N°264 / Oral Communication
TOPIC(s) : Biomass Conversion / Energy

Hydrodeoxygenation of Waste Cooking Oil over CNT-based catalysts

AUTHORS

Karoline Kaiser Ferreira / ALiCE/LSRE-LCM
Christian Di Stasi / Instituto de Carboquímica, CSIC
Alejando Ayala-Cortés / Instituto de Carboquímica, CSIC
Lucília Ribeiro / LSRE-LCM/ALiCE
José Luís Pinilla / Instituto de Carboquímica, CSIC
Isabel Suelves / Instituto de Carboquímica, CSIC
M. Fernando R. Pereira / LSRE-LCM/ALiCE

PURPOSE OF THE ABSTRACT

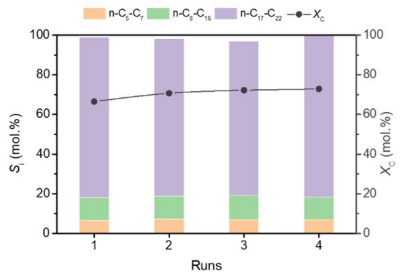
New alternatives for fuel production are essential to replace fossil energy sources and reduce carbon emissions. Renewable sources such as waste cooking oil (WCO) present a promising option for biofuel production, but the high oxygen content in WCO triglycerides poses a significant challenge. To address this, effective catalytic systems are needed to deoxygenate these compounds, yielding hydrocarbons suitable for liquid fuels like gasoline, jet fuel, and diesel [1-4]. This work focused on developing and evaluating bimetallic catalysts based on carbon nanotubes (CNT) for the deoxygenation of WCO. Due to their outstanding textural properties, thermal stability, and surface modification flexibility, CNT were used as supports, including original CNT (Nanocyl-7000) and CNT oxidized with HNO_3 (CNTox). Co or Ni (2.5 wt.%) and Mo (10.5 wt.%) were impregnated on the supports by incipient wetness impregnation method, dried at 110 °C overnight, and subsequently thermally treated in furnaces with N2 followed by a reduction under H2 at the same temperature (550 °C for Ni-Mo and 600 °C for Co-Mo materials). The catalysts (Co-Mo/CNT, Co-Mo/CNTox, Ni-Mo/CNT, Ni-Mo/CNTox) were characterized using nitrogen adsorption at -196 °C, total acidity determination by chemical titration, inductively coupled plasma-optical emission spectroscopy, elemental analysis, X-ray diffraction (XRD) and transmission electron microscopy (TEM). After that, a screening of the catalysts was performed. In a typical run, 2.5 g of WCO, 25 g of n-decane and 0.25 g of catalyst were loaded into a stainless steel 100 mL autoclave batch reactor. After purging the reactor with N2, 70 bar (at 25 °C) of H2 were loaded into the reactor. The experiments were carried out at 350 °C and 1000 rpm for 3 h. Liquid and gas samples were analyzed by gas chromatography (GC) with a flame ionization detector (FID) and GC-FID/thermal conductivity detector, respectively. The carbon content of the WCO used was determined by elemental analysis. According to the results, all the catalysts exhibited mesoporous properties and elevated specific surface areas. However, the oxidation step of the supports was insufficient to introduce large amounts of oxygen groups on their surface due to the decomposition of some of the oxygen content following the thermal and reduction treatments. All the catalysts presented mainly MoO2 species, but an alloy of Co and Mo was observed by XRD patterns in the Co-Mo catalysts. Moreover, by TEM analysis, it is possible to see the introduction of MoO2 species inside the inner cavities of CNTox catalysts. According to the catalytic screening, the results revealed that Ni-Mo/CNTox demonstrated superior

catalytic performance, with a selectivity (Si) for light alkanes (6.6 mol.% of C5-C7), jet fuel (11.4 mol.% of C8-C16), and diesel fuel (81.2 mol.% of C17-C22), with a carbon conversion (XC) of 67 mol.%. Cycling experiments were conducted to assess the stability of this catalyst (Fig. 1), and after 4 consecutive runs, no significant deactivation was observed. On the other hand, it was necessary to extend the reaction time to 5 h for the Co-Mo catalysts to achieve similar results to those obtained over the Ni-Mo/CNTox catalyst. The high amount of MoO2 species leads the pathway by hydrodeoxygenation route (Fig. 2).

Acknowledgments

This work was supported by national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020). The authors thank for the financial support from the I+D+i project PID2020-115053RB-I00, funded by Spanish Ministry of Science and Innovation (MCIN/ AEI/10.13039/501100011033). K.K.F. acknowledges her Ph.D. scholarship (2022.12949.BD) from FCT. C.D.S is grateful for the Juan de la Cierva (JdC) fellowship (Grant Number: JDC2022-048765-I) funded by MICIU/AEI /10.13039/501100011033 and by FSE+.

FIGURES



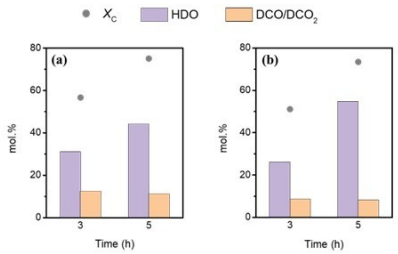


FIGURE 1

Products distribution after four consecutive runs over Ni-Mo/CNTox. Reaction Conditions: 350 °C, 70 bar H2 (at room temperature), 1000 rpm, 3 h, 0.25 g of catalyst, 2.5 g of WCO, 25 g of n-decane.

FIGURE 2

Progression of the conversion, HDO and DCO/DCO2 through the time over (a) Co-Mo/CNT and (b) Co-Mo/CNTox. Reaction conditions: 350 °C, 70 bar H2 (at room temperature), 1000 rpm, 3 - 5 h, 0.25 g of catalyst, 2.5 g of WCO, 25 g of n-decane.

KEYWORDS

Waste cooking oil | Co-Mo and Ni-Mo catalyst | Carbon nanotubes | Liquid Fuels

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