Evaluation of the catalytic deoxygenation process applied to waste cooking oil for the production of biofuels

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Abstract

New alternatives for fuel production are becoming increasingly urgent to replace fossil energy sources and slow down the environmental impacts caused by carbon emissions. In this context, the use of renewable sources, such as waste cooking oil (WCO), is an outstanding option for obtaining bio-based fuels. However, it is necessary to remove the oxygen content present in the triglyceride structures of the oil to enhance its properties and use this feedstock as a fuel. To this end, Ni-Mo and Co-Mo bimetallic catalysts were synthesized on carbon nanotubes (CNT). The catalysts exhibited excellent textural properties for WCO deoxygenation. Evaluation of their catalytic performance, particularly the Ni-Mo catalyst supported on oxidized CNT(Ni-Mo/CNT_{ox}) catalyst, demonstrated superior product distribution into liquid fuel products in the range of gasoline, diesel and jet fuels alkanes, displaying minimal alkenes production and high selectivity to the diesel range compared to other tested materials.

Keywords: Waste cooking oil, deoxygenation, bimetallic catalysts, carbon nanotubes

1. Introduction

In a world struggling with environmental degradation and energy sustainability, innovative solutions are needed to minimize the dependency on traditional fossil fuels. Lipid based feedstock, such as vegetable oils, have been studied to obtain liquid fuels used in the transportation sector (land and air) [1]. However, it is necessary to prioritize the use of non-edible sources, as well as waste cooking oil (WCO). Composed of triglycerides with a carbon chain between C_{16}-C_{24}, the use of WCO provides several advantages such as promoting the circular economy by recycling and reducing waste disposal in the environment and carbon footprint [2,3]. Moreover, the similitude of triglycerides with diesel and jet fuel in terms of carbon length makes them an attractive feedstock for its conversion into biofuels. Nevertheless, the oxygen atoms on its structure must be removed in order to improve the properties of triglycerides into a liquid fuel, since they are responsible for the low heat of combustion, high acidity and viscosity, obstacles that need to be solved to its direct application as a fuel [2].

Catalytic deoxygenation involves a serie of reactions classified as hydrodeoxygenation (HDO), decarbonylation (DCO) and decarboxylation (DCO_2), in which oxygen is removed in the form of H_2O, CO and CO_2, respectively. This process improves the physicochemical properties of WCO. Current catalytic systems include batch and fixed bed reactors using high temperature, hydrogen pressure and supported metal catalysts [4]. In this context, the catalyst plays a fundamental role in the deoxygenation of triglycerides, fatty acids and oxygenated reaction intermediates, as well as performing functions such as cracking and isomerization of the paraffinic hydrocarbons produced. Currently, bimetallic catalysts, with metallic sites and Brønsted-Lowry acidity made of non-noble metals such as Ni, Co, W and Mo supported on zeolites, oxides and mesoporous silica are widely used in studies to evaluate their performance in the reactions [4,5]. However, few studies address the use of carbon nanotubes (CNT). This class of carbon material stands out for its textural properties (high mesoporosity), excellent thermal stability and the possibility of incorporating heteroatoms into its surface [6].

Overall, there is still a great need to develop technologies that enable the application of renewable sources for the production of fuels, but especially the development of new efficient and selective catalysts. Therefore, the aim of this work was to evaluate the catalytic performance of different bimetallic catalysts supported on CNTs for the deoxygenation of WCO into fuel range hydrocarbons.

2. Experimental

Ni-Mo and Co-Mo (2.5 wt.% of Ni and Co, and 10.5 wt.% of Mo) bimetallic catalysts were synthesized by incipient wetness impregnation method using as supports the original CNT and CNT modified by a oxidation treatment with HNO_3 (7 mol L^{-1}) heated to the boiling temperature for 3 h. The oxidized CNT (CNT_{ox}) was subsequently washed with distilled water until neutral pH and dried in the oven at 110 °C for 24 h. After that, the materials were thermally treated under N_2 flow for 3 h followed by a reduction under H_2 flow for 3 h. The same temperature was adopted in both steps, which was determined by temperature programmed reduction (TPR). The produced catalysts (named CoMo/CNT, CoMo/CNT_{ox}, NiMo/CNT and NiMo/CNT_{ox}) were characterized by and N_2 adsorption isotherms at -196 ºC. In addition, a commercial Co-Mo/Al_2O_3 (2.5 wt.% Co and 10.5 wt.% Mo) was also tested.

A screening of the catalysts was performed to determine their activity in the deoxygenation of WCO. In a typical reaction, 2.5 g of WCO, 25 g of n-decane (99%) and 0.25 g of catalyst were loaded into a stainless steel 100 mL Ilshin autoclave batch reactor. After purging the reactor with N_2, 70 bar (at 25 °C) of H_2 were loaded inside the reactor. The experiments were carried out at 350 ºC, 1000 rpm of stirring rate and 3 h of residence time once reached the desired temperature. At the end of the reaction, the reactor was quenched in cold water and the gas and liquid products were properly collected. The liquid samples were analyzed by gas chromatography (Perkin Elmer – GC, Clarus® 690) with a flame ionization detector. Moreover, the peaks were confirmed by the GC-MS (Clarus-690-SQ8T). The gas samples were also analyzed by gas chromatography (Perkin Elmer – GC Refinery Gas Anlyzer – 1157). The carbon content of the WCO used was determined by elemental analysis using a Thermo Electron Flash 1112 Analyzer.

The carbon conversion was estimated by Equation 1 since the triglycerides present in WCO can not be identified by the GC-FID-MS.

$$\text{Carbon conversion } = \frac{C_{\text{products}}}{C_{\text{WCO}}} \times 100\ \% \qquad (1)$$

Where C_{WCO} is the carbon moles content in the WCO fed in the reactor and C_{products} is the total carbon moles in the identified components in the final liquid and gas products.

The selectivity was also calculated as shown in Equation 2 as follows:

$$\text{Selectivity} = \frac{\text{moles of each product}}{\text{moles of total products}} \times 100\ \% \qquad (2)$$

3. Results and Discussion

According to the TPR analysis, Co-Mo/CNT catalysts presented a reduction range temperature between 500 – 600 °C, while Ni-Mo/CNT catalysts showed a broad peak at 550 °C. Thus, CoMo/CNT and CoMo/CNT_{ox} were reduced at 600 °C, whereas NiMo/CNT and NiMo/CNT_{ox} were reduced at 550 °C. The textural properties determined by N_2 adsorption at -196 °C are presented in Table 1. As described, all the CNT-supported catalysts showed high specific area and no micropores in their structure. The elevated mesoporosity and pore volume are crucial to the conversion of the triglyceride's compounds present in WCO in hydrocarbons, mainly to avoid mass transfer limitation. On the other hand, the commercial catalyst showed inferior textural properties compared with the other carbon material, exhibiting a small amount of micropores (0.01 $cm^3\ g^{-1}$) and lower mesopores surface area (144 $m^2\ g^{-1}$).

Table 1. Textural properties of the samples

Sample	S_{BET} **($m^2\ g^{-1}$)**	S_{meso} **($m^2\ g^{-1}$)**	V_{micro} **($cm^3\ g^{-1}$)**	$V_p{}^a$ **($cm^3\ g^{-1}$)**
CNT	229	229	-	1.54
CNT_{ox}	262	262	-	1.44
Co-Mo/CNT	198	198	-	1.51
Co-Mo/CNT_{ox}	227	227	-	1.24
Ni-Mo/CNT	201	201	-	1.55
Ni-Mo/CNT_{ox}	199	199	-	1.28
Co-Mo/Al_2O_3	169	144	0.01	0.42

[a] Pore volume calculated from the amount of N_2 adsorbed at $P/P_0 = 0.98$

According to the results of the catalysts screening (Figure 1), Co-Mo/CNT and Ni-Mo/CNT catalysts presented a carbon yield between 56 – 70 %. Although the major products obtained were n-alkanes in the carbon range of $C_5 – C_{24}$, some intermediates such as alkenes and oxygenate compounds ($C_{18}H_{36}O$ and $C_{18}H_{38}O$) are still present in the liquid products after the 3 h of reaction. Ni-Mo/CNT_{ox} stands out in the overall performance for only producing a small amount of alkenes and being selective to $C_{17} – C_{24}$ n-alkanes (diesel range). As expected, the presence of micropores in Co-Mo/Al_2O_3 was detrimental to the deoxygenation of WCO.

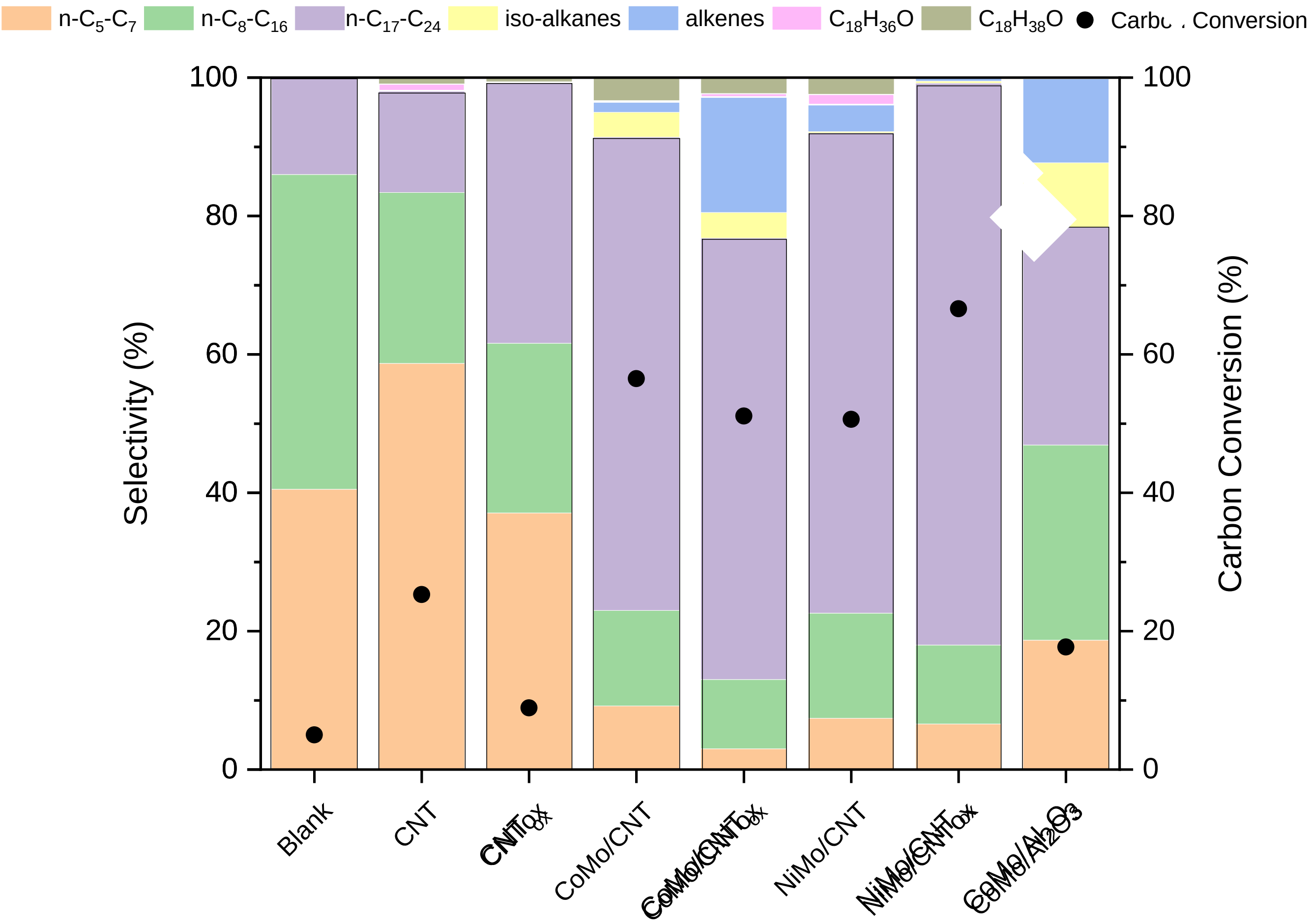

Figure 1. Liquid products distribution and carbon yield of different catalysts and supports. Reaction conditions: 350 °C,, 70 bar of initial H_2 pressure, 3 h of residence time of WCO, 0.25 g of catalyst, 2.5 g WCO, 25 g of n-decane.

4. Conclusions

In this work, Co-Mo and Ni-Mo bimetallic catalysts supported in CNT and CNT_{ox} were synthesized and tested in the deoxygenation reaction of WCO. The textural properties of the catalysts proved to be excellent for the WCO deoxygenation reaction. These results were reflected in the evaluation of the catalytic performance of the synthesized materials, which, combined with the presence of the metal oxides, contributed to the formation of most n-alkanes. In this context, Ni-Mo/CNT_{ox} catalyst showed the best performance, with a minimum percentage of alkenes compared to the other materials tested and being selective to diesel range.

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