

Article

Valorization of Coal Fly Ash Cenospheres as Catalyst Supports for Green Diesel Synthesis

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Abstract

To reduce dependence on fossil fuels and limit their environmental impact, the development of biofuels represents an effective strategy. Green diesel is a biofuel synthesized from vegetable oil that is fully compatible with conventional diesel engines and therefore represents a promising alternative to mineral diesel. In addition, the use of waste-derived catalysts can further improve the sustainability of the process. In this study, fly ash cenospheres (FAC), an abundant industrial waste, were used as a support to synthesize several transition-metal-based catalysts. The catalysts were tested for the catalytic deoxygenation of vegetable oils in a batch reactor at 320 °C and 40 bar H₂ using 10 wt% catalyst and *n*-hexane as the solvent. Among the tested catalysts, NiMo(5/15)/FAC exhibited the best performance, achieving complete conversion and producing a biofuel containing 91.7% C₁₅–C₁₈ hydrocarbons. The physicochemical properties of the catalyst were investigated using ICP-MS, FT-IR, XRD, and BET-BJH analyses. The effects of the solvent, feedstock, and catalyst reuse were also evaluated. In the recycling tests, the catalyst activity rapidly decreased; however, the regeneration step fully restored its catalytic performance. These results show that FAC can be effectively valorized as a catalyst support for green diesel synthesis.

Keywords: coal fly ash cenospheres; waste valorization; heterogeneous catalyst; green diesel; catalytic deoxygenation reaction; vegetable oil

1. Introduction

Today, more than 80% of global energy demand is still met by fossil fuels [1]. Their extensive use results in well-known problems, including environmental pollution and depletion of reserves. In particular, fossil-fuel combustion releases large amounts of greenhouse gases, mainly CO₂, as well as VOCs, SO_x, and NO_x, which are well-known air pollutants [2]. In addition, fossil fuels are a non-renewable energy source and therefore subject to depletion. This issue is further intensified by the continuous increase in global energy demand, driven by population growth, technological development and economic expansion [3]. In particular, the transport sector greatly contributes to fossil fuel consumption; indeed, 95% of transport energy demand is provided by oil (accounting for 60% of total oil consumption) and also contributes to around 24% of total CO₂ and greenhouse gas emissions [4,5]. To overcome these drawbacks, the scientific community has strongly focused on the development of renewable energy sources, and, in the transport sector, biofuels represent one of the main renewable alternatives. Biofuels can be obtained from



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different types of biomass, including sugars–starch, lignocellulosic and triglyceride-based biomass. Among these, triglyceride-based biomass, like vegetable oils, is widely used because it has similar chemical-physical characteristics to those of petroleum derivatives (triglycerides are composed of fatty acids with carbon atom chains similar in length to those of oil-derived hydrocarbons) [6]. Vegetable oil-derived biofuels can provide environmental benefits over conventional fossil fuels, since their use can reduce greenhouse gas emissions and lower the release of pollutants such as SO_x , carbon monoxide, unburned hydrocarbons and particulate matter [7]. In addition, they are a renewable energy source and therefore not subject to depletion. Moreover, the use of waste oil can also provide further benefits in terms of waste management. The most common strategy for triglyceride biomass upgrading is the transesterification of vegetable oil, in which triglycerides are converted into a biofuel consisting of fatty acid methyl esters (FAMES) commonly known as biodiesel. Biodiesel was introduced in 1992 by the National Soy Diesel Development Board and is still among the most widely used biofuels [8]. Despite its wide use, however, biodiesel has several drawbacks, including storage instability, high oxygen content (which results in lower energy density than petroleum diesel), high corrosivity and limited compatibility with conventional diesel engines, since it can generally be used only in blends with petroleum diesel [9,10]. Green diesel (trade name given by UOP/Eni), also known as hydrotreated vegetable oil (HVO) or renewable diesel, is a hydrocarbon biofuel consisting exclusively of hydrocarbons and was first marketed by Neste Oil in 2007 [11]. Green diesel can be obtained through the catalytic deoxygenation reaction (CDO) of vegetable oils, in which triglycerides are thermally treated, typically in a hydrogen atmosphere and with a heterogeneous catalyst and converted into hydrocarbons. The reaction scheme for green diesel formation is shown in Figure 1 [12].

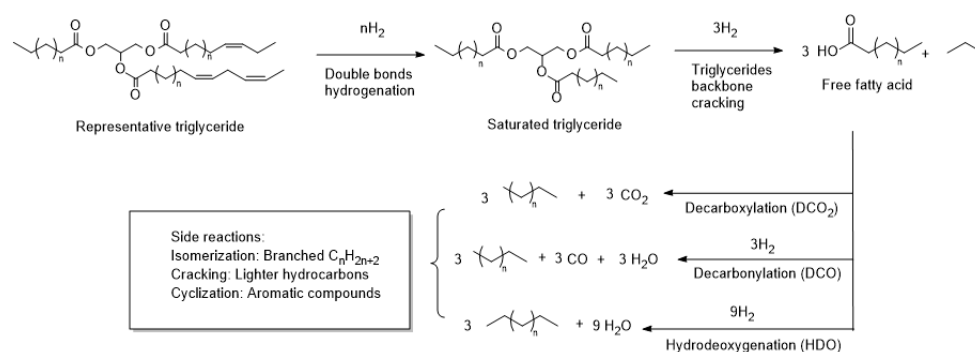


Figure 1. CDO reaction.

Briefly, triglycerides are first hydrogenated and then cleaved to form free fatty acids and propane through a β -elimination reaction (most common mechanism) [13]. The resulting fatty acids are then converted into hydrocarbons through three different reaction pathways: hydrodeoxygenation (HDO), decarbonylation (DCO) and decarboxylation (DCO_2). In the HDO pathway, oxygen is removed as H_2O and a hydrocarbon with the same number of carbon atoms as the starting fatty acid is formed. In contrast, DCO and DCO_2 lead to the formation of a hydrocarbon with one carbon atom less than the starting fatty acid; oxygen is removed as CO and H_2O in DCO, and as CO_2 in DCO_2 [14,15]. Side reactions, such as cracking, isomerization, oligomerization and gas-phase reactions, are also possible during the reaction. Cracking produces short-chain hydrocarbons, which are more suitable for jet-fuel-like biofuel production [16–18]. Isomerization forms branched hydrocarbons, which improve the cold-flow properties of the biofuel [19–21]. Oligomerization, on the other hand, is an undesirable reaction because it leads to the formation of coke and long-chain hydrocarbons, which can deactivate the catalyst and negatively affect the properties of

the final biofuel [22]. In the gas phase, water–gas shift and methanation reactions may also occur, contributing to the overall reaction by producing or consuming H_2 [23]. The overall process is influenced by many factors, including temperature, hydrogen pressure, reactor configuration, feedstock type and, especially, the catalyst. The most commonly used catalysts are noble- or transition-metal-based catalysts (like Pd, Pt, Ru, Ni, Mo, Co, W), supported on different materials such as Al_2O_3 , SiO_2 , zeolites, and activated carbon [23–29]. Noble-metal-based catalysts are particularly active; however, their high cost limits their practical application. For this reason, reduced or sulfided transition-metal catalysts have been developed as alternative systems. Sulfided catalysts are very active in the catalytic deoxygenation reaction, and the most commonly used systems are based on Ni and Co promoted with Mo and W [30–33]. However, sulfided catalysts can suffer from rapid deactivation due to sulfur leaching, and, to maintain their activity, it is necessary to use sulfiding agents that pollute the biofuel produced [34,35]. Reduced transition metal catalysts are able to overcome these limitations, since they can show activity comparable to that of sulfided catalysts, while reducing deactivation and avoiding sulfur contamination of the biofuel, as suggested by Harnos et al. [36]. Among these catalysts, Ni- and Co-based systems promoted with W or Mo and supported on Al_2O_3 , SiO_2 and zeolites are the most widely investigated [36–40]. In a recent study, we synthesized a NiMoAl-based catalyst using the co-precipitation method [41]. This catalyst proved to be highly active, representing a viable alternative to conventional sulfided or noble-metal-based catalysts. However, to further improve process sustainability, we decided to shift our research towards the development of catalysts derived from waste materials. Recently, increasing efforts have been made to synthesize catalysts from waste materials, with the aim of valorizing a waste that would otherwise require disposal [7,42–45]. Coal fly ash (CFA) is a waste product generated during coal combustion, and it has been reported that one ton of coal fly ash is produced for every two tons of coal [46]. Because of its large-scale production and environmental impact, CFA disposal represents an important issue. For this reason, considerable attention has been paid to CFA recycling. Indeed, CFA has been widely used as an additive in cement and construction, as fertilizers, as an adsorbent for wastewater treatment and as a catalyst or catalyst precursor [47–49]. CFA can be used as a precursor of high-added-value materials, including zeolites and mesoporous silica, or directly used as a support for metal catalysts [50–53]. As catalysts, CFA has been widely used for biodiesel synthesis [53–58]. However, to the best of our knowledge, no studies have reported the use of fly-ash-derived catalysts for green diesel production. In this work, we report the synthesis of several metal transition-based catalysts supported on fly ash cenospheres (FAC) (the fly ash cenospheres are a component of the coal fly ash) and zeolites, obtained from FAC. These catalysts were subsequently tested in catalytic deoxygenation reactions in a batch reactor under fixed reaction conditions. The most efficient catalyst was selected for further studies to evaluate the effects of the reaction solvent and feedstock type. In addition, it was tested to assess its activity over multiple reaction cycles. Finally, the catalyst was characterized using FT-IR, XRD, ICP-MS, and N_2 physisorption.

2. Results

2.1. Oil Characterization

Sunflower oil (SO), rapeseed oil (RO), peanut oil (PAO), corn oil (CO) and palm oil (PO) were purchased from local suppliers, while soybean oil (SBO) was purchased from Merck KGaA. Waste cooking oil (WCO) was collected from households. The oils were characterized by transesterification in accordance with the AOAC 969.33 standard [59]. In the transesterification reaction, the fatty acids of the triglycerides (TGs) were converted into fatty acid methyl esters (FAMES), which were subsequently analyzed by GC-FID. FAME

identification was performed by comparing the retention times of the sample with those of a C₁₄–C₂₂ FAME reference standard (see experimental section). The fatty acid compositions of the vegetable oils are reported in Table 1.

Table 1. Fatty acid composition of the oils used.

Oils	FAME (Area %)								
	C ₁₄	C ₁₆	C ₁₈	C _{18:1c} ¹	C _{18:2c}	C _{18:3c}	C ₂₀	C _{20:1c}	C ₂₂
Sunflower	--	6.5	3.2	38.6	51.5	0.2	--	--	--
Rapeseed	--	4.9	1.7	64.5	19.5	7.3	0.6	1.2	0.3
Soybean	0.2	11.3	3.9	21.4	55.3	7.2	0.3	--	0.4
Peanut	--	7.4	2.5	74.6	9.7	--	0.2	2.4	3.2
Corn	--	11.8	1.9	30.5	54.2	0.9	0.4	--	0.3
Palm	0.9	38.8	5.3	42.7	11.6	0.3	0.4	--	--
Waste	0.1	8.7	4.8	35.3	49.6	0.3	--	0.2	1.0

¹ C_n:m:c: n is the number of carbon atoms; m is the number of double bonds; c means cis.

The composition of the oil is important for the CDO reaction because a high content of unsaturated fatty acids can lead to higher H₂ consumption. In addition, the composition of the starting oil affects the product distribution. For example, palm oil produces a biofuel richer in C₁₆ alkanes and therefore with a high cetane number.

2.2. Catalyst Synthesis

Several transition metal catalysts supported on fly ash cenospheres (FAC) and on zeolites synthesized from FAC were prepared and evaluated in the catalytic deoxygenation (CDO) reaction. The FAC employed in this study were sourced from a coal-fired power plant located in Kolkata, India. After catalyst screening, the most performing catalyst was characterized. Its elemental composition was determined by ICP-MS, while specific surface area and pore size distribution were investigated by N₂ physisorption analyses. The crystalline structure and surface functional groups were investigated by XRD and FT-IR, respectively.

2.2.1. Synthesis of FAC-Based Catalysts

Before being used, the FAC were treated with an acid solution to remove impurities and soluble metals, following the procedure described by Sutarno et al. [60]. After acid treatment, the solid, named FAC-HCl, was filtered, washed with deionized water until neutral, and dried in an oven at 110 °C overnight. The catalysts were then synthesized via excess wet impregnation. Appropriate amounts of metal salts were dissolved in an aqueous suspension containing FAC-HCl and stirred at room temperature for 3 h. Water was then removed using a rotary evaporator, and the resulting solid was dried in an oven at 110 °C overnight. Finally, the dried material was calcined in a muffle furnace at the decomposition temperature of the corresponding metal salts, as reported in the literature [61–65]. Catalyst reductions were carried out in a tubular fixed-bed reactor under an H₂/N₂ flow (10%/90%). The reduction conditions were selected based on hydrogen consumption measurements using an ABB gas analyzer. After reduction, the catalysts were stored in sealed containers under an argon atmosphere to maintain inert conditions and prevent possible oxidation. The catalysts were labeled as MNX(m,n,x)/FAC, where M, N, and X represent the impregnated metals, while m, n, and x indicate the nominal loading of the impregnated metals of the corresponding metal oxides. For example, NiMo(5/15)/FAC refers to a catalyst prepared by impregnating FAC-HCl with Ni and Mo salts to obtain nominal loadings of 5 wt% of NiO and 15 wt% of MoO₃ after calcination. The nominal wt% of the impregnated metals of all the FAC-supported catalysts are reported in Table 2. The catalysts were further

distinguished according to their treatment stage: non-calcined samples were labeled as MNX(m,n,x)/FAC N.C., calcined samples as MNX(m,n,x)/FAC C., and reduced samples as MNX(m,n,x)/FAC R. For instance, NiMo(5/15)/FAC R. denotes the reduced form of the catalyst containing 5 wt% of NiO and 15 wt% of MoO₃. Further experimental details are provided in the Experimental section. Table 2 summarizes the synthesized FAC-supported catalysts and their respective calcination and reduction conditions.

Table 2. FAC-supported catalysts synthesized.

Catalyst	Wt% of Impregnated Metals	Calcination Conditions ¹	Reduction Conditions ²
NiMo(5/15)/FAC	5% NiO, 15% MoO ₃	400 °C (5 °C/min), 4 h	700 °C (5 °C/min), 3 h
CoMo(6/15)/FAC	6% CoO, 15% MoO ₃	600 °C (5 °C/min), 4 h	800 °C (10 °C/min), 3 h
NiW(5/15)/FAC	5% NiO, 15% WO ₃	600 °C (5 °C/min), 4 h	800 °C (10 °C/min), 3 h
NiMoCe(5/15/5)/FAC	5% NiO, 15% MoO ₃ , 5% CeO ₂	400 °C (5 °C/min), 4 h	820 °C (5 °C/min), 3 h
NiMoLa(5/15/5)/FAC	5% NiO, 15% MoO ₃ , 5% La ₂ O ₃	800 °C (10 °C/min), 4 h	700 °C (5 °C/min), 3 h
NiMoCa(5/15/20)/FAC	5% NiO, 15% MoO ₃ , 20% CaO	800 °C (20 °C/min), 4 h	800 °C (5 °C/min), 3 h

¹ Chosen after a literature review on the decomposition temperature of the used salts [61–65]. ² Chosen after ABB analysis.

2.2.2. Synthesis of Zeolite-Based Catalysts

FAC-derived zeolite support was synthesized by the alkali fusion method proposed by Sutarno et al. [60]. FAC were fused with NaOH in a muffle furnace. The resulting solid was suspended in Milli-Q water and aged overnight under stirring. The suspension was then subjected to hydrothermal treatment, after which the formed solid was filtered and dried. Metal impregnation was carried out via excess wet impregnation, following the same procedure described for FAC-supported catalysts. To evaluate the influence of the support, the zeolite-based catalysts were synthesized using the same metal species and loadings chosen for the FAC-supported counterparts. For all the zeolite-supported catalysts, the wt% of the oxide metals are reported in Table 3. Calcination was performed under the same conditions used for the corresponding FAC-based catalysts. Reduction conditions were determined using an ABB gas analyzer, as previously described. The catalysts were labeled using the same convention adopted for FAC-based materials, i.e., MNX(m,n,x)/Zeo, where M, N, and X refer to the impregnated metals and m, n, and x represent the nominal loadings of the corresponding metal oxides. The catalyst forms were also distinguished by the suffixes N.C. (non-calcined), C. (calcined), and R. (reduced). Table 3 reports the synthesized zeolite-based catalysts and their respective calcination and reduction conditions.

Table 3. Zeolite-supported catalysts synthesized.

Catalyst	Wt% of Impregnated Metals	Calcination Conditions ¹	Reduction Conditions ²
NiMo(5/15)/Zeo	5% NiO, 15% MoO ₃	400 °C (5 °C/min), 4 h	700 °C (5 °C/min), 3 h
NiW(5/15)/Zeo	5% NiO, 15% WO ₃	600 °C (5 °C/min), 4 h	750 °C (10 °C/min), 3 h
NiMoCe(5/15/5)/Zeo	5% NiO, 15% MoO ₃ , 5% CeO ₂	400 °C (5 °C/min), 4 h	720 °C (5 °C/min), 3 h
NiMoLa(5/15/5)/Zeo	5% NiO, 15% MoO ₃ , 5% La ₂ O ₃	800 °C (20 °C/min), 4 h	850 °C (5 °C/min), 3 h
NiMoCa(5/15/20)/Zeo	5% NiO, 15% MoO ₃ , 20% CaO	800 °C (10 °C/min), 4 h	780 °C (5 °C/min), 3 h

¹ Chosen after a literature review on the decomposition temperature of the used salts [61–65]. ² Chosen after ABB analysis.

2.3. CDO Reaction and Product Characterization

The catalytic activity of the synthesized materials was evaluated in a high-pressure batch reactor system (4590 Micro Bench Top Reactor, equipped with magnetic drives and a 4848 Reactor Controller). Catalyst screening was performed under fixed reaction conditions: temperature of 320 °C, hydrogen pressure of 40 bar measured at room temperature, 2.00 g

of sunflower oil, 0.200 g of catalyst (corresponding to a catalyst-to-oil ratio of 10 wt%), and 20.0 g of hexane as solvent, 6 h of reaction time and 200 rpm of stirring. Further details on the experimental setup are provided in the Experimental section. Based on the results obtained from this preliminary screening, the catalyst exhibiting the highest activity was selected for further investigations, including solvent screening, oil screening and recycling tests. At the end of each reaction, the catalyst was recovered by vacuum filtration and dried under vacuum overnight. The resulting reaction mixture, namely Organic Liquid Product (OLP), was concentrated with a rotary evaporator and weighed to determine the yield. The OLP yield, expressed as OLP wt%, was calculated according to Equation (1):

$$OLP \text{ wt\%} = \left(\frac{gOLP}{gOil} \right) \times 100 \quad (1)$$

where gOLP is the mass of OLP (in grams) recovered, and gOil is the initial mass of oil (in grams) used in the reaction.

The obtained OLP was preliminarily characterized by Fourier-transform infrared spectroscopy (FT-IR) to qualitatively assess the extent of reaction conversion. FT-IR is a rapid and effective analytical technique for this purpose, as it allows the identification of specific functional groups associated with the reactants and products. In particular, the spectral region between 1750 and 1700 cm^{-1} was examined, where the characteristic stretching vibrations of the ester carbonyl group, approximately at 1745 cm^{-1} , and the carboxylic acid carbonyl group, around 1710 cm^{-1} , can be observed. These signals provide information on the relative presence of triglycerides and free fatty acids and can therefore be used as qualitative indicators of reaction progression. Furthermore, the presence of oxygenated compounds in the product mixture was further assessed from the absorption bands in the 1350–900 cm^{-1} region, which correspond to C–O stretching vibrations typically associated with esters, alcohols, and other oxygen-containing functionalities [66].

The OLP was further analyzed by gas chromatography coupled with flame ionization detection (GC-FID) to determine its composition and quantify the components in the mixture. Prior to GC-FID analysis, an aliquot of the OLP was subjected to a transesterification reaction, following the same protocol employed for oil characterization. This step was performed to assess the presence of unreacted oil species, such as triglycerides and free fatty acids, through the formation of their corresponding methyl esters. The components present in the mixture were identified by comparing their retention times with those of a reference mixture of *n*-alkanes (C_7 – C_{40}). To identify any unknown chromatographic peaks observed in the GC-FID profiles, the transesterified mixture was subsequently analyzed by gas chromatography coupled with mass spectrometry (GC-MS). Unknown compounds were identified by comparing the acquired mass spectra with those in the NIST spectral library. In addition, Kovats retention indices were calculated and used as a complementary tool to support the structural identification of the unknown components. The investigated reaction parameters were the organic liquid product yield (OLP (%)), reaction conversion (X), the green diesel yield (GD %) and the selectivity (S) [67,68]. The reaction product distribution was assessed in terms of the relative percentages of the main hydrocarbon classes and unreacted or intermediate compounds. Specifically, the analysis focused on the quantification of olefins, linear alkanes in the ranges C_8 – C_{14} , C_{15} – C_{18} and $\text{C} > 18$, branched hydrocarbons, and unconverted feedstock components, such as free fatty acids and triglycerides, identified and quantified in the form of their corresponding fatty acid methyl esters (FAME).

Equation (2) was used to determine the conversion (X), where FAME represents the sum of the chromatographic peak area percentages assigned to fatty acid methyl esters, and

g_{OLP} and g_{Oil} represent the mass of crude reaction mixture recovered after the reaction and the initial mass of oil used as feedstock, respectively.

$$\chi = 1 - \left(\frac{FAME \times g_{OLP}}{g_{Oil}} \right) \times 100 \quad (2)$$

The green diesel yield (GD %) was calculated using Equation (3), where $A_{nC_{15}-C_{18}}$ is the sum of the chromatographic peak area percentages assigned to linear alkane in the C_{15} – C_{18} range (green diesel fraction)

$$GD (\%) = \frac{A_{nC_{15}-C_{18}} \times g_{OLP}}{g_{OIL}} \times 100 \quad (3)$$

Finally, the preference of the catalysts toward HDO and DCO_x reaction (see Figure 1) was evaluated according to Equation (4). Selectivity was calculated as the ratio between the sum of the peak areas corresponding to hexadecane and octadecane, $C_{16} + C_{18}$, derived from HDO, and the sum of the peak areas related to pentadecane and heptadecane, $C_{15} + C_{17}$, derived from DCO_x .

$$S = \frac{C_{16} + C_{18}}{C_{15} + C_{17}} \times 100 \quad (4)$$

An S-value greater than 1 indicates a preference for HDO, whereas an S-value lower than 1 suggests that the reaction proceeds mainly through the DCO_x pathway.

2.3.1. Catalyst Screening

As previously reported, the catalyst screening experiments were conducted under the following reaction conditions: temperature of 320 °C, hydrogen pressure of 40 bar (measured at room temperature), 2 g of sunflower oil as feedstock, 20 g of hexane, 0.200 g of catalyst (corresponding to a catalyst-to-oil ratio of 10 wt%), reaction time of 6 h and stirring at 200 rpm. Figure 2 shows the FT-IR spectra of the reaction mixtures obtained using bimetallic, on the left, and trimetallic catalysts, on the right, compared to the FT-IR spectrum of the sunflower oil.

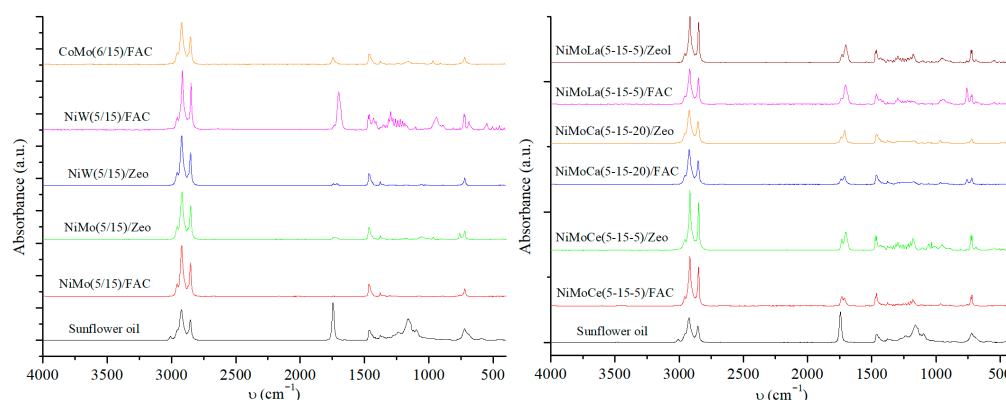


Figure 2. FT-IR of the OLP obtained after catalyst screening (bimetallic catalysts on the left, trimetallic catalysts on the right).

The FT-IR of sunflower oil displays a strong absorption band in the carbonyl region, attributed to triglyceride ester groups at approximately 1745 cm^{-1} , along with several bands in the $1350\text{--}800 \text{ cm}^{-1}$ region corresponding to C–O vibrations. A decrease in the intensity or disappearance of these peaks in the reaction mixtures can therefore be used as a qualitative indicator of triglyceride conversion. For the bimetallic catalysts, Figure 2 left side, only the spectrum of the reaction mixture obtained with NiMo(5/15)/FAC shows the complete disappearance of both the ester carbonyl band and the C–O stretching

region. This observation, coupled with the presence of characteristic C–H stretching and bending vibrations ($3050\text{--}2750\text{ cm}^{-1}$, 1460 cm^{-1} , 1377 cm^{-1} , and 720 cm^{-1}), suggests nearly complete conversion of triglycerides into hydrocarbons. Based on the intensity of the carbonyl band, NiMo(5/15)/Zeo and NiW(5/15)/Zeo also showed good activity, but in these cases, two small peaks are present in the $1750\text{--}1710\text{ cm}^{-1}$ range, indicating incomplete conversion of triglycerides and partial formation of free fatty acids. The spectrum obtained using NiW(5/15)/FAC is dominated by an intense absorption band centered at 1710 cm^{-1} , suggesting efficient conversion of triglycerides into free fatty acids, but limited activity in their subsequent deoxygenation to hydrocarbons. An opposite trend is observed with CoMo(6/15)/FAC, where the band at 1745 cm^{-1} suggests lower triglyceride conversion; however, the catalyst appears to promote the further transformation of free fatty acids into hydrocarbons more effectively. Regarding the trimetallic catalysts (Figure 2 right side), FT-IR spectra consistently show the presence of both ester and carboxylic acid carbonyl peaks, indicating limited overall conversion. Therefore, trimetallic catalysts appear to be less active than bimetallic ones. FT-IR spectra provide only a qualitative interpretation of the catalytic activity of the catalysts; a more detailed analysis of the reaction mixtures was performed by GC-FID and GC-MS analysis (Table 4).

Table 4. Distribution of reaction products and catalytic performance parameters for the tested catalysts.

Entry	Catalyst ¹	Alkenes	<i>n</i> -C ₈ –C ₁₄	<i>n</i> -C ₁₅ –C ₁₈	C > 18	FAME	Other	S	X	OLP (wt%)	GD (wt%)
1	blank	--	--	--	--	81.9	18.1	--	15.0	85.1	--
2	FAC	2.4	1.0	1.6	0.2	79.4	15.4	--	15.0	95.3	1.8
3	NiMo(5/15)/FAC	--	4.4	91.7	3.9	--	--	1.5	100.0	72.2	66.2
4	NiMo(5/15)/Zeo	12.5	2.6	39.1	0.9	12.9	32.0	1.5	87.7	96.1	37.0
5	CoMo(6/15)/FAC	20.6	5.0	67.1	--	3.4	3.9	6.3	97.3	75.5	50.6
6	NiW(5/15)/FAC	11.3	0.6	11.0	--	72.2	4.9	0.4	32.5	87.4	9.6
7	NiW(5/15)/Zeo	1.9	3.5	90.0	1.5	2.3	0.8	0.4	97.3	82.6	74.3
8	NiMoCe(5/15/5)/FAC	22.7	1.4	22.9	0.2	52.8	--	0.9	52.3	90.3	20.7
9	NiMoCe(5/15/5)/Zeo	12.6	0.5	8.1	--	78.8	--	0.6	35.4	82.0	6.6
10	NiMoLa(5/15/5)/FAC	4.3	0.3	2.7	--	82.2	10.5	0.3	17.6	88.9	2.4
11	NiMoLa(5/15/5)/Zeo	17.4	1.3	10.8	0.2	57.4	12.9	0.7	31.7	97.2	10.2
12	NiMoCa(5/15/20)/FAC	15.0	2.8	28.6	0.8	52.4	0.4	0.6	54.7	86.4	24.7
13	NiMoCa(5/15/20)/Zeo	7.5	1.5	5.5	--	85.5	--	0.6	26.0	86.4	4.8

¹ All the reactions were performed at $320\text{ }^{\circ}\text{C}$, 40 bar H_2 , 20 g of *n*-hexane, 2 g of sunflower oil, 0.200 g of catalyst and 6 h of reaction time.

To evaluate the effect of the FAC support on the CDO reaction, two different blank tests were addressed (entries 1 and 2, Table 4). In the first blank test, the CDO reaction was carried out in the absence of catalyst and support (entry 1), while in the second (entry 2) only the HCl-treated FAC support was used. The results indicate that the FAC support shows negligible activity in the CDO reaction because the results for entry 1 and entry 2 are very similar (the reaction in entry 2 shows only a small amount of hydrocarbons, 5.2%). As also evidenced by the FT-IR spectra, the data in the table clearly show that bimetallic catalysts exhibit higher activity than trimetallic ones. In all cases, trimetallic catalysts display high FAME content, exceeding 50%, indicating incomplete deoxygenation. Among the screened catalysts, NiMo(5/15)/FAC (entry 3) exhibited the highest activity, achieving complete conversion and producing 91.7% diesel-range hydrocarbons. This corresponds to an OLP yield of 72.2 wt% and indicates the formation of a fully hydrocarbon biofuel with high selectivity toward diesel-range products. The significant influence of the support is evident when comparing NiMo(5/15)/FAC with NiMo(5/15)/Zeo (entry 3 vs. entry 4). Despite having the same nominal metal loading, the zeolite-supported catalyst showed lower activity, with 87% conversion compared with 100% for NiMo(5/15)/FAC. After NiMo(5/15)/FAC, the most active catalysts were CoMo(6/15)/FAC and NiW(5/15)/Zeo (entry 5 and 7). CoMo(6/15)/FAC achieves 97.3% conversion and a biofuel yield of 75.5 wt%. However, it

shows lower hydrogenation activity than NiMo(5/15)/FAC, resulting in a higher amount of unsaturated hydrocarbons (20.6%) and, therefore, lower n -C₁₅–C₁₈ hydrocarbon content (67.1%). CoMo-based catalysts have often been associated with higher selectivity toward unsaturated products, as reported in the literature [30,69]. The NiW(5/15)/Zeo system (entry 7) shows a comparable conversion to that of CoMo(6/15)/FAC, but the resulting biofuel contains a higher concentration of alkanes in the diesel range, approximately 90%. This indicates a higher degree of hydrogenation than that observed for the CoMo catalyst. In contrast to the NiMo-based systems, for which the FAC-supported catalyst was more active than the zeolite-supported analogue, the opposite trend was observed for the NiW system. In this case, NiW(5/15)/Zeo was more active than NiW(5/15)/FAC, highlighting a support-dependent behavior specific to the NiW formulation (entries 3 and 4 vs. entries 6 and 7). For all the catalysts tested, low cracking activity is observed. In any case, less than 5% of n -C₇–C₁₄ hydrocarbon is produced.

Focusing on product distribution and HDCO/DCO_x selectivity, NiMo(5/15)/FAC promoted both hydrodeoxygenation (HDO, yielding C₁₈ + C₁₆ alkane) and decarbonylation / decarboxylation (DCO/DCO₂, yielding C₁₇ + C₁₅ alkane) pathways, with a slight preference for the HDO route (S value = 1.5). This is consistent with previous observations by Kubička et al. [33]. Interestingly, in agreement with several authors [70–72], CoMo(6/15)/FAC shows notable selectivity toward HDO products (S = 6.3), whereas NiW(5/15)/Zeo strongly prefers the DCO_x pathway. A detailed mechanistic explanation of the observed reaction selectivity would require an extensive physicochemical characterization of all the tested catalysts. Such an investigation is beyond the scope of the present work; however, the different selectivity trends observed may be tentatively interpreted on the basis of literature on related deoxygenation catalysts. Moreover, the discussion was limited to catalysts showing significant catalytic activity, since selectivity values obtained at low conversion are less representative and may be strongly affected by incomplete reaction progress. For NiMo(5/15)/FAC, the interpretation is partially supported by the XRD results (see Section 2.4.3). No crystalline Ni–Mo mixed phase was detected, whereas Ni was identified as Ni⁰ and NiO and Mo mainly as MoO₂. The coexistence of Ni species and MoO₂ species may explain its intermediate HDO/DCO_x selectivity. Metallic Ni can promote H₂ activation and hydrogenation, while Mo-containing species may provide more oxophilic sites for oxygenated-group adsorption and C–O bond cleavage [73]. Conversely, at sites where only Ni is present, DCO_x may be more strongly favored, as observed by Kubička and Kaluža [33]. The CoMo system shows very high selectivity for the HDO reaction; it seems that the catalyst may behave more like conventional hydrotreating-type catalysts, where Co-promoted Mo sites provide a more integrated hydrogenation/C–O cleavage function [15]. Therefore, the higher HDO contribution of CoMo-based catalysts may be related to more effective Co–Mo synergy, whereas NiMo(5/15)/FAC appears to contain partially separated Ni and MoO₂ phases. For NiW/Zeo, the higher DCO_x contribution may arise from the combined effect of Ni–W functions and the acidic zeolitic support. Gosselink et al. report that WO₃-based catalysts preferentially promote DCO_x [74]. At the same time, the acidic and microporous zeolitic support can favor dehydration, cracking, isomerization and secondary transformations, increasing the formation of C_{n-1} and lighter hydrocarbons [75]. A schematic representation of the observed selectivity trends is presented in Figure 3.

It should be noted that the best-performing catalysts, NiMo(5/15)/FAC, CoMo(6/15)/FAC and NiW(5/15)/Zeo, resulted in lower OLP yields. This behavior may be related to the nature of the catalytic deoxygenation reaction. As conversion increases, the formation of volatile products also increases, including propane derived from the triglyceride backbone, light hydrocarbons from cracking, and CO and CO₂ from DCO-DCO₂ [38].

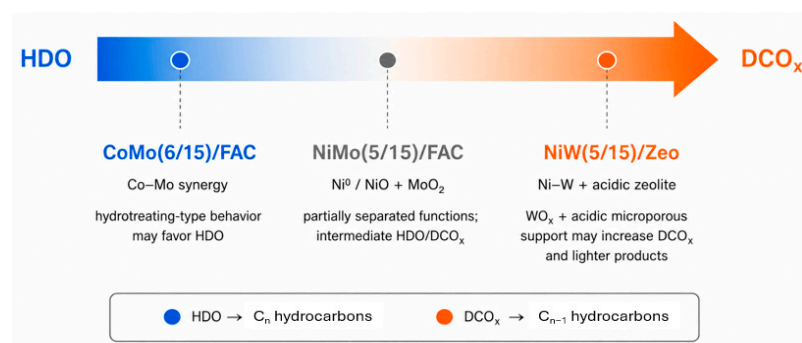


Figure 3. Reaction selectivity trends of the most active catalysts.

In the case of incomplete conversion, and after transesterification, several reaction mixtures report high FAME concentrations, indicating the presence of significant amounts of unconverted triglycerides and/or free fatty acids. The main detected compound was methyl stearate, small percentages of methyl palmitate, and, in a few cases, also methyl elaidate (this reflects the composition of vegetable oils, which, except in the case of palm oil, consist mainly of fatty acids with 18 carbon atoms). These compounds were identified after GC-MS analysis. Although vegetable oils consist of fatty acids with a *cis* configuration, the presence of methyl elaidate is not unexpected, since *cis-trans* isomerization may occur during the reaction [76,77]. In addition, by analyzing the reaction mixture via GC-MS before the transesterification step, other oxygenated compounds such as 1-octadecanol, propyl stearate, and propyl palmitate were observed. CDO proceeds through a sequence of reduction reactions; therefore, the observed 1-octadecanol may derive from the reduction of octadecanal (not observed in any reaction mixture). Several studies report the presence of 1-octadecanol as a reaction intermediate [14,33,34,75,78–80]. Conversely, octadecanal is rarely observed due to its rapid conversion into heptadecane or 1-octadecanol [81–83]. Finally, the detection of propyl stearate and propyl palmitate supports the occurrence of the initial triglyceride cleavage through β -elimination. Indeed, propyl stearate (and propyl palmitate) can be formed when the β -elimination reaction stops after the second hydrogenation step [14,33].

In conclusion, according to the catalytic screening, the activities of the synthesized catalysts follow the order: NiMo(5/15)/FAC > NiW(5/15)/Zeo > CoMo(6/15)/FAC > NiW(5/15)/FAC trimetallic catalysts. Given its higher activity, the NiMo(5/15)/FAC catalyst was used for further studies.

2.3.2. Solvent Effect

The activity of NiMo(5/15)/FAC was evaluated under solvent-free conditions and using *n*-dodecane instead of *n*-hexane as solvent. *n*-hexane and *n*-dodecane were selected to compare hydrocarbon solvents with markedly different volatility and phase behavior. *n*-hexane, under the investigated conditions, is close to its critical region and can significantly influence mass transfer and hydrogen solubility. On the other hand, its high volatility contributes significantly to the autogenous pressure of the reactor. *n*-dodecane was included as a heavier and less volatile hydrocarbon solvent, which remains more closely associated with the liquid phase and provides a thermally stable and persistent liquid hydrocarbon medium. In addition, *n*-dodecane is widely used in the HDO reaction [37,73,84]. The two solvents may therefore generate different fluid densities, hydrogen solubilities, mass-transfer conditions and liquid-phase compositions. Their properties may also indirectly affect catalyst stability by influencing the accumulation of heavy intermediates and coke precursors. Finally, the solvent-free reaction may offer important process advantages, including elimination of solvent recovery, lower downstream separation costs and reduced

solvent consumption. The reactions were carried out at 320 °C, 40 bar H₂, 10 wt% catalyst and 6 h reaction time. The results of the experiments are shown in Figure 4.

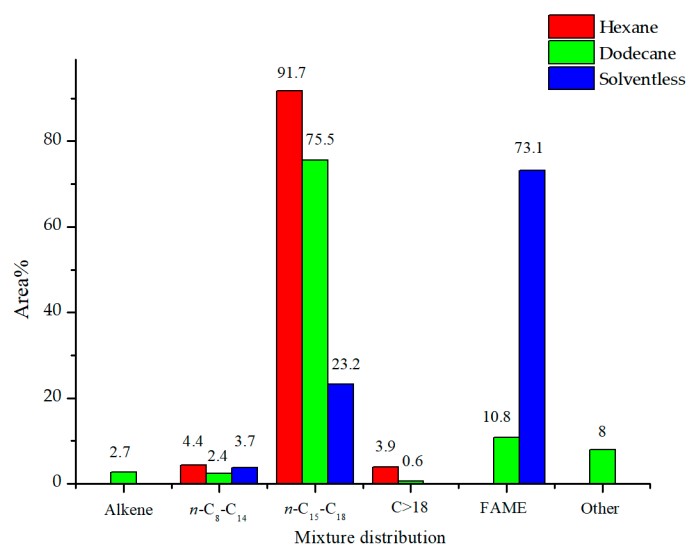


Figure 4. Effect of the solvent on the CDO reaction with NiMo(5/15)/FAC catalyst.

As shown in Figure 4, the reaction performed under solvent-free conditions did not give satisfactory results. The catalyst shows low activity, and the resulting biofuel contains high FAME content, 73.1%, indicating a large amount of unconverted oil. Conversely, the use of a solvent significantly enhances catalytic activity; however, 100% conversion was observed only when *n*-hexane was used. When *n*-dodecane was used, the reaction product contained 10.8% FAME and a green diesel fraction of 75.5%. In contrast, the reaction performed in *n*-hexane achieved complete conversion and produced 91.7% diesel-range hydrocarbons. The solvent did not significantly affect reaction pathway selectivity, since the catalyst showed an *S* value of 1.5 in *n*-hexane and 1.4 in *n*-dodecane. The higher activity observed in *n*-hexane can be correlated to the physical state of the solvent under the reaction conditions employed. *n*-hexane has a critical temperature of 234 °C and a critical pressure of 30 bar; therefore, under the investigated reaction temperature, it is above its critical temperature and may behave as a supercritical fluid [85]. In this state, the lower viscosity, enhanced diffusivity and improved phase contact of the medium may favor hydrogen availability at the catalyst surface and reduce gas–liquid mass-transfer limitations. Numerous studies have reported the beneficial effect of supercritical *n*-hexane in the CDO reaction [86–90]. Furthermore, the use of *n*-hexane results in easy work-up, since it can be easily separated from the reaction product via vacuum evaporation and reused in subsequent reactions, improving the overall sustainability of the process.

2.3.3. Feedstock Effect

The type of feedstock used in the reaction can influence both conversion and product distribution. In practical applications, oil selection is often governed by local availability and cost; therefore, an efficient catalyst should also be active with feedstocks of different origin and composition. To assess catalyst robustness, the performance of NiMo(5/15)/FAC was evaluated using different oils at the same reaction conditions used in catalyst screening. The FT-IR spectra and the GC-FID analysis of the OLP obtained with different oils are shown in Figure 5 and Table 5 respectively.

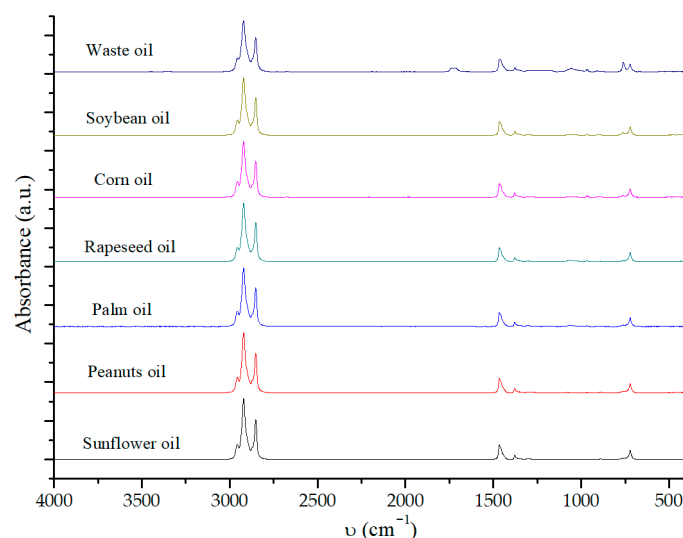


Figure 5. Effect of the feedstock on the CDO reaction with NiMo(5/15)/FAC catalyst.

Table 5. Distribution of reaction products and catalytic performance of NiMo(5/15)/FAC with different oils.

Entry ¹	Oil	Alkenes	<i>n</i> -C ₈ –C ₁₄	<i>n</i> -C ₁₅ –C ₁₈	C > 18	FAME	Other	S	X	OLP (wt%)	GD (wt%)
1	Sunflower	--	4.4	91.7	3.9	--	--	1.5	100.0	72.2	66.1
2	Peanut	0.4	4.4	87.4	7.7	--	--	3.5	100.0	88.0	77.0
3	Palm	2.9	6.3	89.5	1.4	--	--	3.2	100.0	82.2	73.6
4	Rapeseed	7.5	5.2	85.2	2.1	--	--	3.9	100.0	84.7	72.0
5	Corn	5.6	5.0	87.5	1.8	--	--	3.4	100.0	80.6	69.8
6	Soybean	5.2	8.5	83.4	2.8	--	--	3.8	100.0	79.1	65.3
7	Waste cooking oil	20.6	11.3	42.0	4.3	16.1	5.7	1.7	83.0	77.9	32.8

¹ All the reactions were performed at 320 °C, 40 bar H₂, 20 g of *n*-hexane, 2 g of feedstock, 0.200 g of NiMo(5/15)/FAC and 6 h of reaction time.

Similar FT-IR spectra were obtained for all the edible oils used, indicating almost complete conversion. Waste cooking oil was the only exception, as its spectrum still showed a weak absorption band in the 1750–1710 cm^{−1} region, suggesting residual carbonyl-containing compounds and therefore lower conversion.

Focusing on product distribution, Table 5 shows that complete conversion is achieved in all cases except for waste oil. With the waste oil, a conversion of 83% was obtained, producing a biofuel with a significant amount of methyl esters (16.1%). Lower conversion when using waste cooking oil is not unusual. Kim et al. reported a decrease in conversion when waste cooking oil was used instead of fresh soybean oil (41.8% vs. 91.0%) and attributed this behavior to the presence of degradation products and other contaminants accumulated during the previous use of the oil, which may promote catalyst deactivation [91]. Similar observations were reported by Ding et al. [92]. In addition, the lower deoxygenation activity may also be associated with the high concentration of unsaturated hydrocarbons in the products, which accounted for approximately 20%. Unsaturated compounds can decrease catalyst activity by adsorbing on the catalyst surface. They can also undergo oligomerization and polymerization reactions, promoting coke formation and consequently causing active-site coverage and pore blockage [93,94].

Sunflower oil gave the highest content of hydrocarbons in the diesel range (91.7%). However, it also showed the lowest OLP yield, 72.2 wt%, and therefore a lower green diesel yield, 66.1 wt%. The lower OLP yield may be related to the catalyst selectivity. In the case of sunflower oil, the catalyst showed an S value of 1.5, while for the other oils, the S value was generally higher than 3. An S value of 1.5 indicates a greater relative contribution of

DCO/DCO₂ pathways, which result in lower carbon retention in the liquid hydrocarbon fraction than HDO [33,95]. However, the markedly lower OLP yield cannot be explained only by the S value and suggests that additional volatile products may have formed. During the deoxygenation of vegetable oils, CO and CO₂ are generated through DCO and DCO₂, while methane, ethane and other light hydrocarbons may also form through secondary reactions such as methanation, cracking, hydrogenolysis and decarbonylation [33,96]. For all the oils used, *n*-C₁₅–C₁₈ hydrocarbon contents higher than 80% were observed; however, some differences can be noted. The highest biofuel yield was obtained with peanut oil (88.0%), but this reaction also produced the highest content of C > 18 hydrocarbons. The higher concentration of long-chain hydrocarbons is related to the feedstock composition, since peanut oil has a relatively high content of long-chain fatty acids, 5.8%, as reported in Table 1. When palm oil was used, no remarkable differences were observed in terms of green diesel yield and OLP yield. However, palm oil is rich in palmitic acid, and the resulting biofuel results in high *n*-C₁₆ hydrocarbon contents (29.8%). A high hexadecane amount is beneficial for green diesel production because it increases the cetane number (the maximum value of cetane number is 100 and is attributed to pure hexadecane).

2.3.4. Recycling Tests and Regeneration of the Catalyst

Catalyst efficiency is also related to its stability over successive reaction cycles. Therefore, the stability of NiMo(5/15)/FAC was assessed through recycling tests performed at 320 °C, 40 bar H₂, 10 wt% catalyst and 6 h reaction time. In the first run, 20 g of *n*-hexane, 2 g of sunflower oil and 0.2 g of catalyst were used. In the subsequent reactions, the amounts of reactants and solvent were adjusted according to the amount of recovered catalyst. Specifically, the oil/catalyst ratio was maintained at 10:1, while the *n*-hexane/oil ratio was kept at 10:1. At the end of each reaction, the catalyst was recovered, dried overnight under vacuum and reused in the subsequent reaction without further treatment. The results obtained in the recycling tests are shown in Figure 6.

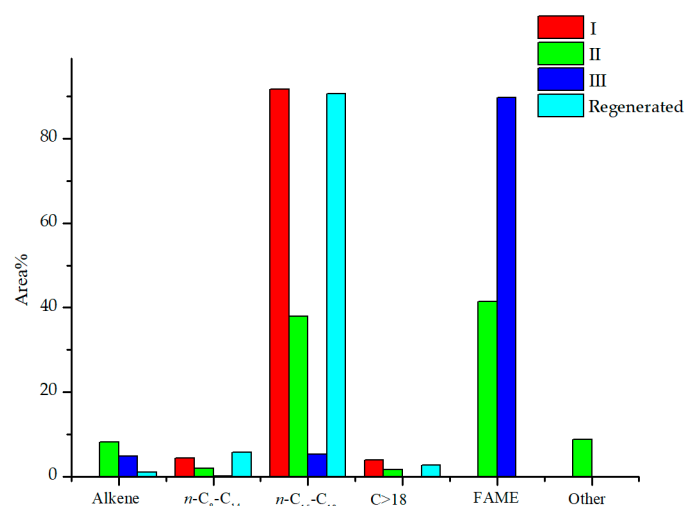


Figure 6. Hydrocarbon distribution over three reaction cycles and after catalyst regeneration.

Unfortunately, the catalyst quickly loses its activity; in the second reaction cycle, it loses about 50% of its activity, leading to a drop in *n*-C₁₅–C₁₈ content from 91.7% to 37.9% and, consequently, in high FAME content (41.5%). At the third reaction cycle, the catalyst completely loses its activity, resulting in a biofuel consisting mainly of FAME (89.7%), of which 85.1% is methyl stearate. This loss of activity was consequently reflected in the conversion degree, OLP yield, and green diesel yield (Table 6).

Table 6. Catalyst activity in the recycling tests.

Entry ¹	Cycle	S	X	OLP (wt%)	GD (wt%)
1	I	1.5	100.0	72.2	66.1
2	II	0.7	61.1	92.7	28.5
3	III	0.5	19.7	89.5	4.5
4	Catalyst regenerated	3.8	100.0	78.9	69.9

¹ All the reactions were performed at 320 °C, 40 bar H₂, sunflower oil:*n*-hexane = 1:10, NiMo/FAC; sunflower oil 10 wt% and 6 h of reaction time.

The results reported in Table 6 show a marked loss of catalytic activity over successive reaction cycles. Conversion decreased from 100% in the first cycle to 19.7% in the third, while the green diesel yield dropped from 66.1 to 4.5 wt%. Typically, catalyst deactivation can be related to three main causes: active metal leaching, active metal sintering, and coke formation, which may cover active sites and reduce catalytic activity [79,93,97–100]. ICP-MS analysis of the spent catalyst, discussed in Section 2.4.1, did not reveal any relevant loss of Ni, while Mo content significantly decreased, from 11.7 wt% in the fresh catalyst to 7.7 wt% in the spent catalyst. This evidence could indicate that the decline in catalytic activity may be partially related to Mo leaching. Furthermore, after the third reaction cycle, the mass of the recovered catalyst was higher than the mass before the reaction. This finding suggests the accumulation of carbonaceous deposits on the catalyst. To verify this hypothesis, the spent material was calcined at 400 °C for 3 h and subsequently reduced before being tested again. The reactant quantities were adjusted according to the amount of catalyst recovered after regeneration. In this case, reduction was carried out in batches at 320 °C under 40 bar H₂ for 8 h. After regeneration, the catalyst recovered its initial activity, achieving 100% conversion and producing a fully hydrocarbon biofuel containing 90.6% diesel-range hydrocarbons. These findings are consistent with a significant contribution of carbonaceous deposition to catalyst deactivation; however, the simultaneous decrease in Mo content indicates that metal leaching may also have contributed.

2.4. Characterization of NiMo(5/15)/FAC Catalyst

After catalyst screening, the physicochemical properties of the NiMo(5/15)/FAC catalyst were investigated using several characterization techniques. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the elemental composition. Fourier-transform infrared spectroscopy (FT-IR) provided information on surface functional groups and chemical bonds, while X-ray diffraction (XRD) was employed to identify the crystalline phases present in the material. Finally, nitrogen adsorption–desorption analysis, evaluated using the BET and BJH methods, was used to determine the specific surface area, pore volume and pore-size distribution. The results obtained from these analyses are discussed in detail in the following sections.

2.4.1. ICP-MS Elemental Analysis

ICP-MS analysis was performed on HCl-treated FAC support and on NiMo(5/15)/FAC to evaluate the actual metal loading impregnated onto FAC. In addition, elemental composition analysis was also carried out on spent NiMo(5/15)/FAC to investigate metal leaching after the deoxygenation reaction; in this case, only Ni and Mo contents were evaluated. Table 7 reports the data obtained after ICP-MS analysis.

FAC are an aluminosilicate material; therefore, it is not surprising that ICP-MS analysis shows 35 wt% Si and 16 wt% Al for the FAC support. The analysis detected 4.4 wt% of Ni and 11.7 wt% of Mo in the NiMo(5/15)/FAC catalyst, confirming the loading of the selected metals. The experimental Ni/Mo molar ratio is slightly higher than the theoretical one, mainly because of the lower Mo content compared with the nominal amount used

in the synthesis. In addition, lower Si and Al contents were observed in the catalyst than in the original FAC support. This decrease is related to the incorporation of Ni and Mo, which contributes to the total mass of the catalyst. In the spent catalysts, the ICP-MS revealed that the Ni content of the catalyst remained essentially unchanged, whereas a noticeable decrease in the Mo content was observed. However, as discussed in Section 2.3.4, Mo leaching does not appear to be the main cause of catalyst deactivation, since the NiMo(5/15)/FAC catalyst recovered most of its initial activity after the regeneration step.

Table 7. Data obtained after ICP-MS elemental analysis.

Catalyst	Si (wt%)	Al (wt%)	Ni (wt%)	Mo (wt%)	Nominal (Ni/Mo) ¹	Experimental (Ni/Mo) ¹
FAC	35 ± 2	16.0 ± 0.4	-	-	-	-
NiMo(5/15)/FAC	20 ± 1	13.0 ± 0.3	4.4 ± 0.1	11.7 ± 0.3	0.54	0.62
NiMo(5/15)/FAC post test ²	-	-	4.2 ± 0.1	7.5 ± 0.3		0.92

¹ Molar ratio. ² For this analysis, only Ni and Mo contents were evaluated.

2.4.2. FT-IR Analysis

FT-IR spectroscopy was performed to evaluate the surface characteristics of the catalyst. The spectrum of the calcined NiMo(5/15)/FAC sample was compared with that of the original FAC support to identify surface changes associated with Ni and Mo impregnation, as shown in Figure 7.

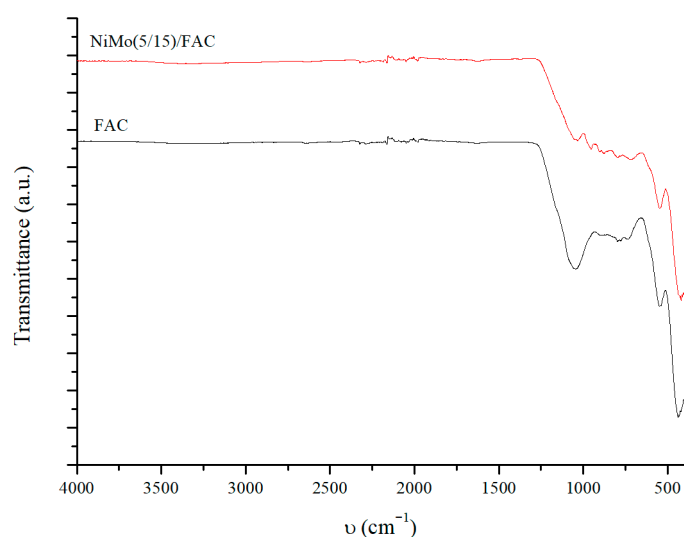


Figure 7. FT-IR spectra of FAC and NiMo(5/15)/FAC (calcined) (spectra recorded in ATR mode and with solids in powder form).

The FAC spectrum shows a band centered at 1055 cm^{−1}, which is related to Si-O-Si asymmetric stretching. The symmetric stretching and bending vibrations of Si-O-Si are attributed to the bands centered at 798 cm^{−1} and 450 cm^{−1} respectively. In addition, asymmetric Si-O-Al stretching is also observed as a weak band at 545 cm^{−1} [101–103]. After the Ni and Mo impregnation, the bands related to Si- and Al-containing phases showed a decrease in intensity, which can be associated with the deposition of NiO and MoO₃ on the support rather than inside the pores. In addition, new bands were observed in the FT-IR of the NiMo(5/15)/FAC catalyst. In particular, the signals at 957 cm^{−1} and 880 cm^{−1} were assigned to the asymmetric and symmetric stretching vibrations of the Mo=O bond, respectively, confirming the presence of MoO₃ [104]. No absorption bands related to NiO were detected. The relatively low NiO loading, together with the overlap with the more

intense bands of the aluminosilicate matrix, may account for the absence of clearly resolved NiO signals.

2.4.3. XRD Analysis

To identify the crystalline phases present in both the catalyst and support, XRD analysis of FAC and NiMo(5/15)/FAC (in reduced state) was carried out. The XRD diffractograms recorded are reported in Figure 8.

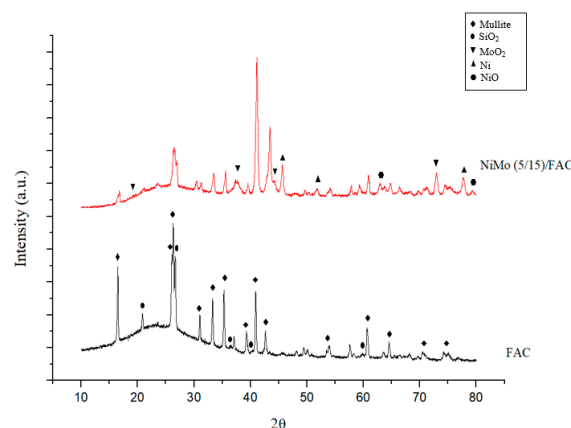


Figure 8. XRD diffractogram of FAC support and NiMo(5/15)/FAC catalyst.

The diffraction pattern of the FAC support shows the typical reflections associated with mullite ($2\theta = 16.4^\circ, 26^\circ, 26.2^\circ, 30.5^\circ, 33.5^\circ, 35.5^\circ, 40.9^\circ$, and 60.8°). This aluminosilicate phase is commonly found in fly ash cenospheres [102,105]. In addition to mullite, quartz is another characteristic phase of FAC and can be present in both crystalline and amorphous forms. The crystalline phase gives reflections at 2θ of $20.9^\circ, 26.6^\circ, 36.5^\circ, 50.1^\circ$, and 59.93° , whereas the amorphous contribution is indicated by the broad background feature extending from approximately 10° to 40° and centered near 25° [106,107]. After synthesis, the reduced NiMo(5/15)/FAC catalyst still exhibits the reflections of the support; however, with lower intensity, indicating a partial loss of crystallinity after metal incorporation. Additional reflections appear in the reduced sample and can be associated with the deposited Ni- and Mo-containing phases. Under the reduction conditions employed, MoO_3 is expected to be converted into MoO_2 , whose characteristic reflections occur at $2\theta = 21.2^\circ, 26.8^\circ$, and 44.3° . In this case, the reflections at 21.2° and 44.3° were observed, while the reflection at 26.8° was not clearly distinguishable, most likely because of overlap with the intense reflections of the support [108,109]. The peaks observed at approximately $45^\circ, 51^\circ$, and 76° are assigned to metallic Ni, confirming the reduction of part of the nickel phase [110,111]. Reflections attributable to NiO are also present at $2\theta = 37.2^\circ, 43.3^\circ, 62.8^\circ$, and 75.5° . Their occurrence may indicate that nickel reduction was incomplete or that partial oxidation took place after the reduction treatment [110].

2.4.4. FAC Particle Size Distribution and BET-BJH Analysis

Particle size analysis showed a decrease in the Sauter mean diameter from $95.6 \mu\text{m}$ for the raw FAC to $87.0 \mu\text{m}$ for the HCl-washed FAC, likely due to the removal of soluble surface components and limited fragmentation during stirring. The resulting particle size should favor particle dispersion and external surface accessibility in the stirred 100 mL batch reactor and may also reduce intraparticle diffusion distances.

Focusing on porosimetry analysis, both the FAC support and the reduced catalyst display adsorption profiles mainly associated with type II isotherms, according to the IUPAC classification, which are generally observed for non-porous or macroporous material. The

reduced NiMo(5/15)/FAC catalyst shows a more pronounced hysteresis loop, suggesting a type IV isotherm, characteristic of mesoporous material (Figure 9) [112]. An increase in the amount of adsorbed nitrogen is observed after impregnation of FAC with Ni and Mo, suggesting a change in the adsorption properties of the material. In both cases, an H3-type hysteresis loop is observed, which is generally associated with capillary condensation in mesopores, often arising from slit-shaped pores or interparticle voids. The loop is narrow for the FAC support, whereas it extends over a broader relative-pressure range for NiMo(5/15)/FAC, suggesting a wider distribution of mesopores after metal deposition, in agreement with the observation of Deka and Bhattacharyya [113].

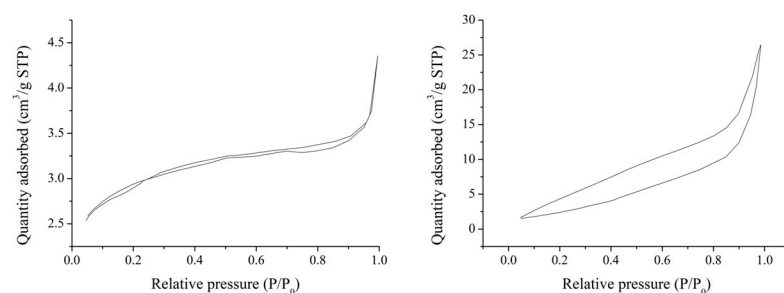


Figure 9. Left side: FAC adsorption isotherm. Right side: NiMo(5/15)/FAC R. adsorption isotherm.

Table 8 shows the textural properties of the materials. After Ni and Mo impregnation, the BET surface area slightly decreased from 10.10 to 8.40 m²/g. Conversely, the BJH pore volume increased from 0.004 cm³/g to 0.05 cm³/g, and the average pore diameter increased from 1.6 nm to 23.3 nm. These findings suggest that Ni and Mo impregnation modified the porous structure of the FAC support, possibly increasing the contribution of mesoporosity or improving the accessibility of existing pores [56,110].

Table 8. Textural properties of FAC and NiMo/FAC R.

Sample	BET Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	Average Pore Diameter (4V/S _{BET})
FAC	10.10 ± 0.01	0.004 ± 0.001	1.59 ± 0.4
NiMo(5/15)/FAC R.	8.4 ± 0.01	0.049 ± 0.010	23.33 ± 4.76

3. Discussion

This study demonstrates that fly ash cenospheres (FAC), a waste residue of coal combustion, can be effectively used as support for catalysts used in the deoxygenation of vegetable oils. FAC were used either directly, after acid treatment, or converted into zeolitic materials. Both supports were employed to synthesize several transition-metal-based catalysts, including bimetallic and trimetallic systems. Catalytic screening was carried out in a batch reactor at 320 °C and 40 bar of H₂, using sunflower oil as feedstock and *n*-hexane as solvent. Among the tested catalysts, the NiMo(5/5)/FAC showed the best catalytic activity, achieving 100% conversion and producing a biofuel rich in diesel-range hydrocarbons (*n*-C₁₅–C₁₈ = 91.7%). Some of the zeolite-supported catalysts also showed appreciable activity. In particular, NiW(5/15)/Zeo reached high conversion and produced a considerable amount of diesel-range hydrocarbons, suggesting that converting FAC into zeolite can also represent an effective strategy for catalyst synthesis. Future work will focus on optimizing zeolite synthesis from FAC in order to tune their composition, pore structure and acidity, making them more effective supports. After catalyst screening, NiMo(5/15)/FAC, which proved to be the most active catalyst, was further investigated. Its activity was evaluated using *n*-dodecane as solvent and under solvent-free conditions.

Its robustness was also investigated by varying the feedstock, and its stability was tested over consecutive reaction cycles.

The solvent-free reaction did not give satisfactory results, as conversion was very low, and the reaction product was rich in FAME. Under the conditions adopted here, the absence of solvent may have limited hydrogen transfer between the gas phase, the oil and the catalyst surface. Further optimization of the operating conditions, metal dispersion, and support properties will therefore be required to obtain satisfactory activity under solvent-free conditions. In addition, one possible strategy could be to perform the reaction in a semi-batch or continuous-flow reactor. These configurations allow continuous hydrogen supply and provide better control of product residence time, limiting side-reactions leading to heavy compounds that can deactivate the catalyst. Some studies report that continuous processes can enhance conversion and stability [96,114,115].

NiMo(5/15)/FAC was active with all the fresh vegetable oils examined. However, waste cooking oil gave a lower conversion of 83% and produced larger amounts of unsaturated hydrocarbons and FAME. The poorer performance observed with waste cooking oil may be related to the impurities present in the waste oil after use that could compete for active sites, hinder mass transfer, or promote carbon deposition. In addition, the high concentration of unsaturated hydrocarbons detected in the mixture can contribute to deactivating the catalyst by promoting oligomerization and polymerization reactions [91,116]. Nevertheless, the catalysts show appreciable activity, offering a starting point for further studies with waste oils. Combining waste-oil upgrading with the valorization of FAC would be particularly attractive from a circular-economy perspective.

The recycling tests revealed a rapid loss of activity, with conversion decreasing to 61.1% in the second cycle. This deactivation was mainly attributed to coke deposition, which is one of the most common causes of catalyst deactivation during the deoxygenation and hydrotreatment of biomass-derived feedstocks. Coke may cover the metal phase, block pore entrances and alter the surface properties of the support [117,118]. Therefore, further studies should focus on improving catalyst formulation to mitigate this phenomenon. Different activation treatments, the addition of other promoters or variation of the metal loading could increase accessible porosity, improve metal dispersion, reducibility, and stability of the active phase [119,120]. In addition, the use of continuous reactors could help remove by-products that deactivate the catalyst, thus preserving catalytic activity. Nevertheless, the regeneration step performed on the spent catalyst fully restored the catalytic activity of the NiMo(5/15)/FAC catalyst, providing further evidence of the effectiveness of this catalytic system.

Despite the limitations reported, NiMo(5/15)/FAC represents a promising starting point for the development of catalysts based on very abundant waste. The system offers several potential advantages over other catalyst families used in vegetable-oil deoxygenation, especially from the perspective of sustainability. Conventional sulfided NiMo and CoMo catalysts are highly active, but maintaining their activity requires the addition of sulfur-containing compounds, which may contaminate the product and increase process complexity [34,35]. In contrast, activation by reduction overcomes this limitation.

Noble-metal catalysts based on Pd, Pt, or Ru are generally highly effective for hydrogenation and deoxygenation and do not require sulfidation. However, their high cost and limited availability can affect the economic sustainability of large-scale applications [121–123]. NiMo/FAC instead combines non-noble metals with support obtained from industrial waste.

Transition-metal carbides, nitrides, and phosphides have also been investigated as alternatives to sulfided catalysts. These catalysts can exhibit high activity, in some cases comparable to that of noble-metal catalysts. However, their synthesis often requires high

temperatures, reactive atmospheres and specific precursors, resulting in more demanding preparation procedures than the synthetic route used for NiMo(5/15)/FAC [120,124].

Table 9 presents a comparison between the catalyst developed in this study and other catalysts reported in the literature, particularly NiMo-based catalysts. The selection of literature studies was based on work conducted in batch reactors using real feedstock.

Table 9. Comparison of NiMo(5/15)/FAC with selected literature.

Catalyst	Feedstock	Best-Performing Conditions	Main Catalytic Result	Reference
NiMo(5/15)/FAC	Sunflower oil	320 °C, 40 bar H ₂ , 6 h, <i>n</i> -hexane as solvent, 10 wt% catalyst	100% conversion; 91.7% <i>n</i> -C ₁₅ –C ₁₈ ; 72.2 wt% OLP	This work
NiMoAl LDH	Rapeseed oil	320 °C, 40 bar H ₂ , 6 h, <i>n</i> -hexane as solvent, 10 wt% catalyst	100% conversion; 92.0% <i>n</i> -C ₁₅ –C ₁₈ ; 72.9 wt% OLP	[41]
Commercial sulfided NiMo/γ-Al ₂ O ₃	Soybean oil	400 °C, 9.2 MPa H ₂ , 2 h, cat/oil = 0.044–0.088, solvent-free	91.9–92.9% conversion; 76.8% <i>n</i> -C ₁₅ –C ₁₈	[15]
NiMo–alumina composite	Karanja oil	340 °C, 30 bar H ₂ , 4 h, <i>n</i> -dodecane as solvent, 20 wt% catalyst	100% conversion; Product distribution: 13% < C ₁₈ , 75% C ₁₈ , 12% > C ₁₈ alkanes	[125]
NiMo/ZSM-5	Palmitic acid	300 °C, 35 bar H ₂ , 4 h, <i>n</i> -dodecane as solvent, 25 wt% catalyst	99% conversion; 70% of C > 12 hydrocarbon	[73]
5 wt% Pd/C	Castor oil FAME	Batch, 340 °C, 10 bar initial H ₂ , 6 h, <i>n</i> -hexane as solvent, 10 wt% catalyst	100% conversion; 95% total alkane yield; 95% C ₁₇ –C ₁₈	[90]
Sulfided Re–Ni–Mo/γ-Al ₂ O ₃	PFAD, refined palm stearin, refined palm olein	370 °C, 4 MPa, 1 h, solvent-free, ca. 2.2 wt% catalyst	100% conversion; diesel yield = 72.5% from PFAD, 69.7% from RPS, and 69.5% from RPO	[126]
Mo ₂ C/AC	FAME, soybean oil, rubber seed oil	370 °C, 3.0 MPa H ₂ , 3 h, <i>n</i> -hexane as solvent, 10 wt% catalyst	FAME: 100.0% conversion, 85% <i>n</i> -C ₁₅ –C ₁₈ ; Soybean: 100% conversion, 74% <i>n</i> -C ₁₅ –C ₁₈ ; Rubber seed oil: 97% conversion 78% <i>n</i> -C ₁₅ –C ₁₈	[127]

Although a direct comparison is not straightforward because of differences in feedstock composition, reactor configuration, catalyst loading, solvent and product-yield definitions, the results show that the NiMo(5/15)/FAC catalyst shows activity comparable to that of many catalysts reported in the literature. In some cases, higher hydrocarbon yields or higher C₁₅–C₁₈ selectivity have been reported, especially for optimized noble-metal catalysts or conventional sulfided systems. However, these catalysts often require more expensive active phases, higher reaction temperatures or pressures, or more controlled catalyst activation procedures. In this context, the NiMo(5/15)/FAC formulation represents an effective alternative, since it combines high conversion and high diesel-range hydrocarbon selectivity with the use of a waste-derived aluminosilicate support. The comparison therefore suggests that the NiMo(5/15)/FAC catalyst is a promising candidate for green diesel production, which combines a simple synthesis route, the valorization of waste

material, and good catalytic activity. It shows 100% conversion with a product containing 91.7% of hydrocarbon in the diesel fraction at 320 °C, 40 bar of H₂ and for 6 h of reaction time. In addition, it maintains activity for all the edible oil feedstocks and recovers its activity after an easy regeneration step. However, further studies are planned to improve the catalytic performance and reduce the limitations observed during reuse.

4. Materials and Methods

4.1. Catalyst Synthesis

4.1.1. Acid Treatment of Raw FAC

Before being used as a support, the cenospheres were subjected to acid treatment to remove impurities. The acid treatment was performed following the procedure proposed by Sutarno et al. [60]. A total of 10 g of FAC were suspended in a 5 M HCl (37%, Carlo Erba, Milano, Italy) aqueous solution, and the suspension was vigorously stirred under reflux for 1 h. After cooling, the solid was separated by vacuum filtration and washed with distilled water until neutral pH was reached. The resulting solid was then dried in an oven at 110 °C overnight and stored before being used for catalyst synthesis.

4.1.2. FAC Zeolitization Process

FAC-derived zeolites were synthesized using the alkali fusion method described in the literature [60]. A total of 10 g of HCl-treated FAC and 12 g of NaOH (NaOH pearl 97%, Lancaster, MA, USA), corresponding to a FAC:NaOH weight ratio of 1:1.2, were mixed in a crucible and ground to uniform the powder. The mixture was then transferred into a muffle furnace and melted at 550 °C (5 °C/min) for 1 h. After cooling, the fused product was ground, transferred with 100 mL of distilled H₂O in a Teflon beaker and stirred overnight at room temperature. The slurry was then hydrothermally treated at 110 °C for 72 h. The resulting solid was vacuum-filtrated, washed with distilled H₂O until neutral and finally dried at 110 °C overnight. The obtained zeolites were collected in a bottle and subsequently used as a support for the synthesis of catalysts.

4.1.3. FAC- and Zeolite-Supported Catalyst Synthesis

The chemicals used for the synthesis of the bimetallic and trimetallic catalysts supported on FAC and zeolite were as follows: Ni(NO₃)₂·6H₂O (98%, Alfa Aesar, Heysham, Lancashire, UK), Co(NO₃)₂·6H₂O (98.0–102.0%, Alfa Aesar, Heysham, Lancashire, UK), (NH₄)₆Mo₇O₂₄·4H₂O (99%, Alfa Aesar, Heysham, Lancashire, UK), (NH₄)₆W₁₂O₃₉·xH₂O (≥85% WO₃ basis (gravimetric), Alfa Aesar, Heysham, Lancashire, UK), Ce(NO₃)₃·6H₂O (99.5%, Alfa Aesar, Heysham, Lancashire, UK), Ca(CH₃CO₂)₂·H₂O (≥99.0%, Sigma-Aldrich, Darmstadt, Germany), La(CH₃CO₂)₃·xH₂O (99.9%, Sigma Aldrich, Darmstadt, Germany).

As an example of catalyst synthesis, the following section reports the synthesis of NiMo(5/15)/FAC catalyst; the same synthesis approach can be extended to all the other bi-metallic and trimetallic catalysts supported on FAC and zeolite.

Ni(NO₃)₂·6H₂O (0.529 g, 1.8 mmol) and (NH₄)₆Mo₇O₂₄·4H₂O (0.501 g, 0.4 mmol) were dissolved in 10 mL of distilled water in a 50 mL round-bottom flask. When trimetallic catalysts were synthesized, Ce(NO₃)₃·6H₂O, La(CH₃CO₂)₃·xH₂O or Ca(CH₃CO₂)₂·H₂O was also added. After the salts were completely dissolved, 2.174 g of HCl-treated FAC (or zeolite) were added, and the suspension was stirred for 3 h at room temperature. The amount of metal salts used was calculated to obtain a catalyst with nominal content of 5 wt% of NiO and 15 wt% of MoO₃ (the quantities of metal salts used for the synthesis of the other catalysts were also selected to obtain the desired nominal metal oxide contents). Afterwards, water was removed using a rotary evaporator (50 °C, 40 torr), and the resulting solid was dried overnight at 110 °C. Once dried, the material was recovered and placed

in a crucible for the calcination process. In the case of NiMo(5/15)/FAC, calcination was carried out at 400 °C (5 °C/min) for 4 h. For the reduction step, the catalyst was placed in a tubular reactor and treated under a 10:90% H₂/N₂ gas flow (20Nml/min of H₂ and 180Nml/min of N₂). The reduction temperature and duration were selected by monitoring H₂ consumption using an ABB gas analyzer. In the case of NiMo(5/15)/FAC, the reduction was performed at 700 °C (5 °C/min) for 3 h. At the end of the reduction process, the reactor was cooled to room temperature under a flow of 200 Nml/min of N₂ to prevent oxidation. Once the reactor had reached room temperature, the catalyst was recovered in a flask and stored under an argon atmosphere to avoid possible oxidation. The same procedure was carried out for all the other FAC- and zeolite-supported catalysts. The same H₂ and N₂ flow rates were used, whereas the reduction temperatures and time varied according to their H₂ consumption. All the information concerning the synthesis of the FAC- and zeolite-supported catalysts is reported in Tables 2 and 3.

4.2. Oil and Catalyst Characterization

4.2.1. Oil Characterization

Edible sunflower oil (SO), rapeseed oil (RO), corn oil (CO), peanut oil (PAO) and palm oil (PO) were purchased from local traders, while soybean oil (SBO) was purchased from Merck (soybean oil is a dietary source of long-chain triglycerides and other lipids); all the oils were used for the CDO reaction without any previous treatment. The fatty acid composition of the used oils was investigated after transesterification reaction according to the AOAC Official Method 969.33 [59].

A total of 0.350 g of oil was placed in a 50 mL flask and refluxed for 10 min with 2 N NaOH methanolic solution (NaOH pearl 97%, Lancaster, MA, USA; CH₃OH anhydrous, 99.8%, Merck, Darmstadt, Germany) After 10 min, a 10 wt% BF₃ methanolic solution (Boron trifluoride-methanol solution ~10% (~1.3 M), for GC derivatization, LiChropur™, Supelco®, Bellefonte, PA, USA) was added and kept under reflux for 1 min. Finally, 5 mL of *n*-hexane (99% Carlo Erba, Milano, Italy) was added and, once the solution reached room temperature, a NaCl (99.7%, Merck, Darmstadt, Germany) saturated solution was transferred into the flask, and the separation of the organic phase from the aqueous phase occurred. An aliquot of 1.3 mL of the organic layer was collected and transferred to a vial containing anhydrous Na₂SO₄ (≥99%, Carlo Erba, Milano, Italy) to remove residual water.

Then, 1 µL of the resulting solution was manually injected into a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Waltham, MA, USA) coupled with a flame ionization detector (FID) and with a Supelco® SP-2380 capillary column (30 m × 0.25 mm × 25 µm, stationary phase = Poly(90% biscyanopropyl/10% cyanopropylphenyl siloxane)). The chromatographic analysis was performed under isothermal conditions at 180 °C for 25 min. Hydrogen was used as the carrier gas, with a split flow of 25 mL/min, while both the injector and detector temperatures were set at 250 °C. The chromatographic peaks were identified by comparison with a commercial FAME reference mixture containing C₁₄–C₂₂ methyl esters (F.A.M.E. Mix, Supelco, Bellefonte, PA, USA). Data acquisition and chromatogram processing were performed using Xcalibur™ software (software version 4.0, Thermo Fisher Scientific, Waltham, MA, USA). The results of the oil characterization are shown in Table 1.

4.2.2. Catalyst Characterization

The NiMo(5/15)/FAC catalyst was characterized to identify the physicochemical characteristics of the material. The elemental composition of the catalyst was investigated with an iCAP™ TQe ICP-MS (Thermo Fisher Scientific, Waltham, MA, USA) with a triple quadrupole MS detector. Hydrogen peroxide solution (≥30%) for ultra-trace analysis

(Sigma-Aldrich, Darmstadt, Germany) and suprapure[®] nitric acid (65%) (Merck, Darmstadt, Germany) were used in sample digestion. Instrument control and data processing were performed using Qtegra[™] Intelligent Scientific Data Solution software (software version 2.14, Thermo Fisher Scientific, Waltham, MA, USA).

FT-IR spectra were recorded in attenuated total reflectance mode using a PerkinElmer Spectrum instrument (Spectrum Two[™] model). The collected spectra were processed with Spectrum software (PerkinElmer Spectrum version 10.03.06). Each spectrum was obtained by averaging 16 scans at a resolution of 4 cm^{−1}.

X-Ray diffraction measurements were performed with a PANalytical X'Pert PRO diffractometer (PANalytical, Almelo, The Netherlands) operating in Bragg–Brentano geometry and equipped with Cu irradiation ($K\alpha_1 = 1.540598 \text{ \AA}$; $K\alpha_2 = 1.544426 \text{ \AA}$; $K\beta = 1.39225 \text{ \AA}$). The X'Pert HighScore Plus software (version software 5.2, Malvern Panalytical, Almelo, The Netherlands) was used to manage the diffractograms obtained with angle 2θ ranging from 10° to 80°. Crystalline phases were identified by ICDD and ICSD reference databases.

The particle-size distributions of the raw FAC and HCl-washed fly ash cenospheres were determined using a Mastersizer 2000 laser diffraction particle-size analyzer (Malvern Instruments, Malvern, Worcestershire, UK). Representative samples were obtained by manual coning and quartering and subsequently dispersed in distilled water and placed in a beaker. The particle retention index was set to 2.08, and the absorption index was set to 1. The data collected from these detectors were processed using Mie's mathematical model.

N₂ physisorption analysis was carried out using a NOVA 1200e Surface Area & Pore Size Analyzer from Quanta-chrome Instruments (Boynton Beach, FL, USA). BET and BJH calculations were performed with Nova Station software (version 11.0). Before the analysis, approximately 100–200 mg of sample was degassed under high vacuum at 200 °C (10 °C/min) for 8 h.

4.3. Set-Up for Catalytic Deoxygenation Reaction and Product Analysis

4.3.1. Catalytic Deoxygenation Reaction

A 100 mL stainless steel autoclave reactor (4590 Micro Bench Top Reactor, equipped with magnetic drives and a 4848 Reactor Controller, Parr Instrument Company, Moline, IL, USA) was used to carry out the deoxygenation experiments. The reactor was initially loaded with 2 g of oil, 20 g of *n*-hexane ($\geq 95\%$, HPLC grade, Sigma-Aldrich, Darmstadt, Germany) and catalyst-to-oil weight ratio = 10 wt% (0.200 g of catalyst). To ensure an oxygen-free atmosphere, the reactor was flushed three times with N₂ and three times with H₂ before the reaction. The deoxygenation tests were performed with 40 bar partial pressure of H₂ (at room temperature), 320 °C, constant stirring and for 6 h (the reaction started when the reactor reached 320 °C). After this, the reactor was cooled and washed with CHCl₃ and *n*-hexane to recover further product. The catalyst was filtered under vacuum by washing with *n*-hexane and CHCl₃ and then dried overnight in a vacuum oven. The reaction mixture was recovered in a previously weighed flask, concentrated using a rotary evaporator, dried under vacuum, and finally re-weighed to assess the yield of the liquid organic product (OLP).

4.3.2. Green Diesel Analysis

To qualitatively assess the degree of conversion of the reaction, a small portion of OLP was analyzed with the same FT-IR ATR used for catalyst characterization (4 scans and 4 cm^{−1}). The degree of conversion can be evaluated by observing the peak at 1745 cm^{−1}, corresponding to the stretching vibration of the carbonyl ester; in addition, the appearance of a peak at 1710 cm^{−1} indicates the occurrence of free fatty acids (peak related to C=O vibration of free fatty acids) [66]. The conversion degree and compound distribution in

the mixture were evaluated by GC-FID and GC-MS analysis. However, before analysis, a small portion of OLP (350 mg) was transesterified to convert residual oil into methyl esters that are easier to analyze by GC-FID and GC-MS; transesterification was performed in the same way as described for oil characterization [59]. A total of 1 μ L of the transesterified mixture was injected into an Agilent 7820A GC gas chromatograph (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a flame ionization detector (FID) and an HP-5 19091J-413 capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 μ m, stationary phase = (5-Phenyl)-methylpolysiloxane). The heat run involves a steady state at 50 $^{\circ}$ C for 5 min, then the temperature is increased to 280 $^{\circ}$ C with a ramp of 10 $^{\circ}$ C/min, and finally this temperature is maintained for 7 min. The FID was set at 300 $^{\circ}$ C while the injector was set at 270 $^{\circ}$ C, and the eluent gas was H_2 . Chromatographic runs were elaborated with the software OpenLAB CDS (version C.01.10, Agilent Technologies, Inc., Santa Clara, CA, USA), and the identification of chromatographic peaks corresponding to *n*-alkanes was performed by comparison with a C_7 – C_{40} linear saturated alkane standard solution (C_7 – C_{40} Saturated Alkanes Standard, 1000 μ g/mL each component, Supelco, Bellefonte, PA, USA). In addition, to evaluate the presence of FAME isomers, the transesterified sample was injected into the same GC-FID used for oil characterization, and the chromatographic run was performed with the same thermic program used for oil characterization. Unidentified chromatographic peaks were identified with a GC-MS system (GC model: Varian Star 3400cx, MS model: Varian Saturn 2000) equipped with an HP-5 column (30 m $\times$ 0.25 μ m $\times$ 0.25 mm stationary phase = 5% phenyl-methyl polysiloxane). The sample was prepared by diluting 20 μ L of the transesterified mixture in 1.5 mL of *n*-hexane; 1 μ L of this sample was injected into the GC-MS. The analysis was carried out over a 35 min run, starting with a 5 min hold at 50 $^{\circ}$ C, followed by a temperature increase of 5 $^{\circ}$ C/min up to 280 $^{\circ}$ C, and ending with a 5 min hold at 280 $^{\circ}$ C. Helium was used as the carrier gas. The trap and injector temperatures were both set at 250 $^{\circ}$ C. Data elaboration was performed with Varian MS Workstation (version 6.9). Unknown peaks were identified by comparing their mass spectrum with a library (NIST). Additionally, Kovats retention indices were calculated to further validate the unidentified compounds. The parameters investigated to evaluate the catalyst's activity are presented in Section 2.3.

5. Conclusions

Coal fly ash cenospheres (FAC) were successfully employed as direct supports or as precursors to zeolitic supports for the synthesis of several catalysts for the deoxygenation of vegetable oil. Among the catalysts tested, NiMo(5/15)/FAC demonstrates the best catalytic activity, achieving 100% conversion and producing a biofuel with 91.7% of *n*- C_{15} – C_{18} , corresponding to a green diesel yield of 66.1 wt%. Furthermore, zeolitic catalysts show acceptable activity in the deoxygenation reaction. The NiMo(5/15)/FAC was tested in solvent-free conditions, with different feedstocks and in multiple reaction cycles. The results obtained show that the catalyst is not active without *n*-hexane as solvent but demonstrates high activity for all the used feedstocks. However, catalytic activity drops to 83% conversion when waste cooking oil was used. The catalyst rapidly lost its activity during the recycling test, but regeneration of the spent catalyst through calcination completely restored catalyst activity; after regeneration, the catalyst reached 100% conversion with a green diesel yield of 69.9 wt%. Based on the results obtained, it can be stated that NiMo(5/15)/FAC represents a promising waste-derived catalyst formulation and a useful starting point for further optimization.

FAC-based catalysts can enhance the sustainability of the overall process by valorizing waste products that would otherwise require disposal. Future work will focus on opti-

mizing FAC-based catalysts and the process setup, evaluating their catalytic activity in continuous-flow reactors and under solvent-free conditions.

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