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Multilayered catalysts for fatty acid ester hydrotreatment into fuel range hydrocarbons

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ABSTRACT

This study aims to investigate Ni–Mo/ γ -Al₂O₃ and Ni–La/Zn-ZSM-5– γ -Al₂O₃ catalysts, which convert methyl esters into various compounds with a similar composition to those found in diesel fuels. The catalysts were synthesized by impregnation using two different routes and characterized by atomic absorption spectrometry, Brunauer–Emmett–Teller, and scanning electron microscopy. The acid strength distribution indicates a relatively high concentration of weak acid centers for both materials. The disposal of the catalysts into the reactor system is an important factor for driving the process toward the desired reaction products. The hydrodeoxygenation becomes important and paraffins are formed as intermediaries when Ni–Mo/ γ -Al₂O₃ is first disposed into the reactor, whereas hydrocracking is poor and the dehydrocyclization does not occur in the case of Ni–La/Zn-ZSM-5– γ -Al₂O₃ as first layer. Triple-layered catalytic systems enhance the production of *n*-paraffins with high carbon number, mainly C17 and C18, which are important as diesel component. The effect of temperature was also studied and it was found that aromatics are mainly formed over double-layered catalytic systems by varying the temperature. In the case of triple-layered catalysts, the change in the product composition from saturated hydrocarbons with 12–18 carbon atoms to aromatics was observed by increasing the temperature from 420 to 445 °C. An interesting finding by the addition of *n*-octane in the feed was observed and the considerable increase in C8 aromatics involved the dehydrocyclization that occurred faster than hydrocracking.

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1. Introduction

The increase in the number of vehicles and stringent regulations regarding the pollutant emissions abatement enforce the finding that alternative fuels and renewables have environmental benefits. Vegetable oils, for example, palm oil, canola, rapeseed oil, and cooking oils, are currently used for producing biodiesel. Resulting from the hydrotreatment of renewable feedstock, green diesel is considered a promising alternative to conventional diesel

and stands out for the high cetane number value, the absence of sulfur and aromatic hydrocarbons, low cold filter plugging point, as well as lower emissions of greenhouse gases. During hydrotreatment, the side chains of triglycerides are fragmented and paraffinic hydrocarbons in the diesel range (C14–C18) are obtained (green diesel) [1].

The bio-oil conversion occurs at relatively high temperatures (above 300 °C) under high pressures over Pd-supported on mesoporous carbon, Ni–Mo/Co–Mo on different supports, or Pd-amorphous SiO₂–Al₂O₃. The triglycerides were subjected to a complex reaction process comprising hydrocracking, hydrogenation, hydrodeoxygenation (HDO), and decarboxylation/decarbonylation [2–4].

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Nomenclature

B	benzene
C15–C18	alkanes with 15–18 carbon atoms
DEB	diethylbenzene
EB	ethylbenzene
Green LPG	green liquid petroleum gas
HDO	hydrodeoxygenation
LHSV	liquid hourly space velocity
MeO	methyl oleate
mX	<i>meta</i> -xylene
pX	<i>para</i> -xylene
SEM	scanning electron microscopy
T	toluene
TCD	thermal conductivity detector

Furthermore, hydrocracking involves destructive hydrogenation and is based on the conversion of compounds with high molecular weight into products with lower molecules. Isomerization reactions simultaneously occur, resulting in hydrocarbons with boiling points in gasoline or diesel distillation ranges. To diminish the possibility of either polymerization or coke formation reactions to occur, high reaction temperatures and hydrogen pressures are required. To accomplish this process, catalysts with acid function, provided by acid supports (e.g., amorphous aluminosilicates, silico-aluminous phosphates, or crystalline zeolites) are used [5–7].

Hydrotreating or hydrefining is considered as a nondestructive hydrogenation reaction, enhancing the properties of petroleum fractions, without distillation range modifications. The process occurs at low temperatures and pressures (300–400 °C, 5–11 MPa), and unstable compounds, which may lead to gums or insoluble materials, are transformed into stable compounds [7–9]. Hydrotreating is favored by the metallic function of catalysts. Noble metals or transitional metals (e.g., Ni, Mo, and Co) supported on alumina were widely investigated [7,10,11]. Contaminants such as nitrogen or metals were removed during the process [7].

The oxygen removal from the triglycerides can be performed by HDO, decarboxylation, or decarbonylation. The *n*-paraffins with long chains are the main reaction products and oxygen is removed either in the form of H₂O (via HDO) or H₂O and CO (via decarbonylation) and CO₂ (via decarboxylation) [12].

The operating conditions (e.g., temperature, pressure, and catalyst type) influence what reaction takes place first during the process, in addition to the yields and compositions of liquid products. Green gasoline (C5–C10), green kerosene (C11–C13), green diesel (C14–C20), or green liquid petroleum gas can be obtained through hydrotreating vegetable oils. To convert vegetable oils into green diesel with higher yield, the catalysts should not induce severe hydrocracking and the temperature range should not be excessive (usually 450–500 °C) [13].

Because the *n*-paraffins with C17 and C18 are the main components of green diesel, the freezing point of green

diesel can be relatively high [14]. For this reason, a selective catalyst (e.g., Ni promoted with transition metals such as Cu and Fe) may favor the hydroisomerization to obtain methyl isoparaffins with better cold properties. Several catalysts were studied for hydrotreating vegetable oils and for various hydroconversion technologies of oils and lubricants [15].

The study performed by Herskowitz et al. [16] shows that soybean oil is converted over Pt/SAPO-11–Al₂O₃ catalyst in a single-step process, at 375–380 °C and 30 atm. The yield in organic liquid product was approximately 80%, and the gas-chromatography coupled with mass spectrometry (GC–MS) proves the presence of straight and branched paraffins, naphthenes, and monoaromatics, producing a high quality diesel component [16].

Hanafi et al. [17] studied the conversion of waste cooking oil into renewable fuel by hydrocracking over NiW/SiO₂–Al₂O₃, in the temperature range of 375–450 °C under pressure below 6 MPa. Liquid products with a chemical composition similar to gasoline, kerosene, and diesel were obtained, and the yield of each fraction depends on the reaction conditions.

Ni–Mo/γAl₂O₃ is one of the most widely used catalysts for hydrotreating medium and heavy fractions because of its high activity and low acidity, which are convenient for the hydroconversion of triglycerides into green diesel [7,18,19]. The effect of a different atomic ratio of the Ni–Mo/γAl₂O₃ reduced catalyst was recently investigated for hydrotreating triglycerides, indicating that changes in the atomic ratio influence the yield to hydrocarbons in the diesel range [12].

On the other hand, Sebos et al. [20] found that the CoMo/Al₂O₃ catalyst exhibits superior performance for the conversion of cottonseed oil–desulfurized diesel mixture into green diesel at 305–345 °C and 30 bar. The conversion of triglycerides was about 100% under the conditions examined [20].

A recent study regarding the bio-oil hydrotreating of diesel-like products over alumina-supported sulfided NiMo and CoMo catalysts was reported [21], suggesting the role of reaction conditions and additives.

Nowadays Ni–Mo catalysts are widely used in the hydrotreating of petroleum products, focusing on hydrogenolysis and HDO of the heterocompounds [22]. This is the reason for choosing the Ni–Mo/γAl₂O₃ catalyst for our study. To our knowledge, there are no studies available on the investigation of nonsulfided Ni–Mo/γAl₂O₃ activity for the hydrotreatment of methyl oleate (MeO).

Several studies have been focusing on the hydrotreatment of vegetable oils mixed with petroleum products. An interesting finding was reported by several investigators [23–26], suggesting that the combination of various catalysts may contribute to the oxygen removal and C=C double bonds, without hydrogenation of aromatics even if this could lead to a lower octane number of gasoline and increased hydrogen consumption [26–29]. The catalysts used to convert triglycerides, methyl esters, or ethyl esters in diesel-like components need to be selective toward deoxygenation, hydrogenation, and hydroisomerization, without coke formation.

The Zn-modified ZSM-5 support decreases the Brønsted acid sites and increases Lewis acid sites [30] while

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