduction

A number of problems associated with the high oxygen content of biodiesel have caused attention to shift towards the conversion of lipids to transportation fuels through catalytic methods in which oxygen is eliminated either as H_2O or as CO_x. These deoxygenation methods have the paramount advantage of producing hydrocarbons that are entirely fungible with petroleum-derived fuels from a great variety of raw materials, including waste and inedible feedstocks that do not compete with the food supply [1–3]. Of these deoxygenation methods, hydrodeoxygenation (HDO) *via* hydrotreating represents the most developed route. Indeed, this route forms the basis of a number of processes – including Neste Oil's NExBTL, UOP/Eni's Ecofining, Petrobras' HBio and Dynamic Fuels' Bio-Synfining – capable of producing hydrocarbon fuels purportedly superior to both biodiesel and fossil diesel in terms of performance, cold flow properties, storability and/or reduced emissions [4–6]. Unfortunately, this approach requires high pressures of H_2 and problematic sulfided catalysts, which risk contaminating

the products with sulfur [7,8] and tend to deactivate in the presence of water [8,9] (one of the products of the HDO reaction).

An alternative lies in the deoxygenation of lipids *via* decarboxylation/decarbonylation ($deCO_x$) – an approach which has recently been reviewed [10] – as these reactions proceed under considerably lower H_2 pressures and over simple metal catalysts. However, most reports have focused on the use of catalysts comprising either Pd [11–20] or Pt [21–23], the cost of which may be prohibitive. In previous work we have demonstrated that carbon-supported Ni catalysts display near comparable performance to that shown by carbon-supported precious metal catalysts in the upgrading of triglycerides and fatty acids to hydrocarbons, both in a batch reactor under inert atmosphere [24] and in a semi-batch reactor under different partial pressures of hydrogen [25]. Albeit these results are quite promising, particularly due to the fact that the cost of Ni is ~1750 and ~3450 times lower than that of Pd and Pt, respectively [26], the nature of the support remains an important issue. Some workers have reported that the use of carbon (as opposed to metal oxides) as the support in $deCO_x$ catalysts leads to better results due to the more favorable adsorption of fatty acids on the catalyst surface [27]. However, $deCO_x$ catalysts are susceptible to deactivation by the accumulation of carbonaceous deposits on their surface [15,17,18,28–33] and the use of a carbon support both complicates the study of spent catalysts *via* thermogravimetric analysis (TGA) and precludes the regeneration of the catalyst through the combustion of these deposits. The latter is particularly unfortunate, given

that calcination in air constitutes the regeneration approach most favored by industry due to its low cost and simplicity.

In view of the foregoing, non-precious metal catalysts comprising supports other than carbon – particularly Ni on oxidic supports and hydrotalcite materials – are beginning to attract attention as practicable catalysts for the conversion of lipids into fuel-like hydrocarbons *via* deCO$_x$ [7,8,34–43]. In a previous contribution we reported that out of a series of hydrotalcite-like materials tested in the batch deCO$_x$ of triglycerides and fatty acids to hydrocarbons under an inert atmosphere, a Layered Double Hydroxide (LDH) including both Ni and Al afforded the best results, rivaling (and in some cases outperforming) carbon-supported Pd, Pt, or Ni [24,40]. Encouraged by these results, in the present study we examined the deoxygenation of triglycerides and fatty acids over this LDH catalyst (and over 20% Ni/Al$_2$O$_3$ for comparison purposes) in a semi-batch reactor, as constantly purging the reactor during deoxygenation has been observed to lead to improved results [25,44]. Given that hydrogen partial pressure has been reported to be an important factor in lipid deoxygenation reactions [11,25], experiments were performed under three different atmospheres (N$_2$, 10% H$_2$/N$_2$ and H$_2$) and the spent catalysts were analyzed using TGA in an effort to test the effect of hydrogen partial pressure on both catalytic performance and on the formation of carbon deposits. Finally, a representative catalyst was regenerated by means of calcination and retested in an effort to determine the recyclability of these formulations.

2. Materials and methods

2.1. Catalyst preparation and characterization

The LDH catalyst and a 20 wt% Ni/Al$_2$O$_3$ reference catalyst were prepared using materials and procedures which have previously been described [40]. The formula of the LDH catalyst was determined to be [Ni$_{0.67}$Al$_{0.33}$(OH)$_2$][CO$_3$]$_{0.17}$·mH$_2$O. For simplicity, this material will henceforth be referred to as Ni–Al LDH.

The surface area, pore volume and average pore radius of the catalysts were determined by means of N$_2$ physisorption. Powder X-ray diffraction (XRD) measurements were performed in order to determine the average crystallite size of the LDH and the average metal particle size of both catalysts. The reducibility of the catalysts in this study was investigated via temperature programmed reduction (TPR) and the Ni metal specific surface area was measured by means of H$_2$ chemisorption. The description of the instrumentation and methods employed in the aforementioned tests has previously been reported [24,25,40].

The acidity and the basicity of the catalysts were assessed through the temperature programmed desorption (TPD) of NH$_3$ and CO$_2$, respectively. TPD measurements were performed using a Micromeritics AutoChem II analyzer loaded with 90 mg of sample. Each sample was pretreated *in situ* under 10% H$_2$/Ar at 350 °C for 3 h, flushed with He at this temperature for 10 min and cooled to 90 °C under He flow prior to adsorption of either NH$_3$ (1000 ppm NH$_3$/He) or CO$_2$ (100%) for 1 h. The system was then flushed with He at 90 °C for 2 h, after which the temperature was ramped at a rate of 10 °C/min to 700 °C and held at that temperature for 15 min. Effluent gases were continuously analyzed using a mass spectrometer (Pfeiffer Thermostar GSD301). While a number of mass-over-charge (m/z) signals commonly attributed to NH$_3$ and CO$_2$ were followed, m/z = 15 and m/z = 44 were found to be free of interference from other species (mainly water in the case of the m/z signals corresponding to NH$_3$) and thus, they were chosen to represent NH$_3$ and CO$_2$, respectively. In order to correct the TPD profiles for the contribution of species stemming from the catalyst samples (*e.g.* residual CO$_2$ remaining from the incomplete decomposition of

Table 1
Acid number and distribution of fatty acids in the tristearin used in this study.

Fatty acid (X:Y)[a]	Tristearin, 95% (wt.%)
Myristic (14:0)	0.2
Palmitic (16:0)	10.6
Stearic (18:0)	87.5
Linoleic (18:2)	0.1
Linolenic (18:3)	0.5
Other	1.0
Acid number	1.31 mg KOH/g

[a] X:Y = carbon number: number of double bonds.

the LDH catalyst during calcination), TPD measurements were also performed on samples which had not been subjected to NH$_3$ or CO$_2$ adsorption. The intensity of the m/z signals used to represent NH$_3$ and CO$_2$ in these experiments – which was negligible in the case of m/z = 15 and noteworthy in the case of m/z = 44 – were subtracted from the amounts desorbed in the corresponding NH$_3$ or CO$_2$–TPD measurements to obtain the corrected profiles.

The nature and the amount of the carbonaceous deposits on the surface of spent catalysts was studied by means of TGA performed under flowing air (50 mL/min) on a TA instruments Q500 thermogravimetric analyzer. The temperature was ramped from room temperature to 800 °C at a rate of 10 °C/min.

2.2. Deoxygenation experiments

Stearic acid (97%) was purchased from Acros Organics and analyzed by means of GC. This analysis showed the sample to be ~99.5% stearic acid and ~0.5% palmitic acid. Tristearin (95%) was purchased from City Chemical and analyzed using instruments and methods which have previously been described [25,40]. The results of these analyses are collected in Table 1. Experiments were performed in a mechanically stirred 100 mL stainless steel autoclave operated in semi-batch mode. Typically, the catalyst (0.5 g) in powder form (particle size <150 μm) was reduced *in situ* at 350 °C under flowing 10% H$_2$/N$_2$ for 3 h prior to purging the reactor with Ar and adding both solvent (dodecane, 25 g) and feedstock (1.75 g). The autoclave was then purged three times with Ar prior to being pressurized with the required gas (N$_2$, 10% H$_2$/N$_2$ or H$_2$) and heated to the reaction temperature. The system was kept at 300 ± 2 °C and 135 psi for 1.5 h or at 355 ± 5 °C and 580 psi for 6 h in deoxygenation experiments involving stearic acid and tristearin, respectively. The autoclave temperature was measured by a type-K Omega thermocouple placed inside the reactor body. The reactions were performed under constant gas flow of 70 mL/min and mechanical stirring of 1000 rpm. Volatile products were collected from the gas stream leaving the reactor by cooling the latter with a condenser kept at room temperature prior to venting. At the completion of each test, forced air and an ice bath were sequentially used to facilitate cooling. Once the reactor reached room temperature, the system was slowly depressurized. Oil and catalyst were removed from the reactor and separated by gravity filtration to isolate the product. The catalyst was then washed twice with chloroform to yield additional material.

2.3. Product analysis

Prior to chromatographic analysis, samples were diluted with chloroform, typically in a 2:1 weight ratio. Simulated distillation-GC analyses were performed according to ASTM D2887, using an Agilent 7890 GC equipped with a Multimode inlet and a J&W Scientific D-2887 capillary column. Separations Systems Inc. SimDis Expert 9 software was used to quench the signal corresponding to the reaction solvent – which was done prior to performing all conversion and selectivity calculations in Table 4 and to process