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Partial Hydrogenation of Soybean and Waste Cooking Oil Biodiesel over Recyclable-Polymer-Supported Pd and Ni Nanoparticles

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Abstract: Biodiesel obtained through the transesterification in methanol of vegetable oils, such as soybean oil (SO) and waste cooking oil (WCO), cannot be used as a biofuel for automotive applications due to the presence of polyunsaturated fatty esters, which have a detrimental effect on oxidation stability (OS). A method of upgrading this material is the catalytic partial hydrogenation of the fatty acid methyl ester (FAME) mixture. The target molecule of the partial hydrogenation reaction is monounsaturated methyl oleate (C18:1), which represents a good compromise between OS and the cold filter plugging point (CFPP) value, which becomes too high if the biodiesel consists of unsaturated fatty esters only. In the present work, polymer-supported palladium (*Pd-pol*) and nickel (*Ni-pol*) nanoparticles were separately tested as catalysts for upgrading SO and WCO biodiesels under mild conditions (room temperature for *Pd-pol* and T = 100 °C for *Ni-pol*) using dihydrogen (p = 10 bar) as the reductant. Both catalysts were obtained through co-polymerization of the metal containing monomer M(AAEMA)$_2$ (M = Pd, Ni; AEEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate)) with co-monomers (ethyl methacrylate for Pd and *N*,*N*-dimethylacrilamide for Ni) and cross-linkers (ethylene glycol dimethacrylate for Pd and *N*,*N'*-methylene bis-acrylamide for Ni), followed by reduction. The *Pd-pol* system became very active in the hydrogenation of C=C double bonds, but poorly selective towards the desirable C18:1 product. The *Ni-pol* catalyst was less active than *Pd-pol*, but very selective towards the mono-unsaturated product. Recyclability tests demonstrated that the Ni-based system retained its activity and selectivity with both the SO and WCO substrates for at least five subsequent runs, thus representing an opportunity for waste biomass valorization.

Keywords: biodiesel; waste cooking oil; partial hydrogenation; palladium; nickel; nanoparticles; recyclable catalysts

1. Introduction

Using biomass instead of fossil sources for producing fuel for automotive applications is essential for reducing greenhouse gas emissions and for overcoming the increasing depletion of petrol supplies [1], which has become significant for the European Union due to recent geopolitical events. In the framework of employing renewable supplies, many fuel companies have so far used fatty acid methyl esters (FAMEs) derived from natural feedstock, such as edible oils, especially palm oil, as a biodiesel for transport purposes [2]. After the ban on palm oil imposed by the European Union until 2030, manufacturing companies have been looking for sustainable alternatives for producing biodiesel. An appealing substitute for palm oil as a feedstock for generating biodiesel is

waste cooking oil (WCO) [3,4]. For example, every year, in Italy, about 280,000 tons of waste vegetable oils from alimentary industries are produced and converting them into valuable sources of energy could eliminate the cost of their disposal [5]. FAMEs obtained through the transesterification of methanol from WCO [6] or any vegetable oil [7] cannot be utilized as a fuel for automotive applications due to the presence of many polyunsaturated compounds, such as linolenic and linoleic methyl esters [8]. A method for making the obtained FAME mixture suitable for use as a biofuel is catalytic partial hydrogenation [9,10], i.e., the conversion of poly-unsaturated fatty esters into mono-unsaturated ones (Scheme 1). In fact, mono-unsaturated fatty esters represent the best compromise between oxidation stability and the fluidity parameters that a high-quality biofuel should possess [10]. The total hydrogenation of C18 esters into methyl stearate should be avoided, as it yields an ester that is solid at room temperature; *cis* to *trans* isomerization of the unsaturated fatty esters should also be prevented, because it adversely affects the pour point of the fuel mixture (Scheme 1).
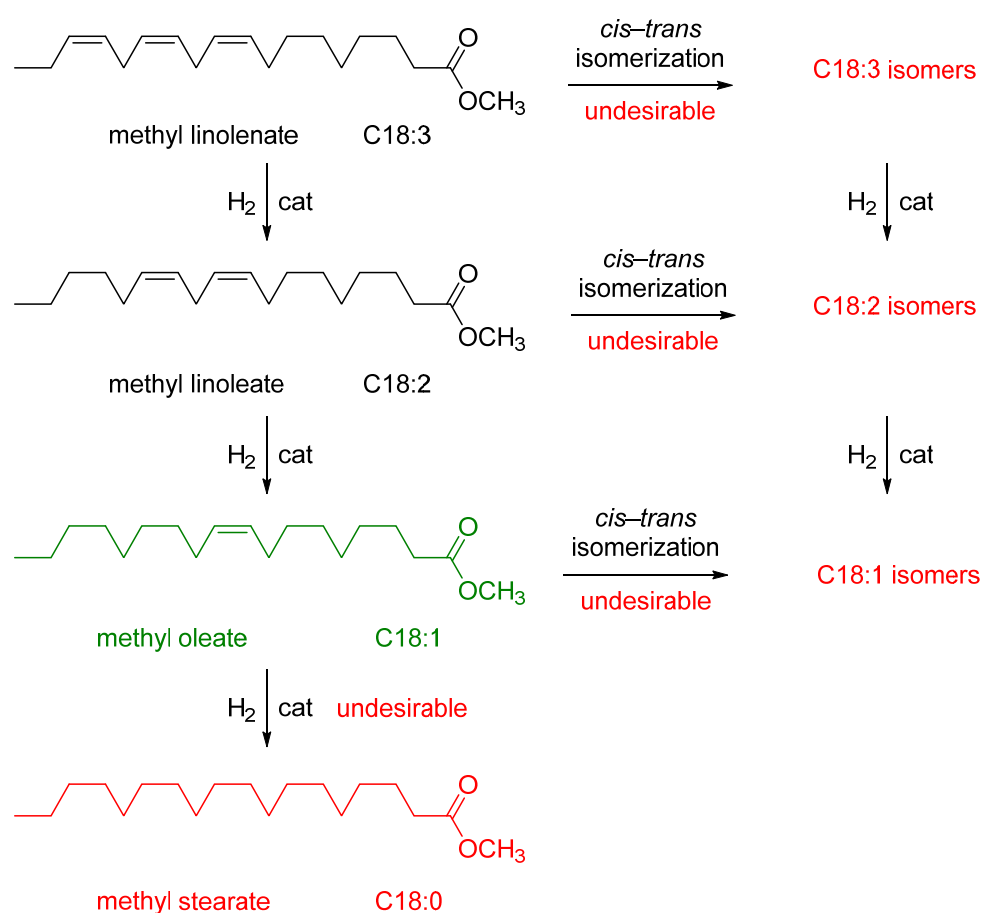
Scheme 1. Hydrogenation of C18 FAMEs.

In recent years, many studies on upgrading FAMEs have been reported [11,12], most of them being catalytic hydrogenation [13,14] or transfer hydrogenation systems [15,16], based on metals such as Ni [17–19], Pd [20–22], Pt [23], or Ir [24]. However, it should be underlined that WCO feedstocks contain several unwanted species, such as free fatty acids (FFAs) and water (not present in fresh vegetable oils), posing serious concerns for the stability of the catalytic systems used for upgrading biofuels [3]. For this reason, developing convenient and effective procedures for converting WCO into a valuable biofuel is still a challenging goal. Recently, we scrutinized new catalytic systems based on polymer-supported palladium (*Pd-pol*) and nickel (*Ni-pol*) nanoparticles in the hydrogenation [25,26] and catalytic transfer hydrogenation [27,28] of several substrates under sustainable conditions, even in aqueous media [29]. Both catalysts were obtained through the co-polymerization of the

metal containing monomer M(AAEMA)$_2$ (M = Pd, Ni; AEEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate)) with co-monomers (ethyl methacrylate for Pd and *N,N*-dimethylacrilamide for Ni) and cross-linkers (ethylene glycol dimethacrylate for Pd and *N,N'*-methylene bis-acrylamide for Ni), followed by reduction. The amphiphilic nature of the supported catalysts and the stability of the latter in the presence of water, air, and free fatty acids (FFAs) prompted us to test the activity of *Pd-pol* and *Ni-pol* as catalysts for the partial hydrogenation of WCO biodiesel, as well as of soybean oil (SO) FAMEs. The main aim of the present work is to highlight the differences between palladium and nickel nanoparticles supported on similar organic matrices in the partial hydrogenation of FAMEs, with the goal of proposing a new catalytic system for upgrading the biodiesel. The results showed that the palladium catalyst appeared to be more active than the nickel counterpart in the hydrogenation reaction, but less selective towards the C18:1 desirable product. Thus, the biodiesel obtained with *Ni-pol* upgrading displayed better fuel parameters with respect to the one achieved with the *Pd-pol* treatment. Both catalytic systems were recyclable and performed in the same way with either the SO or WCO feedstock.
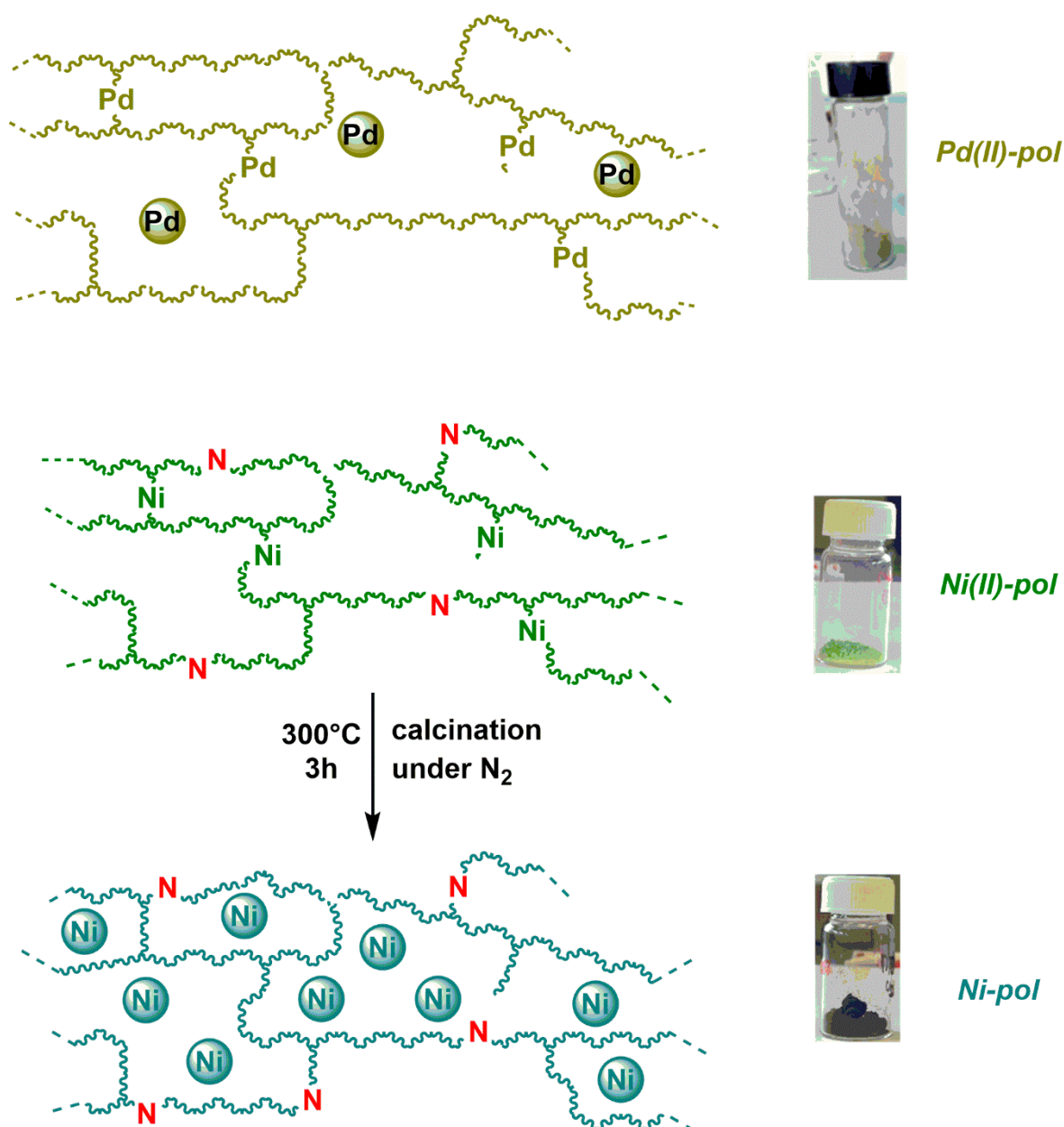
2. Results and Discussion

2.1. Catalysts

As mentioned in the previous paragraph, both Pd- and Ni-based catalysts were prepared by co-polymerizing the metal containing monomers M(AAEMA)$_2$ (AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate; M = Pd, Ni) with suitable co-monomers (ethyl methacrylate (EMA) for Pd and *N,N*-dimethylacrilamide (DMA) for Ni) and cross-linkers (ethylene glycol dimethacrylate (EGDMA) for Pd and *N,N'*-methylene bis-acrylamide (MBAA) for Ni; Scheme 2), thus obtaining porous amphiphilic resins supporting homogeneously dispersed M(II) centers (*Pd(II)-pol* and *Ni(II)-pol*) [30].

Both *Pd(II)-pol* and *Ni(II)-pol* needed to be reduced to afford polymer-supported metal(0) nanoparticles, which constitute the catalytically active species for hydrogenation reactions. As the reduction of Pd centers from the +2 to 0 oxidation state is very easy, the transformation of *Pd(II)-pol* into polymer-supported Pd(0) nanoparticles (referred to as *Pd-pol*) occurred smoothly during the first cycle of FAMEs hydrogenation. In the case of *Ni(II)-pol*, no reduction from Ni(II) to Ni(0) could be achieved under the reaction conditions used in the FAMEs hydrogenation; therefore, the polymer-supported Ni(0) nanoparticles (referred to as *Ni-pol*) were obtained through the calcination of *Ni(II)-pol* at 300 °C under nitrogen flow. The full characterization of *Pd(II)-pol, Pd-pol, Ni(II)-pol,* and *Ni-pol* has been reported in the literature [31,32]. Figure 1 summarizes the structure of *Pd(II)-pol, Ni(II)-pol,* and *Ni-pol* [31,32], showing the following: (i) *Pd(II)-pol* is a resin containing mainly Pd(II) species and few Pd nanoparticles (mean size diameter of 9 nm) formed during thermal polymerization (Figure S5); (ii) *Ni(II)-pol* does not bear any metal nanoparticles; and (iii) *Ni-pol* is composed of acrylamide-based polymer-supported Ni nanoparticles with a diameter ranging from 10 to 37 nm, except for Ni nanocubes and ellypsoids (Figure S3). As we previously observed that *Pd(II)-pol* quickly transformed into *Pd-pol* under reductive reaction conditions [29], in the following, *Pd-pol* will be referred to as both *Pd(II)-pol* and *Pd-pol*, without distinctions.

The reason for the choice of methacrylic and acrylamide supports for Pd and Ni catalysts, respectively, stemmed from the necessity to enhance the catalytic activity of Ni and to "moderate" the catalytic activity of Pd towards C=C hydrogenation. In fact, as a noble metal, Pd is very active in hydrogenation reactions of carbon−carbon double bonds, and therefore needs a support able to stabilize itself in the form of nanoparticles, preventing aggregations and avoiding the formation of unactive Pd black. At the same time, given that the goal of the present work is the partial hydrogenation of FAMEs, Pd did not require a matrix that enhanced its activity. In fact, a too high activity in the catalytic hydrogenation could be detrimental for selectivity towards the formation of mono-alkene products. On the contrary, as Ni is much less active than Pd in hydrogenations, it needs a support suitable to improve its catalytic activity. Many studies have been reported on

the importance of N-doping earth abundant metal-based catalysts for increasing their catalytic activity [33,34]. In fact, N impurities dispersed onto the support can achieve the following: (a) promote electron transfer towards the metal centers; (b) co-adjuvate the solvent assisted heterolytic splitting of dihydrogen, due to Brønsted basic properties of the nitrogen sites; and (c) facilitate the formation of metal−hydride intermediates in the catalytic pathway. The acrylamide matrix of *Ni-pol* contains several nitrogen centers, even after calcination, and for this reason, acrylamide *Ni-pol* has been found much more active than its methacrylic analogous in the hydrogenation of nitroarenes [35]. On the basis of all of the reported considerations, no partial hydrogenation tests were performed by cross-switching the organic supports between Ni- and Pd-based catalysts.

Scheme 2. Synthesis of *Pd(II)-pol* and *Ni(II)-pol*.

Figure 1. Schematization of *Pd(II)-pol*, *Ni(II)-pol*, and *Ni-pol* structures.

2.2. Fatty Acid Methyl Esters (FAMEs)

Commercial soybean oil (SO) and waste cooking oil (WCO) were analyzed after transesterification in methanol, and the resulting FAMEs compositions are reported in Figure 2.

SO and WCO have a similar FAMEs composition (Figure 2), being rich in polyunsaturated methyl esters, such as C18:2 (methyl linoleate, 48.2–46.9%) and C18:3 (methyl linolenate, 4.8–5.8%), which should be converted into the more valuable monounsaturated C18:1 product, avoiding the further formation of C18:0 methyl stearate, which is present in raw SO and WCO FAMEs in a low amount (5.8–6.8%), except for methyl palmitate (C16:0, 9.8–10.9%) and a negligible quantity of methyl arachidate (C20:0, 0.3%). The biodiesel upgrading aims at converting C18:3 and C18:2 starting esters into C18:1 methyl oleate (*cis* configuration), trying to prevent the formation of methyl elaidate (C18:1, *trans* configuration), which has a melting point higher than its *cis* isomer, with detrimental effects on the cold flow properties of the whole mixture. However, it has been demonstrated that

biodiesel enriched with the *trans*-C18:1 isomer has better lubricity features than FAMEs mixture containing C18:1 species in only a *cis* configuration [36].
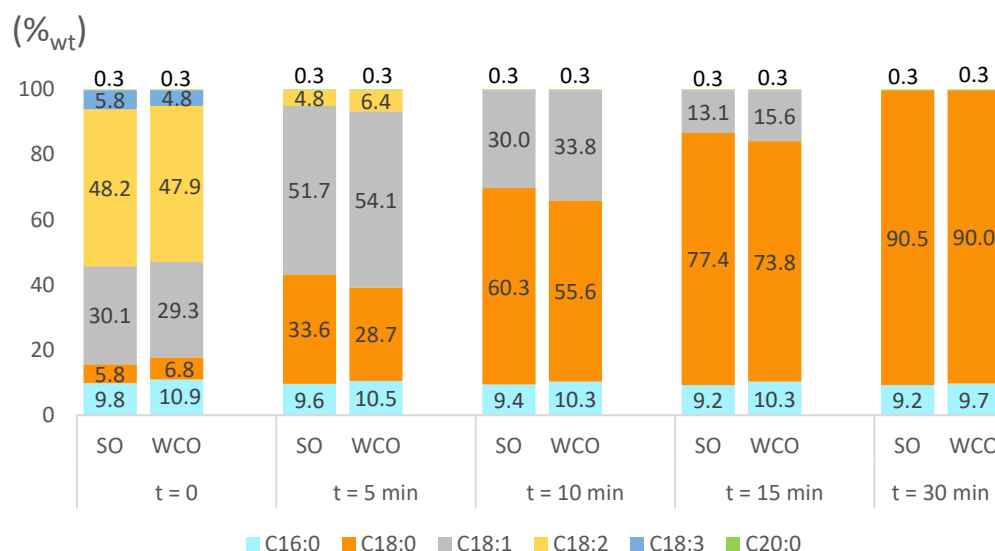
FAMEs composition (%$_{wt}$)
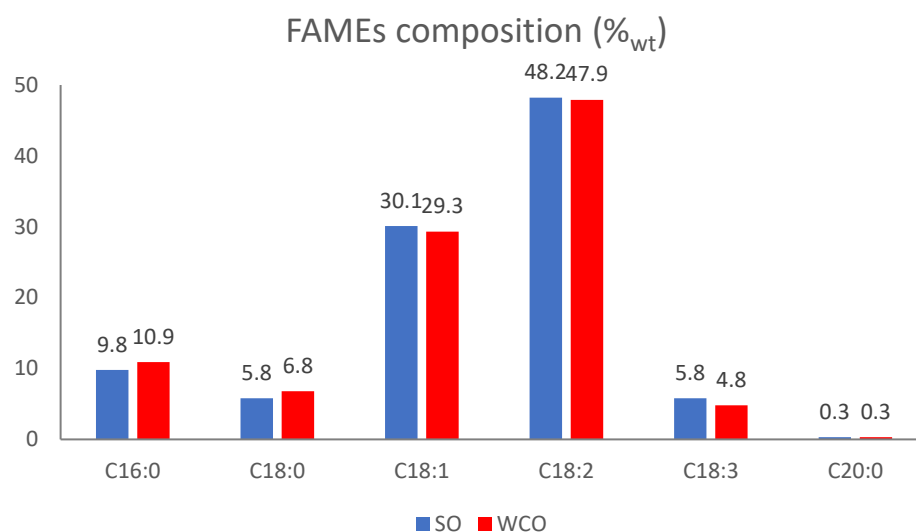
Figure 2. SO and WCO FAMEs composition (%$_{wt}$).

2.3. Catalytic Tests

2.3.1. Pd Catalyst

Based on the catalytic activity of *Pd-pol* in C=C double bond hydrogenation reactions [25], preliminary experiments were carried out using a metal/biodiesel molar ratio equal to 0.028, under 10 bar of dihydrogen in methanol at room temperature (RT). Figure 3 shows the composition of the SO and WCO FAMEs mixtures at different reaction times.


Figure 3. SO and WCO FAMEs compositions (%$_{wt}$) at different reaction times during hydrogenation with *Pd-pol* (2.8 mol% of Pd with respect to biodiesel (0.5 mmol, 125 mg), CH$_3$OH (5 mL), RT, under H$_2$ (10 bar)).

A close inspection of Figure 3 reveals that the *Pd-pol* catalytic system was able to convert almost quantitatively polyunsaturated fatty acid methyl esters (PFAMEs) into mono-unsaturated and even totally hydrogenated FAMEs after a 5-min reaction. In fact, at t = 5 min the most abundant compound in the biodiesels was C18:1 ester (51.7% and 54.1% for SO and WCO mixtures, respectively), and the quantity of methyl stearate was not

negligible (33.6% of SO and 28.7% of WCO) in both biooils. Notably, at t = 5 min, the C18:1 *cis/trans* molar ratio was equal to 0.83, suggesting that *Pd-pol* was able to simultaneously catalyze hydrogenation and alkene isomerization from a *cis* to *trans* configuration, considering that C18:3, C18:2, and C18:1 FAMEs in the starting SO and WCO biodiesels had only *cis* geometry for all C=C double bonds. After a 10-min reaction (Figure 3), the amounts of methyl stearate were 60.3% and 55.6% in SO and WCO, respectively, and both C18:3 and C18:2 compounds disappeared, while the C18:1 compound accounted for approximately one third of the biodiesel amount. At t = 10 min, the SO and WCO FAMEs compositions were too rich in saturated esters for use as an automotive biofuel because of the high value of the methyl stearate melting point (37 °C), which is detrimental for cold flow properties. As expected, the amounts of saturated products increased after a 15 min reaction, and both SO and WCO mixtures were totally hydrogenated after a 30 min reaction (Figure 3). These catalytic tests prompted us to consider 5 min as the best reaction time for obtaining the highest amount of desired C18:1 product, even if *cis* to *trans* isomerization could not be avoided. Remarkably, the *Pd-pol* performance was similar with both SO and WCO FAMEs, and no metal deactivation was observed when using waste oil as a starting material.

Recyclability tests were carried out on *Pd-pol* recovered after a 5 min reaction, which were re-used for further subsequent runs. Figure 4 shows the recyclability of *Pd-pol* catalytic system in the SO and WCO biodiesel partial hydrogenation.
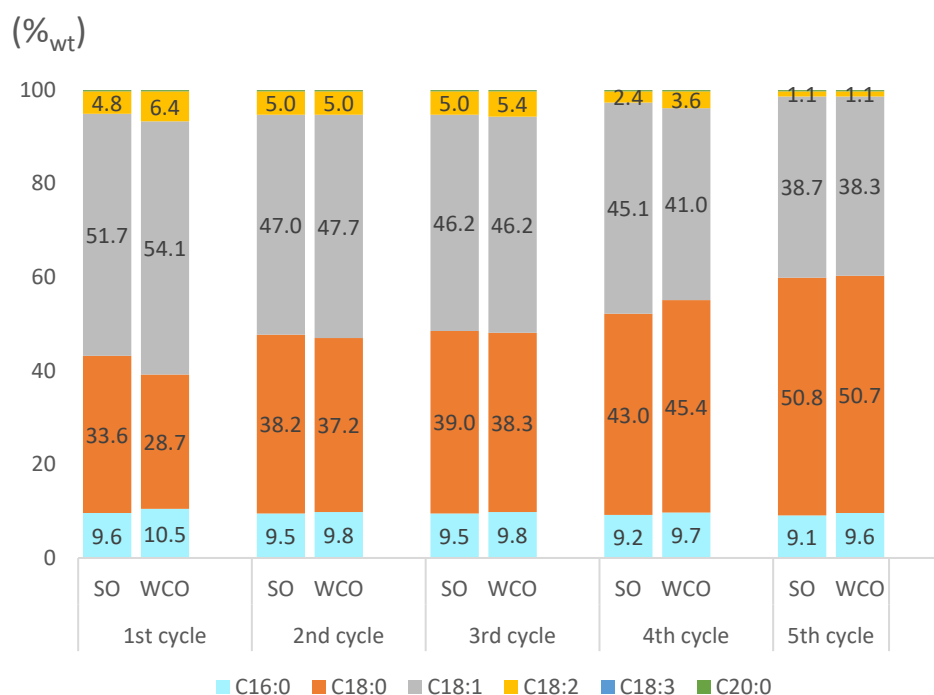

Figure 4. SO and WCO FAME composition (%$_{wt}$) after each of five subsequent runs with the same *Pd-pol* catalyst. Reaction conditions: SO or WCO biodiesels (125 mg), *Pd-pol* (0.014 mmol of Pd), CH$_3$OH (5 mL), RT, H$_2$ (10 bar), t = 5 min. In all histograms, the percent of C20:0 methyl ester is equal to 0.3%.

The *Pd-pol* catalyst was recyclable for at least five subsequent runs for both SO and WCO substrates, as unwanted C18:3 and C18:2 methyl esters were almost quantitively converted in a 5 min reaction, even in the fifth cycle with the same catalyst (Figure 4). Indeed, the catalytic activity of *Pd-pol* seemed to increase after recycling, enhancing the amount of undesirable totally hydrogenate methyl stearate product. In fact, the quantity of the latter passed from one third of the upgraded biodiesel obtained after the first run to half of the hydrogenated FAMEs mixtures recovered after the fifth cycle (Figure 4). Conversely, the selectivity towards the C18:1 product decreased with the increase in cycles, rendering the partially hydrogenated blends obtained after the second run not suitable as

automotive fuels, as the amounts of totally hydrogenated esters were too high for acceptable viscosity and cold flow features. In addition, the undesirable *cis/trans* isomerization was not negligible and the C18:1 methyl ester was mainly in the thermodynamically more stable *trans* configuration. Elemental analyses carried out on the recovered resin after five subsequent runs revealed that Pd leaching from the supported catalyst was negligible.

2.3.2. Ni Catalyst

The initial experiments of the hydrogenation of SO and WCO blends with *Ni-pol* were carried out using the same reaction conditions adopted for the *Pd-pol* partial hydrogenation system, but no C18:3, C18:2, and C18:1 conversion was observed after either the overnight reaction or after increasing the metal amount employed. Only by using a Ni/biodiesel molar ratio equal to 0.12 and by increasing the reaction temperature up to 100 °C (although the dihydrogen solubility in methanol is lower at higher temperature), was a high concentration of C18:1 methyl ester obtained after a 10 h reaction (68.7%$_{wt}$ for SO blend, Figure 5). Figure 5 shows the composition of SO mixtures analyzed at different reaction times under the above-mentioned conditions, revealing that the undesirable formation of a high amount of C18:0 methyl ester did not occur during the reaction (methyl stearate %$_{wt}$ passed from 5.8 in the pristine feedstock to 15.9 after 10 h reaction).

(%$_{wt}$)
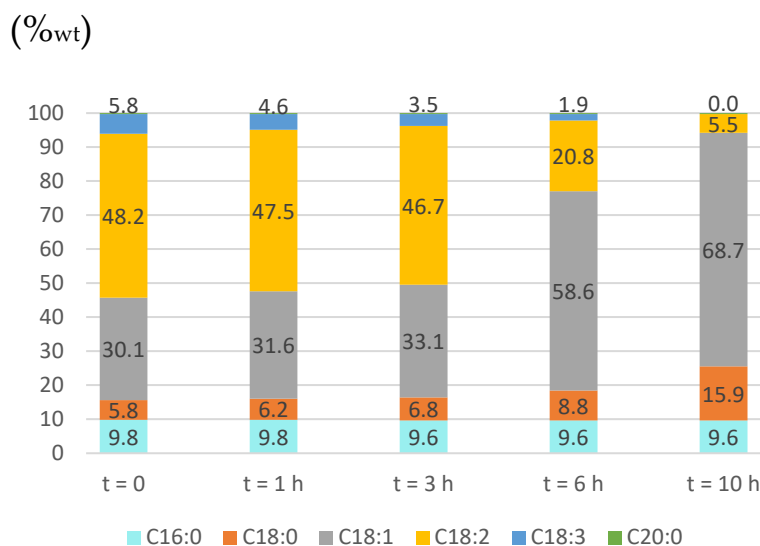
Figure 5. SO FAMEs composition (C) at different reaction times during hydrogenation with *Ni-pol* (0.059 mmol of Ni), biodiesel (0.5 mmol, 125 mg), and CH$_3$OH (5 mL), at 100 °C under H$_2$ (10 bar). In all of the histograms, the percent of C20:0 methyl ester is equal to 0.3%.

Once optimized for the reaction time of 10 h, recyclability tests were performed for both SO and WCO FAME feedstocks (Figure 6). The weight percent of C18:1 FAMEs was 68.7 in the SO blend and 68.1 in the WCO mixture (first cycle of Figure 6), with both values being higher than the ones obtained with the *Pd-pol* system. Clearly, *Pd-pol* was too active for the purposes of the present work, as it was poorly selective towards the mono hydrogenated product. On the contrary, *Ni-pol* was less active in the hydrogenation reaction than *Pd-pol*, thus requiring a longer reaction time and higher reaction temperature, but it turned out to have a higher selectivity towards the desirable C18:1 product. Recyclability tests performed on *Ni-pol* revealed that the catalyst could be re-used at least five times without losing its activity and selectivity towards the C18:1 product. Figure 6 shows the weight percent composition of the partially hydrogenated SO and WCO biodiesel after each of the five subsequent runs performed after recycling the Ni supported catalyst.
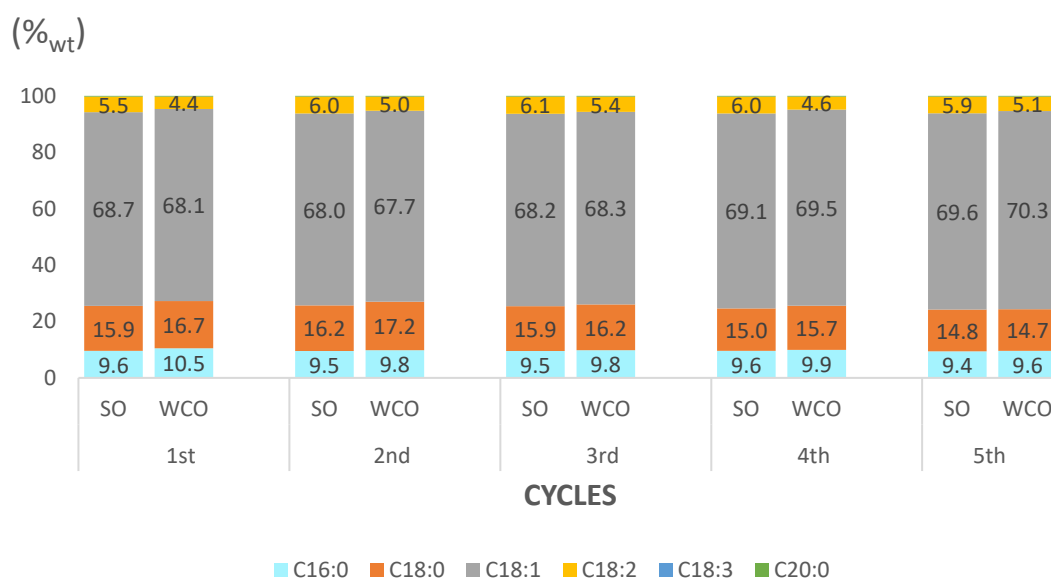
Figure 6. SO and WCO FAMEs compositions (%$_\text{wt}$) after each of the five subsequent runs with the same *Ni-pol* catalyst. Reaction conditions: SO or WCO biodiesels (125 mg), *Ni-pol* (0.059 mmol of Ni), and CH_3OH (5 mL), at 100 °C, H_2 (10 bar), and t = 10 h. In all of the histograms, the percent of C20:0 methyl ester is equal to 0.3%.

The compositions of partially hydrogenated blends were very similar for both SO and WCO starting materials in all of the cycles. The main compound present in the blends was always C18:1 methyl ester, the amount of which ranged from 68.0%$_\text{wt}$ to 70.3%$_\text{wt}$ (Figure 6). In addition, C18:3 methyl esters disappeared in the blends after partial hydrogenation, and small amounts (about 5%$_\text{wt}$) of the C18:2 compound was always detectable in all runs (Figure 6). The *Ni-pol* system appeared to retain its activity and selectivity over several recycles for both SO and WCO starting materials, although with some differences as discussed in the following. Elemental analyses carried out on the recovered resin after five subsequent runs revealed that Ni leaching from the supported catalyst was negligible.

2.3.3. Partially Hydrogenated Biodiesel Features

The main physical−chemical characteristics of the partially hydrogenated blends derived the quantity of the poly-unsaturated compounds and the value of the C18:1 *cis/trans* molar ratio from their composition. Unfortunately, during partial hydrogenation reactions, *cis* to *trans* isomerization occurred in both *Pd-pol* and *Ni-pol* catalytic systems, and a mixture of *cis* and *trans* C18:1 methyl isomer was invariably obtained in all blends. However, the *Ni-pol* catalytic system was less active towards *cis* to *trans* isomerization with respect to the *Pd-pol* catalyst. In fact, after the first run with *Ni-pol*, the *cis/trans* C18:1 molar ratio was 1.30 and 1.37 for the SO and WCO partially hydrogenated blends, respectively, indicating that the relative amount of methyl oleate was higher than that of methyl elaidate (first cycle in Figure 7). On the contrary, with *Pd-pol* catalytic system after the first run, the amount of *cis*-C18:1 was lower than the quantity of *trans*-C18:1, with a *cis/trans* molar ratio of 0.83 for both the SO and WCO partially hydrogenated FAMEs (1st cycle in Figure 7). However, the *cis/trans* molar ratio increased with the subsequent cycles for *Pd-pol* and decreased for *Ni-pol*. Figure 6 shows the C18:1 *cis/trans* molar ratio over five cycles for both *Pd-pol* and *Ni-pol* catalysts in SO and WCO biodiesels, indicating that for *Pd-pol* hydrogenated blends, the C18:1 methyl ester was mostly in the thermodynamically favoured *trans* configuration, while for the *Ni-pol* partially hydrogenated FAMEs, the *cis* configuration was prevalent over the *trans* one. Considering that the melting point of *cis*-C18:1 (−19.9 °C) was much lower than that of *trans*-C18:1 (10 °C), the isomerization of *cis*-C18:1 to *trans*-C18:1 should be avoided if the final mixture is addressed to cold regions. However, FAMEs enriched

by *trans*-C18:1 could be used as an automotive biofuel in warm countries [37], as they are characterized by excellent lubricating features [36].
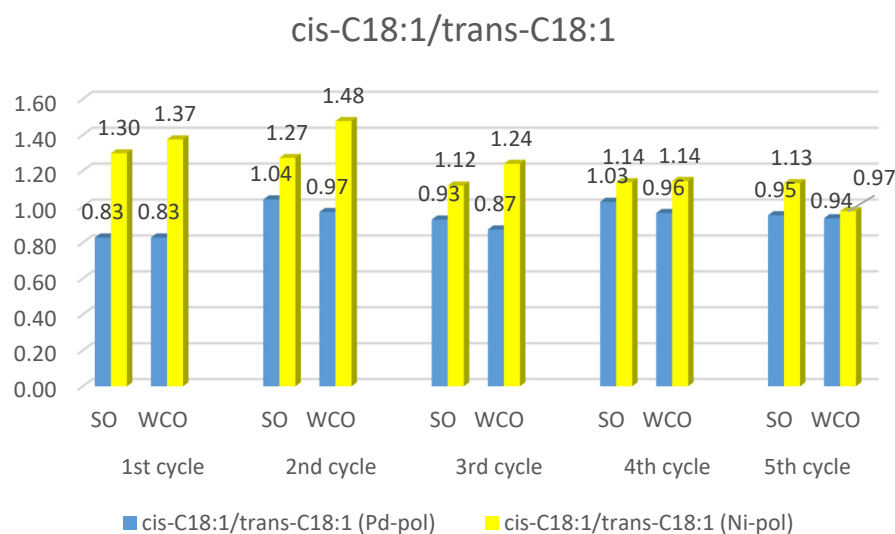
cis-C18:1/trans-C18:1

Figure 7. The *cis*-C18:1/*trans*-C18:1 molar ratio in SO and WCO partially hydrogenated biodiesel over five subsequent cycles with *Pd-pol* and *Ni-pol*.

Based on the FAMEs profiles of the upgraded mixture, some key parameters for defining biodiesel quality and properties, such as cold filter plugging point (CFPP), iodine value (IV), and oxidation stability (OS), could be predicted using the Biodiesel Analyzer© Software [38]. CFPP represents the lowest temperature at which fuel still flows through a specific filter, while IV is a measure of the unsaturation of biodiesel and is correlated to its stability, because the presence of many unsaturated features renders the material sensible to oxidation. Namely, IV indicates the mass in grams of iodine to be reacted with 100 g of a given oil by stoichiometric addition to double bonds. OS parameters depend on IV values, but there are many other factors not included in the iodine value affecting the stability of the bio-oil (such as the presence of saturated free fatty acids, length of the carbon chains, location of the double bonds, *cis* or *trans* configuration, and allylic double bonds that are more oxidable than not allylic ones). However, IV could give an idea about the stability of the biodiesel, and according to European laws, it should not be higher than 120 [39], while OS should exceed 8 h [40]. The best value for CFPP depends on the considered country and climate, and it always goes in the opposite direction with respect to the OS index. In fact, the CFPP value improves with increasing the number of double bonds in the FAMEs chain, whereas OS rises when the unsaturation number decreases.

Table 1 reports the CFPP, IV, and OS for SO and WCO diesel samples before the reaction and after each cycle of the partial hydrogenation test with *Pd-pol* and *Ni-pol*.

Table 1. CFPP, IV, and OS for SO and WCO diesel samples treated with *Pd-pol* or *Ni-pol* catalytic systems.

Biodiesel	Cat	Cycle	CFPP (°C)	IV (g/100 g)	OS (h)
	-	-	−3.3	130	4.7
	Pd-pol	1st	40.3	55.2	27.2
	Pd-pol	2nd	47.5	51.3	26.2
SO	*Pd-pol*	3rd	48.7	50.6	26.2
	Pd-pol	4th	54.9	44.9	51.7
	Pd-pol	5th	67.1	36.8	109.8

Table 1. *Cont.*

Biodiesel	Cat	Cycle	CFPP (°C)	IV (g/100 g)	OS (h)
	-	-	−1.4	126	4.8
	Pd-pol	1st	32.8	60.2	21.0
	Pd-pol	2nd	46.0	51.9	26.2
WCO	*Pd-pol*	3rd	47.7	51.3	24.4
	Pd-pol	4th	58.8	43.4	35.3
	Pd-pol	5th	67.1	36.4	109.8
	Ni-pol	1st	12.5	71.7	24.0
	Ni-pol	2nd	12.8	72.9	22.2
SO	*Ni-pol*	3rd	12.4	72.4	21.9
	Ni-pol	4th	11.0	73.0	22.2
	Ni-pol	5th	10.6	73.3	22.6
	Ni-pol	1st	14.0	69.2	29.4
	Ni-pol	2nd	14.6	69.9	26.1
WCO	*Ni-pol*	3rd	13.0	71.2	24.4
	Ni-pol	4th	12.2	70.8	28.2
	Ni-pol	5th	10.6	72.5	25.7

Before upgrading, SO and WCO FAMEs had good CFPP values (−3.3 °C and −1.4 °C, respectively, Table 1) and very bad IV and OS parameters, due to the high number of unsaturations in the material. By using Pd-pol as the upgrading catalyst, the IV and OS values improved, making the SO and WCO biodiesels very stable, but unfortunately the CFPP temperature increased significantly (ranging from 32.8 °C to 67.1 °C), rendering the partially hydrogenated mixtures unsuitable as a fuel for automotive applications (Table 1). Finally, SO and WCO *Ni-pol* partially hydrogenated FAMEs were stable enough (OS >> 8 h and IV << 120 g/100 g in all cases), but their CFPP values still exceeded the European limit (10 °C), ranging from 10.6 °C to 14.6 °C (Table 1). Thus, SO and WCO mixtures upgraded with the *Ni-pol* system could be useful as a biodiesel only in warm countries or by adding substances that could improve their fluidity [40].

2.4. Possible Explanation of the Different Performances of Pd-pol and Ni-pol Systems

By analyzing the data reported in previous paragraphs, it appears that *Pd-pol* is unsuitable for upgrading as a biodiesel, because it is too active in hydrogenation reactions and has detrimental effects on both selectivity towards C18:1 fatty acid esters as well as *cis* to *trans* isomerization. This high activity is not unexpected, as noble metals are very susceptible to form metal hydride intermediates, which in turn coordinate C=C double bonds to give additional hydrogen. Indeed, in some cases, palladium catalysts have been poisoned with sulfur or lead, aiming at lowering their activity in hydrogenation reactions, and thus improving their selectivity [13]. On the contrary, the increase of *Pd-pol* catalytic activity with the subsequent cycles seems to be quite uncommon, because, generally, a catalyst deactivates or at least retains its catalytic activity with reuse. As the increasing activation of *Pd-pol* with reuse is an occurrence never observed before in other *Pd-pol* catalyzed reactions taking few hours [25,27], we argue that in the present work, during the first run under dihydrogen, *Pd-pol* did not have enough time to transform the whole amount of palladium(II) species into Pd nanoparticles (NPs), because of the short reaction time (5 min). In fact, as the active species in these kinds of reactions are metal nanoparticles, an increased catalytic activity with the subsequent reuse might be associated with an increased density of Pd nanoparticles on the catalyst support. Indeed, *Pd-pol* was mainly constituted by Pd(II) centers prior to their use in catalysis, which were reduced to Pd NPs during hydrogenation under reaction conditions [25,26]. Given that the time of permanence of *Pd-pol* under dihydrogen became longer with reuse, more Pd(II) sites had the possibility to transform into Pd NPs, increasing the amount of catalytically active sites. To confirm this hypothesis, we employed *Pd-pol* recovered after five subsequent runs for an extra cycle

of partial hydrogenation, observing that the catalytic activity of the supported catalyst did not increase further (Figure 8). In fact, the quantity of C18:1 FAMEs was half of the hydrogenated mixtures recovered after both the fifth and sixth cycles, becoming most (70%wt *ca.*) of the blend after 10-min hydrogenation with the same catalyst when used six times (Figure 7), suggesting that after five runs (25 min under dihydrogen in total) *Pd-pol* was composed only of Pd NPs supported onto an organic matrix.
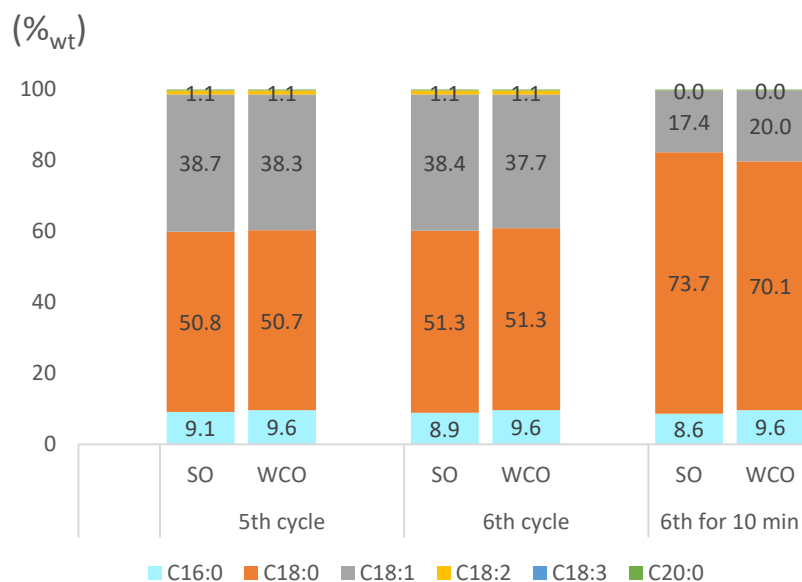
Figure 8. SO and WCO FAMEs compositions (%wt) after the fifth and the sixth runs with the same *Pd-pol* catalyst. Reaction conditions: SO or WCO biodiesels (125 mg), Pd-pol (0.014 mmol of Pd), and CH3OH (5 mL), at RT, H_2 (10 bar), and t = 5 min. The last two histograms refer to the sixth cycle over a 10-min reaction. In all of the histograms, the percent of C20:0 methyl ester is equal to 0.3%.

Ni-pol did not show the same high activity of *Pd-pol*, but it was more selective towards the formation of the desirable *cis*-C18:1 FAME than its palladium analogue (Figures 4, 6 and 7), because nickel nanoparticles have a lesser tendency to form metal hydrides. In addition, as expected, for the *Ni-pol* system, an increase in its catalytic activity with the subsequent re-use was not observed.

Regarding the *cis* to *trans* isomerization and the different performances of *Pd-pol* and *Ni-pol* catalytic systems towards it, it could be useful to recall the mechanism of the heterogeneous hydrogenation reaction. In fact, the catalytic cycle started with the interaction between the unsaturated C=C bond and the catalyst, followed by homolytic dihydrogen splitting into the atomic hydrogen bound to the catalyst (Figure 9). Then, a hydrogen attached to the substrate in a reversible step (a) (Figure 9), followed by the addition of a second hydrogen atom (step b), rendering the hydrogenation process irreversible (Figure 9). During the reversible step (a) (Figure 9), isomerization could occur, forming the thermodynamically more favourable *trans* isomer, which is less prone to be hydrogenated with respect to the *cis* geometric isomer, because the interaction between the double bond and the metal catalyst is sensitive to steric hindrance [10].
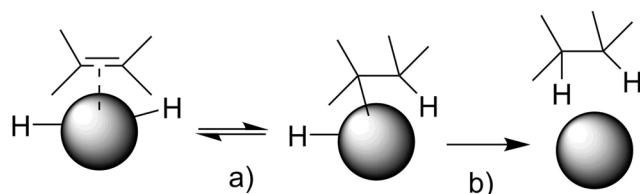
Figure 9. Mechanism of the heterogeneously catalysed hydrogenation of C=C bond.

As *Pd-pol* was more active than *Ni-pol* in the hydrogenation, it also hydrogenated the less sterically hampered C18:1 *cis* isomer faster than the *trans* one, leading to a *cis*-C18:1/*trans*-C18:1 molar ratio of less than 1 in the final mixture.

In addition, as conjugate dienes are easier to be hydrogenated than monoenes [41], the less active *Ni-pol* system was able to more rapidly hydrogenate methyl linoleate and methyl linolenate than methyl oleate, thus resulting in being selective towards the formation of C18:1 methyl ester.

Notably, both Pd and Ni systems performed in the same way for upgrading FAMEs from SO and WCO feedstocks, because they were stable to impurities (water, FAAs, oxidized functionalities, etc.) usually found in vegetable oils recovered from fried-food industries.

Finally, *Pd-pol* and *Ni-pol* were more active than conventional activated carbon supported Pd and Ni catalysts in the partial hydrogenation of FAMEs, using dihydrogen as the reductant. In fact, Pd/C 5% has been reported to hydrogenate SO FAMEs under H_2 (p = 75 atm) at 85 °C for 4 h, resulting in a mixture containing 23% of C18:2, 24% of C18:1, and 40% of C18:0, with a *cis*-C18:1/*trans*-C18:1 molar ratio of 0.5, thus using harsher conditions with respect to the ones employed in the present work, except for the metal/substrate molar ratio [42]. Ni/C did not show an impressive catalytic activity in the hydrogenation of FAMEs derived from palm oil under 6 bar dihydrogen, at 120 °C for 2.5 h, as C18:3 and C18:2 amounts passed from 0.23% and 0.28%, respectively, in the pristine blend to 0.14% and 0.10% in the hydrogenated one, while C18:1 increased from 38.63%.to 39.81% after the reaction [43]. However, Ni-based nanomaterials are promising catalysts for the catalytic transfer hydrogenation of FAMEs using isopropanol, glycerol, and so on, as hydrogen donors [15,19].

3. Materials and Methods

3.1. General Considerations

All of the chemicals were purchased from commercial sources and were used as received. Soybean oil and WCO were obtained from food market and domestic waste, respectively. Tap water was de-ionized by ionic exchange resins (Millipore) before use. *Pd-pol* [31] and *Ni-pol* [32] were synthesized according to the procedures described in the literature. The metal content in the catalysts (before and after their use) was assessed with an atomic absorption spectrometer (AAS; Perkin–Elmer 3110) after sample mineralization. The experimental error on the assessed value was ±0.3%. Mineralization of the catalysts was performed in the microwave ETHOS E-TOUCH Milestone applicator in an HCl/HNO$_3$ (3:1 *v*/*v*) solution (12 mL). Gas chromatography−mass spectrometry (GC-MS) data (EI, 70 eV) were acquired on a HP 6890 instrument using an HP-5MS cross-linked 5% phenyl methyl siloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column coupled with a HP 5973 mass spectrometer. The products were identified by comparing their GC-MS characteristics with those of the pure samples. Gas chromatography analyses were carried out using an HP 6890 instrument equipped with a flame ionization detector (FID) and an HP-1 (Cross linked Methyl Siloxane) capillary column (60.0 m × 0.25 mm × 1.0 μm).

3.2. Synthesis of FAMEs

FAMEs were prepared from SO and WCO through a transesterification reaction according to the procedure reported in [22]. First, 50 g of vegetable oil was heated at 60 °C. Then, a solution of methanol (16.9 g) and potassium hydroxide (0.5 g) in a MeOH/oil molar ratio equal to 9:1 was added to the heated oil and left under stirring at 600 rpm for 2 h under refluxing conditions. Afterwards, the mixture was poured into a separating funnel, and was left standing overnight to separate the FAMEs from the glycerol. Once separated, the FAMEs phase was washed several times with distilled water at 60 °C and dried over Na$_2$SO$_4$. The average molar weights of the SO and WCO FAMEs mixtures were calculated on the base of their composition.

3.3. Catalytic Tests

3.3.1. Upgrading with *Pd-pol*

Biodiesel (125 mg) and *Pd-pol* (60.3 mg, Pd%$_{wt}$ = 2.50) were mixed in CH$_3$OH (5.0 mL) in a 50 mL stainless-steel reactor under dihydrogen (10 bar) at room temperature. The whole mixture was left under stirring for the appropriate amount of time. The progress of the reaction was monitored by GLC and GC-MS.

At the end of the reaction, the catalyst was filtered off and washed with methanol (3 × 5 mL) and n-hexane (3 × 5 mL). Then, it was dried under vacuum, weighed, and employed for subsequent catalytic runs, by using a proper amount of fresh reagent, in order to keep the metal/substrate molar ratio steady over subsequent cycles.

3.3.2. Upgrading with *Ni-pol*

Biodiesel (125 mg) and *Ni-pol* (64.5 mg, Ni%$_{wt}$ = 5.35) were mixed in CH$_3$OH (5.0 mL) in a 50 mL stainless-steel reactor under dihydrogen (10 bar) at 100 °C. The whole mixture was left under stirring for the appropriate amount of time. The progress of the reaction was monitored by GLC and GC-MS.

At the end of the reaction, the catalyst was filtered off, and washed with methanol (3 × 5 mL) and n-hexane (3 × 5 mL). Then, it was dried under vacuum, weighed, and employed for subsequent catalytic runs by using a proper amount of fresh reagent in order to keep the metal/substrate molar ratio steady over subsequent cycles.

4. Conclusions

Polymer-supported palladium (*Pd-pol*) and nickel (*Ni-pol*) nanoparticles were employed as catalysts for the partial hydrogenation of FAMEs obtained from soybean and waste cooking oils. *Pd-pol* was very active under mild conditions (10 bar dihydrogen, room temperature, 5 min reaction time), but unfortunately it was poorly selective towards the formation of a desirable C18:1 product, which guaranteed good cold flow and oxidative stability parameters for the upgraded biodiesel. In fact, the main product of the *Pd-pol* catalytic system was methyl stearate, resulting from total hydrogenation. On the contrary, the *Ni-pol* catalyst was less active than *Pd-pol*, requiring longer reaction times (10 h) and higher temperatures (100 °C) under 10 bar dihydrogen, but still not severe conditions. However, the *Ni-pol* system showed good selectivity towards the formation of C18:1 methyl ester, although the unwanted *cis* to *trans* isomerization could not be avoided. Both catalysts were recyclable for at least five subsequent runs and retained the metal charge over the cycles. By comparing the Pd and Ni polymer-supported catalysts reported here, the best performances were achieved with the nickel material. Considering the high cost of palladium, the present work demonstrates that nickel catalysts could represent a compelling alternative to noble metals for the synthesis of renewable biofuels.

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