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Esterification, transesterification and hydrogenation reactions of polyunsaturated compounds catalyzed by a recyclable polymer supported palladium catalyst.

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Abstract

Aliphatic and aromatic carboxylic acids were converted into their corresponding esters using a polymer supported palladium(II) β -ketoesterate complex under hydrogen atmosphere in the presence of catalytic bromobenzene in alcohols. This method was also applicable to the transesterification of esters. Good to excellent yields were obtained for different aliphatic or aromatic starting materials. The esterification (or transesterification) was promoted by the *in situ* generation of HBr from bromobenzene, which provided a mild acidic reaction environment. Pd(II) centers were converted into polymer stabilized metal nanoparticles (the true active species) under reaction conditions. The palladium catalyst exhibited a remarkable activity and was reusable for eight consecutive cycles. The present system was also tested for the preparation of partially hydrogenated fatty acid methyl esters, starting from a mixture composed by highly polyunsaturated esters and free carboxylic acids, taken as a model acidic feedstock for biodiesel upgrading.

Keywords

Esterification; palladium nanoparticles; transesterification; recyclable catalyst; hydrogenation; biodiesel upgrade.

1. Introduction

Esterification of carboxylic acids and transesterification of esters are important reactions having wide industrial applications for the synthesis of fragrances, flavors, polymers, pharmaceutical and agricultural compounds [1,2,3]. In this regard, many useful and reliable catalytic systems for the synthesis of esters [4,5,6,7] and for transesterification reactions [8,9,10,11,12,13] have been reported in the literature. In addition, esterification and transesterification reactions are of great interest for the preparation of biodiesel [14], which is commonly produced from either transesterification of natural triglycerides (animal fats or vegetable oils) or from esterification of free fatty acids (FFAs) with methanol to give fatty acid methyl esters (FAMEs) [15]. Another important aspect in biodiesel synthesis is the amount of polyunsaturated compounds in the feedstock. Products that comprise large amounts of highly unsaturated FAMEs are more susceptible to oxidation (rancidity) but, on the other hand, have better cold flow properties than highly saturated products [16], so a useful biodiesel should have a large amount of monounsaturated FAMEs and low quantities of both saturated and polyunsaturated FAMEs. Many efforts have been recently made to design catalytic systems aiming at biodiesel upgrading by partial hydrogenation of FAMEs [17,18], also with palladium based catalysts [19,20,21,22].

On the basis of the above considerations, we could argue that a catalytic system able to simultaneously promote esterification, transesterification and partially hydrogenation reactions would be interesting both for fine chemicals synthesis and for biodiesel production.

Recently, it has been reported that the esterification of carboxylic acids and the transesterification of esters could be smoothly achieved using Pd/C under hydrogenation conditions (1-4 bars H₂) in the presence of small amount of bromobenzene in alcohols [23]. However, the reported Pd/C catalytic system could be improved (Pd/C is even pyrophoric) mainly from a recyclability point of view, being the catalyst re-usable only up to three times [23].

Aiming at developing a more active system, we decided to evaluate the catalytic activity of a polymer supported palladium catalyst (in the following *Pd-pol*) for the esterification of carboxylic acids and transesterification of esters. In order to obtain a material with a uniform distribution of the active sites, the pre-catalyst was synthesized in an unusual procedure [24], i.e., by co-polymerization of the β -ketoesterate metal-containing monomer Pd(AAEMA)₂ [AAEMA⁻= deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with suitable co-monomer (ethyl methacrylate, EMA) and cross-linker (ethylene glycol dimethacrylate, EGDMA) [25] (Scheme 1).

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Pd-pol pre-catalyst was successfully employed in several palladium promoted reactions [26,27,28,29,30,31,32,33,34,35]. In all cases, the pristine Pd(II) supported complex was reduced *in situ* under reaction conditions to Pd(0), forming palladium nanoparticles (NPs) (the real active species) immobilized onto the insoluble support (*Pd-pol*, Scheme 1) and stabilized by the macroporous and reticulated polymer matrix [36]. These NPs showed a size distribution centered around 4 nm (when formed under 1 atm H₂ in methanol as the solvent), retaining their morphology and roughly their dimension even after several catalytic runs in hydrogenation reactions [30].

Herein, we report on the catalytic activity and recyclability of *Pd-pol* system in the esterification (and transesterification) reaction by a simple condensation of a carboxylic acid with an alcohol under mild hydrogenation conditions in the presence of catalytic amount of bromobenzene. Since

the present system was incidentally able to catalyze also the C=C double bond hydrogenation, we tested the developed protocol in the simultaneous esterification, transesterification and partially hydrogenation of a mixture of free acids and polyunsaturated fatty esters, taken as a model acidic feedstock for biodiesel upgrading.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and used as received. Pd-pol was synthesized according to the procedure described in ref. [30]. Commercial edible oil was composed by all cis-5,8,11,14,17-eicosapentaenoic acid ethyl ester (40%), all cis-4,7,10,13,16,19docosahexaenoic acid ethyl ester (20%_w), α -linolenic, linoleic and oleic acid ethyl esters (30%_w), excipients (10%_w). Palladium content in *Pd-pol* was assessed after sample mineralization by atomic absorption spectrometry using a Perkin-Elmer 3110 instrument. The experimental error on the palladium percentage was ±0.3. Palladium amount in the crude product (after removal of the catalyst) was assessed after sample mineralization by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo ICAP 6000) analysis. For the corresponding calibration curve the limit of detection was 50 ppb. Mineralization prior to Pd analyses was carried by microwave irradiation with an ETHOS E-TOUCH Milestone applicator, after addition of 12 mL HCl/HNO3 (3:1, v/v) solution to each weighted sample. GC-MS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP-5MS crosslinked 5% PH ME siloxane(30.0 m \times 0.25 mm \times 0.25 mm) capillary column coupled with a mass spectrometer HP 5973. Reactions were monitored by GLC or by GC-MS analyzes. GLC analysis of the products was performed using a HP 6890 instrument equipped with a FID detector and a HP-1 (Crosslinked Methyl Siloxane) capillary column (60.0 m $\times 0.25 \text{ mm} \times 1.0 \text{ }\mu\text{m}$). Yields were calculated by GLC analysis as moles of ester product per mole of starting acid by using biphenyl as internal standard.

2.2. General procedure for catalytic esterification of carboxylic acid and transesterification reaction

In a typical run, a 50 mL stainless steel autoclave equipped with a transducer for online pressure monitoring was charged under air of *Pd-pol* (10.6 mg, Pd: 0.5 mol%), the substrate (carboxylic acid or ester, 1.0 mmol), bromobenzene (0.1 mmol, 15.7 mg) and alcohol (5.0 mL). The autoclave was then purged three times with hydrogen, then pressurized with 2 bars H_2 , set on a magnetic stirrer and heated to 40 °C. After the minimum time needed to reach reaction completion, the autoclave

was let to reach room temperature, the hydrogen was vented and the autoclave opened. When necessary, 3.0 mL diethyl ether was added to the mixture at the end of reaction in order to dissolve organic reactants and products. The catalyst was recovered by centrifugation. The yields were assessed by GLC analysis of the organic solution by using biphenyl (50.0 mg) as internal standard.

2.3. Recycling experiments

The catalyst recovered by centrifugation was washed with methanol and diethyl ether and dried under vacuum. The recovered catalyst was thus weighed and reused for a new cycle employing appropriate amount of carboxylic acid, assuming that the palladium content remained unchanged with the recycles. Iteration of this procedure was continued for eight reuses of the catalyst.

2.4. Isolated Yield

3-phenylpropionic acid (751.0 mg, 5.0 mmol), bromobenzene (78.5 mg, 0.5 mmol), *Pd-pol* (53.0 mg, Pd: 0.5 mol%), and methanol (10 mL) were placed in autoclave vessel. Autoclave was pressurized with 2 bars of hydrogen gas. The reaction mixture was then warmed to 40 °C temperature and stirred for 3 h. After reaction, the catalyst was filtered through celite bed. Filtrate was added of water (30 mL). The reaction mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with 5% aqueous sodium bicarbonate solution (3 x 15 mL), dried over anhydrous Na₂SO₄ and filtered. The filtrate was evaporated under vacuum to give methyl 3-phenylpropionate as a pale yellow oil (763.5 mg, yield = 93 %). Comparison of its MS and NMR features with those reported in literature [37] confirmed the purity of the obtained product.

2.5. One pot hydrogenation, transesterification and esterification

A 50 mL stainless steel autoclave equipped with a transducer for online pressure monitoring was charged under air with *Pd-pol* (10.6 mg, Pd $%_w = 5.0$), the commercial oil (323.5 mg), octanoic acid (0.50 mmol, 72.1 mg, when present), bromobenzene (0.10 mmol, 15.7 mg) and methanol (5.0 mL). The autoclave was then purged three times with hydrogen, then pressurized with 2 bars H₂, set on a magnetic stirrer and heated to 40 °C. The reaction course was monitored by submitting to GLC analysis 0.2 mL samples (diluted with 3.0 mL diethyl ether) drawn at proper time from the reaction mixture.

3.Results and Discussion

3.1. Esterification

In preliminary experiments we selected the esterification of 3-phenylpropionic acid to the corresponding methyl ester as the model reaction to study the catalytic activity and selectivity of *Pd-pol*, being 3-phenylpropionic acid methyl ester an intermediate for drug synthesis [38]. The relevant results are reported in Table 1.

 Table 1. Esterification of 3-phenylpropionic acid to methyl 3-phenylpropionate under different reaction conditions ^a



Entry	P (bar) ^b	T (°C)	t (h)	Conv. (%) ^c	Selectivity
					(%) ^c
1 ^d	5	40	3	0	0
2^{e}	5	40	3	1	>99
3	_f	40	3	0	0
4	5	40	2	>99	>99
5	3	40	2.5	>99	>99
6	5	RT	2.5	83	>99
7	2	40	2.5	90	>99
8 ^g	2	40	3	>99	>99 (93) ^h

^a3-phenylpropionic acid (1.0 mmol), CH₃OH (5.0 mL), *Pd-pol* (Pd: 0.5 mol% of Pd, 10.6 mg), bromobenzene (0.1 mmol, 15.7 mg) under H₂. ^b H₂ pressure. ^c Calculated by GLC analysis. ^d In the absence of *Pd-pol*. ^e In the absence of bromobenzene. ^f Under air. ^g Bold typing refers to best reaction conditions. ^h Isolated yield of the reaction carried out on a 5.0 mmol scale.

The best conditions were found to be those employed in entry 8, that is: 3-phenylpropionic acid (1.0 mmol), *Pd-pol* (0.5 mol% of Pd), hydrogen (2 bar) in methanol (5 mL) at 40 °C for 3 h. The

preliminary experiments revealed that in methanol at 40 °C after 3 h the conversion into the ester product was negligible in the absence of *Pd-pol* (entry 1), or in the absence of a catalytic amount of bromobenzene (entry 2) or when the reaction was carried out under air (entry 3), thus confirming that *Pd-pol*, bromobenzene and hydrogen gas were all essential for the desired transformation. On the contrary, by increasing the pressure of H₂ up to 5 bars in the presence of both *Pd-pol* and bromobenzene, the acid conversion raised up to 99% at 40 °C after 2 h (entry 4) and up to 83% at room temperature after 2.5 h (entry 6). By decreasing the dihydrogen pressure to 3 bars the minimum time to reach quantitative conversion was 2.5 h at 40 °C (entry 5). Since in terms of "safe" chemistry the use of a low hydrogen pressure is more convenient, we decided to carry out the catalytic esterification of 3-phenylpropionic acid under 2 bars hydrogen at the temperature of 40 °C, achieving quantitative substrate conversion after 3 hours (entries 7 and 8). Using the optimized reaction conditions, the activity and the scope of the catalytic system was explored in the esterification reaction of some aliphatic and aromatic acids in different alcohols as solvents (Table 2).

Table 2. Esterification	n of carbo	xylic acids	with alcohols ^a
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<i>Pd-pol</i> (0.5 mo	1%)
RCOOH —	RCOOR'
additive	
H_2 (2 bar)	$R' = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, CH_2Ph$
40°C R'OH	

entry	substrate	product	t(h)	Yield (%) ^b
1	б соон	COOCH ₃	2	98
2^{c}	M7 COOH	16 COOCH ₃	2	95
3	СООН	COOCH ₃	3	98
4	СООН	COOCH ₃	14	91



^acarboxylic acid (1.0 mmol), R'OH (5.0 mL), *Pd-pol* (Pd: 0.5 mol% of Pd), bromobenzene (0.10 mmol, 15.7 mg) under H₂ (2 bars), T = 40 °C. ^b Calculated by GLC analysis. ^c diethyl ether (3.0 mL) was added to the reaction mixture prior GLC analysis, in order to dissolve residual substrate and methyl stearate. ^d reaction carried out in the presence of HBr (0.1 mmol) under air at T = 40 °C, in the absence of both *Pd-pol* and PhBr. ^e 3-phenylpropionic acid (5.0 mmol), CH₃OH (5.0 mL), *Pd-pol* (Pd: 0.10 mol% of Pd, 10.6 mg), bromobenzene (0.10 mmol, 15.7 mg) under H₂ (2 bars), T = 40 °C.

The esterification with methanol of octanoic acid, a substrate frequently taken as a model reactant for the synthesis of "green diesel" [39], proceeded smoothly, producing the relevant methyl ester in 2 h (entry 1). On the other hand, the methylation of oleic acid (entry 2) occurred together with the C=C bond hydrogenation, yielding a 95% of methyl stearate. This result is significant, because there is an increasing interest in the fully hydrogenation process of FAMEs [40,41].

The methylation of 2-phenylpropionic acid was quantitative in 3 h (entry 3, Table 2), and followed the same course observed for its isomer 3-phenylpropionic acid (entry 8, Table 1). As expected on the basis of the proposed mechanism (*vide infra*), the methylation of aromatic acids was more sluggish, requiring 14 h to achieve acceptable conversions (entries 4-6, Table 2). The esterification of 1-naphtoic acid (entry 5, Table 2) was incomplete due to the detrimental steric effect of the hydrogen atom in position 8 [42].

To explore the reaction scope, 3-phenylpropionic acid (the model acid) was reacted with different alcohols (ethanol, *n*-propanol, *i*-propanol, benzyl alcohol) in the presence of bromobenzene. The obtained results in the esterification of the model acid under the optimized reaction conditions were excellent when linear alkyl alcohols were used (entries 7 and 8, Table 2). However, when a more hindered hydroxyl group (entry 9, Table 2) was employed, poor results were observed. Finally, the use of benzyl alcohol gave a good yield (entry 10, Table 2).

3.2. Recyclability

The reusability of *Pd-pol* catalyst in the esterification of 3-phenylpropionic acid to methyl 3phenylpropionate was investigated under the reaction conditions described for entry 8 of Table 1. After the first use, the supported catalyst was recovered by simple centrifugation and reused in the next run after a washing workup. The recovered catalyst was successfully employed in subsequent eight cycles with a high catalytic activity, giving the product in excellent yields (94-99%, Figure 1). The samples of *Pd-pol* recovered either during reaction (filtered off when the substrate conversion was 30 % ca.) and after the first and the eighth runs were mineralized and analyzed by atomic absorption spectrometry showing the same palladium content (in the range of the experimental error) of the pristine catalyst (Table 3). In addition, the crude product (after removal of the supported catalyst) was mineralized and submitted to ICP-OES analyses revealing the absence of palladium in the organic phase (Pd amount was below the detection limit of 50 ppb). All these experiments proved that the metal leaching into solution was negligible.



Figure 1: Recyclability of *Pd-pol* (0.5 mol% of Pd) in the esterification of 3-phenylpropionic acid to methyl 3-phenylpropionate in methanol under H₂ (2 bars) at 40 °C (t = 3 h) using bromobenzene as additive.

Table 3. Palladium	amount on	the s	supported	catalyst	recovered	after	different	cycles	of the	model
reaction.										

Pd-pol	Pd wt%
Pristine	5.0 ± 0.3
Recovered during reaction (30% conv.)	5.1 ± 0.3
Recovered after the first run	$4.9\ \pm 0.3$
Recovered after the eight run	4.8 ± 0.3

3.3. Mechanistic considerations

To gain insights into the reaction mechanism, the following test was performed. The solid catalyst was hot filtered off after the esterification of 3-phenylpropionic acid in methanol under dihydrogen had run for 15 min and the conversion had reached 30% ca. The clear filtrate was then stirred under air at 40 °C. After 3 h, the GLC analysis of the catalyst-free mixture showed quantitative conversion into methyl 3-phenylpropionate, and the atomic adsorption analysis carried out on the digested filtered catalyst revealed a palladium content equal to that found in *Pd-pol* before use. However, a color change of the palladium based polymer from yellow (before use) to dark gray was observed at the very beginning of the reaction, suggesting that dihydrogen transformed the precatalyst into the active species, *i.e.* palladium nanoparticles. In fact, the polymeric support of *Pd-pol* was proven to stabilize palladium nanoparticles (with diameters ranging from 2 to 6 nm) formed under dihydrogen in methanol, as revealed by TEM analysis [30]. It is thus clear that the catalytically active species were not the original monomeric Pd(II) species, *i.e.* [Pd(AAEMA)₂], but

the *in situ* generated palladium nanoparticles. The reaction pathway could be similar to the one proposed by Aavula and co-workers [23] starting with an oxidative addition of bromobenzene additive to the coordinately unsaturated palladium(0) at the nanoparticle edge, affording Pd(II)-phenyl bromide intermediate, which in contact with hydrogen gas leads to generation of HBr and Pd(II) phenyl hydride species that, in turn, restores the initial Pd(0) by elimination of benzene (Scheme 2). Proton transfer from the generated HBr to the carbonyl oxygen of the carboxylic acid increases the electrophilicity of the carbonyl carbon, promoting the well-known Fischer esterification with alcohol [43] (Scheme 2).



Scheme 2: Possible reaction mechanism for the esterification with alcohol promoted by *Pd-pol*.

This mechanism was confirmed by the high catalytic activity showed by the hot filtered mother liquor let under stirring at 40 °C under air in the absence of metal catalyst. The following observations also substantiated the proposed reaction pathway: the esterification of 3-phenylpropionic acid with methanol proceeded smoothly *i*) when the methanol solution containing the substrate was stirred under air at 40 °C without the Pd catalyst in the presence of catalytic amount of HBr (entry 11, Table 2), and *ii*) when in the model reaction system (3-phenylpropionic

acid, methanol, PhBr additive, dihydrogen atmosphere) the amount of *Pd-pol* was decreased up to 0.10 mol% of Pd (entry 12, Table 2).

In addition, the proposed mechanism explains why aromatic acids took longer time to react (entries 4-6, Table 2). In fact, the electro-donating capability of the aromatic group decreases the electrophilicity of the carboxylic carbon, thus slowing the reaction rate.

3.4. Transesterification

Since it is known that the acid promoted esterification runs the same pathway followed by the transesterification reaction in the presence of excess alcohol, the present catalytic system was applied to the transesterification of ethyl octanoate with methanol. The obtained results were excellent (yield = 95 % after 3 hour reaction, Scheme 3).



Scheme 3: Transesterification with methanol promoted by *Pd-pol*.

The transesterification carried out on ethyl benzoate gave poor results (yield = 15 % after 20 hours).

3.5. Simultaneous hydrogenation, transesterification and esterification

This catalytic system is able also to reduce C=C double bonds, as it is clear from entry 2 of Table 2, thus promoting simultaneously esterification and hydrogenation reactions, which is really interesting for production of high quality biodiesel. In fact, for example fatty acid methyl esters derived from algae or fish oils have good cold flow properties, but suffer from very poor oxidation stability, which makes these products unsuitable for the use as biodiesel. All these features arise from the presence of highly polyunsaturated esters. Many efforts have been made to date to partially hydrogenate polyunsaturated methyl esters (biodiesel upgrading) in order to increase the oxidation stability, while maintaining satisfying cold flow properties [44]. Another important problem in biofuel production is the undesirable presence of large amount of FFAs in certain biodiesel (acidic oils) feedstocks (mostly those coming from waste cooking oils), which lowers the fuel quality [13]. For this reason, we decided to test the catalytic activity of *Pd-pol* system in the simultaneous partial hydrogenation, transesterification and esterification with methanol of a mixture constituted by an

edible commercial oil containing highly polyunsaturated fatty acid ethyl esters (FAEEs) added of octanoic acid, in order to simulate an acidic biodiesel feedstock. The majority of the esters in the chosen edible oil included acids with many unsaturations, such as eicosapentaenoic acid (EPA, C20:5, 40%_w) and docosahexaenoic acid (DHA, C22:6, 20%_w) (scheme 4). The remaining part of the oil comprised ethyl esters of α -linolenic acid (ALA, C18:3, scheme 4), linoleic acid (C18:2) and oleic acid (C18:1) and minor amounts of ethyl esters of C17 and C16 fatty acids.



Scheme 4: ALA, EPA and DHA ethyl esters.

The model mixture was suspended in methanol and subjected to *Pd-pol* catalytic hydrogenation/esterification/transesterification using PhBr as the additive.

The octanoic acid was quantitatively converted into its corresponding methyl ester after 2 hours.

Time course of the reaction for C18, C20 and C22 species is reported in Figures 2a, 2b and 2c, respectively.



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Figure 2: Percentage composition during reaction of (a) C18; (b) C20; (c) C22 species.

Before the reaction started (t = 0 h, Figure 2a), the C18 fraction of the mixture was constituted by α -linolenic acid ethyl ester (34%, FAEE C18:3), linoleic acid ethyl ester (13%, FAEE C18:2) and oleic acid ethyl ester (53%, FAEE C18:1). For α -linolenic acid ethyl ester (FAEE C18:3) the C=C double bond hydrogenation reaction was faster than the transesterification, and after 2 h the conversion of the initial C18:3 FAEE into C18:2 and C18:1 methyl and ethyl esters was quantitative (Figure 2a). The transesterification of ethyl esters into methyl esters reached completion after 22 hours, when C18:1 FAME isomers and methyl stearate (FAME C18:0) were the sole C18 species, being in 4:1 ratio. Their relative ratio remained almost the same even after 46 h reaction.

Also for EPA ethyl ester (FAEE C20:5), the C=C double bond hydrogenation was fast, and the conversion into less unsaturated species was 83% after 2 h reaction (Figure 2b). Actually, a plethora of species formed during reaction due to partial hydrogenation, isomerization and esterification. It was not possible to distinguish these species by GLC techniques, because they gave rise to overlapping broad peaks. They were classified in figure 2b as "unresolved mixture". Their quantity decreased down to 10% of the total amount of C20 species after 22 hour reaction and disappeared

after 46 hours, when the C20 fraction was made up mainly of di-unsaturated FAMEs (48%) and monounsaturated FAMEs (32%), being minor (20%) the amount of fully hydrogenated FAME.

DHA ethyl ester (FAEE C22:6) disappeared after 2 h stirring under reaction conditions (Figure 2c). Also in this case, as it happened for EPA derivatives, an "unresolved mixture" formed, whose amount decreased down to 13% of the total amount of C22 species only after 22 h. After 46 hour reaction, the C22 portion contained di-unsaturated FAMEs (62%), monounsaturated methyl ester isomers (23%) and a minor quantity of fully hydrogenated product (15%).

For all polyunsaturated FAEEs, this catalyst provided satisfactory transesterification capability and good partial hydrogenation activity with consecutive C=C double bond reductions, which might result in an improvement of the oxidative stability of the obtained FAME mixture. The lower catalytic activity showed by *Pd-pol* system in hydrogenating the present mixture with respect to the activity observed in hydrogenating (and esterifying) oleic acid (entry 2, Table 2) might be found in the low purity of the considered mixture. Palladium based catalysts are known to be sensitive to impurities. In fact, it has been reported that, in the presence of a Pd sol-gel heterogeneous catalyst, squalene (a terpene with six C=C double bonds) was fully hydrogenated in 4 h if its purity was > 98 %_w, while complete hydrogenation did never occur under the same reaction conditions, if the substrate was the 82 %_w squalene olive oil (after 24 hour reaction only four double bonds were hydrogenated, and no further reaction took place even at longer reaction times) [45].

In order to ascertain whether the presence of free octanoic acid could affect the course of the hydrogenation/transesterification reaction of the model mixture, the same experiment was carried out in the absence of octanoic acid. The product distribution did not change, revealing that the initial presence of a free carboxylic acid had no influence on the overall reaction, being the acid quickly esterified.

4.Conclusion

Polymer supported palladium nanoparticles promoted the esterification of carboxylic acids with alcohol under dihydrogen gas in the presence of catalytic amount of bromobenzene. This procedure could also be applicable to the transesterification of esters. The role of bromobenzene consisted in generating *in situ* catalytic amount of HBr which provided a mild acidic environment and started the Fischer esterification (or transesterification) reaction. The palladium catalyst exhibited a remarkable activity and was reusable for eight consecutive cycles. The present method resulted also able to simultaneously catalyze the hydrogenation and the esterification of oleic acid to methyl

stearate, a valuable industrial product. The strength of this system stands in its simplicity and environmentally benignity (avoid of strong acidic conditions and use of a recyclable catalyst). The *Pd-pol* method was also tested in the one-pot partial hydrogenation, transesterification and esterification with methanol of a low purity mixture of ethyl esters of highly polyunsaturated fatty acids, added of a free carboxylic acid (octanoic acid), in order to simulate a FFA containing biodiesel feedstock to be upgraded. Esterification of the carboxylic acid and transesterifications were quantitative, while the hydrogenation led to mono- and di-unsaturated products, which are more suitable for biofuel application than fully hydrogenated or highly polyunsaturated FAMEs. Therefore, this study suggests that the addition of catalytic amount of bromobenzene to acidic oils eliminates the undesirable free fatty acids, when upgrading biodiesel under palladium catalyzed hydrogenation conditions.

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Highlights

- Esterification and transesterification were promoted by a Pd catalyst (*Pd-pol*).
- Reactions occurred in the presence of PhBr (additive) under H₂.
- The catalyst could be reused at least eight times without loss of activity.
- The system was able to catalyze also hydrogenation reactions.
- The system killed free carboxylic acids when used for upgrading acidic biodiesel.