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Transforming levulinic acid into surfactants and biolubricants by chemoselective reductive etherification with fatty alcohols

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Abstract

Biomass derived surfactants with very good surface tension and critical micellar concentration properties have been obtained by conversion of methyl levulinate into methyl 4-alkoxypentanoates, via reductive etherification with aliphatic alcohols. Among different bifunctional acid/metal catalysts best results have been obtained with Pd on carbon bearing acid sites. The reaction occurs through the formation of enol ether intermediate followed by hydrogenation. Pd in high density planes are the active hydrogenation species and, following this, an optimum crystal size was found at ~10 nm.

The reductive etherification with aliphatic alcohols has been extended to other aliphatic and cyclic ketones and aldehydes obtained from biomass and excellent results have been obtained on Pd supported catalysts and the reaction route and experimental conditions described in this work.

Keywords: reductive etherification, methyl levulinate, biobased surfactants, biobased lubricants, fatty alcohols

Introduction

Starting from sustainability concepts, efforts have been made to produce fuels, chemicals and fine chemical from biomass as renewable, widespread, abundant and cheap source of carbon compounds. Through feasible catalytic or thermal processes, biomass can be easily converted into intermediate compounds called platform molecules for downstream synthesis of fuels and chemicals.^[1] Among them, levulinic acid (LA) or 4-oxopentanoic acid has been classified by DOE US as one of the twelve promising platform molecules for the synthesis of several chemicals with multiple applications. ^[2, 3] LA can be obtained from lignocellulosic biomass that does not compete with food. This can be achieved by the hydrolysis of the cellulose fraction into glucose monomers which are dehydrated in acidic media into 5-hydroxymethylfurfural, that subsequently hydrolyzes into levulinic and formic acids. In the last years important advances in producing LA have been reported, ^[4-8] and have converted levulinic acid into a striking platform molecule. In fact, currently the global demand of LA is $2.5 \cdot 10^3$ Tm/year and it is estimated that it will increase up to 3.8 Tm/year in 2020, being Biofine International Inc. the main manufacturer.

Levulinic acid bearing a ketone and a carboxyl groups is a molecule with high chemical versatility, and one of the most studied reactions to valorize LA is the reduction to γ -valerolactone which possesses excellent properties for applications as biofuel and solvent. ^[9] Recently, Tulchinsky et al.^[10] reported the production alkyl 4-alkoxypentanoates, useful as solvents, by the reductive etherification of LA with primary alcohols using a commercial 5%Pd/C catalyst.

The process involves the autocatalyzed esterification of levulinic acid with short chain alcohols (methanol, ethanol butanol and heptanol) followed by the reductive etherification of the ester formed with the primary alcohol. The reactions were performed using an excess of alcohol (alcohol/LA molar ratio =20), at 200-220 °C, keeping a pressure of hydrogen of 7-49 bar, during 18-24h giving 54-77 % yield of the alkyl 4-alkoxypentanoates. This process suffers from several disadvantages such as the high temperatures and hydrogen pressure, and long reaction times required to achieve moderate yields of the target compounds. Inspired by this precedent on the reductive etherification of LA, and following our ongoing interest to produce high added value compounds,^[3, 11] we propose here the valorization of methyl levulinate (ML) by its conversion into methyl 4-alkoxypentanoates through the reductive etherification of methyl levulinate with fatty alcohols (see Scheme 1). These compounds have potential applications as solvents, fuel additives and particularly when a fatty alcohol is involved in the etherification, a fatty acid methyl ester analog can be produced. These methyl 4-alkoxypentanoates can be interesting intermediates for a new class of surfactants since they could be converted into anionic surfactants by saponification or the methyl ester, that can be easily transesterified with glycerol, polyethyleneglycols, sugars, etc. to obtain non-ionic surfactants.

In fact, in the last decade, a significant interest has been focused on the production of surfactants from a variety of renewable products such as 5-hydroxymethylfurfural, carbohydrates, organic acids or amino acids.^[12-15]

Reductive etherification of carbonyl compounds with alcohols using metal supported solid catalysts such as platinum^[16, 17] palladium^[18-21] or rhodium^[22] under hydrogen pressure is an interesting protocol to produce ethers from

carbonyl compounds. In this reaction the formation of acetals, hemiacetals and/or enol ethers, which requires acid catalysis, has been suggested as possible intermediates (Scheme 2)^[21] and, in some cases, an additional acid is required as co-catalyst.

Pd supported on carbon (usually the commercial 5%Pd/C) has been the most used catalyst for the reductive etherification of aldehydes and ketones with primary alcohols, but, the use of high hydrogen pressures (40 bar)^[18] along with the requirement of an acid as co-catalyst are the main disadvantages of these process.^[19, 20, 23] It is interesting to point out that in the case of the reductive etherification of ML with fatty alcohols the presence of an acid co-catalyst can promote the transesterification reaction between ML and the fatty alcohol decreasing the selectivity to the methyl 4-alkoxypentanoates that is our target product. Therefore, the control of the acidity of the catalytic system to produce the reaction intermediate (hemiacetal/acetal or enol ether) while avoiding transesterification reaction will be mandatory to produce the desired methyl 4-alkoxypentanoates.

In this work we have prepared different bifunctional acid-metal catalyst by supporting Pd on supports of different acidity. It will be showed that among the different supports used, carbon support, with very mild acidity is the most adequate to produce the bifunctional acid-metal catalyst. Then, we have designed an optimized catalyst by selecting the adequate support and Pd crystal size based on Pd/C that is able to perform under mild reaction conditions the reductive etherification of methyl levulinate with a variety of fatty alcohols with excellent yields to produce surfactant precursors. Moreover, the catalyst has also

been applied successfully to the reductive etherification of biobased aldehydes and ketones with fatty alcohols to produce biolubricants. [23]

Results and discussion

Although it has been proposed that high hydrogen pressures are required to obtain good results in the reductive etherification of aldehydes and ketones with primary alcohols,^[18, 24] Fuji et al. [21] proposed an alternative protocol to obtain ethers in good yields. The authors used commercial Pd/C as catalyst, under mild reaction conditions and in absence of solvent and acids as cocatalyst. In this protocol the reaction is performed under atmospheric pressure in a continuous stream of hydrogen, removing in such a way the water formed during the reaction. This process was limited to monofunctional carbonyl compounds, requires an excess of the carbonyl compound, and involves large time of reaction (24 h). However we thought that the mild reaction conditions required and the possibility to recirculate the hydrogen, makes this a very attractive process from the point of view of green chemistry, and it was worth to be further explored for achieving surfactants from levulinic acid.

Thus, in this study we chose the reductive etherification of methyl levulinate (ML) with octanol as reaction model. Using the Fuji protocol, the reactions were first performed under atmospheric pressure in a continuous stream of hydrogen using a molar ratio ML/octanol= 2 at 160 °C in presence of different catalysts. Considering the reaction mechanism proposed by Fuji et al. [21] (see Scheme 2), the reductive etherification of carbonyl compounds occurs by either hydrogenolysis of hemiacetal/acetal intermediates (route A) or by hydrogenation of an enol ether (route B). Then, in principle, a bifunctional catalyst bearing acid sites (to promote the formation of intermediates) and metal sites (to promote

hydrogenolysis or/and hydrogenation of intermediates) will be required. However, we have to consider that ML is a molecule with a keto and ester functions. As commented above, the ester group, in presence of an acid catalyst, can undergo transesterification with the primary alcohol, while in presence of a reducing atmosphere, the carbonyl group can be reduced to alcohol and the resultant 4-hydroxymethyl ester can cyclize to γ -valerolactone decreasing considerably the selectivity to the target compound. Therefore, the catalytic properties of both active sites (acid and metal) have to be mastered in order to design an active catalyst able to produce selectively methyl 4-alkoxypentanoates from methyl levulinate and fatty alcohols.

In order to design an adequate bifunctional acid-metal catalyst, first of all we prepared a catalyst based on 5 wt % Pd supported on a weak acid support such as TiO₂ (5%Pd/TiO₂). Pd was selected as the hydrogenating metal, due to its low activity for reducing carbonyl groups. As can be seen from Table 1, 5%Pd/TiO₂ gave high conversion of alcohol, but the selectivity to the target compound, methyl 4-octyloxylevulinate (**1**), (Scheme 3) was very low (8 %), while the transesterified ketoester **2** was the main compound produced. These results indicate that the acid centers on the support are able to catalyze the transesterification much faster than the metal catalyzes the hydrogenation to the ether derivative. Other supports with different acid-base character such as CeO₂ and Al₂O₃ gave very poor conversions, being also the transesterified ketoester the main product obtained. These results indicate that a support with very mild acidity able to promote the formation of enol ether and/or acetal intermediates while avoiding transesterification reaction could be more convenient for the process.

Most carbonaceous supports possess very weak acidity which is associated to the presence of acid oxygenated functions on the surface (carboxylic, phenolic groups). Therefore, we have prepared a catalyst bearing a 5 wt% of Pd on carbon following the procedure described in the experimental section. As can be observed in Table 1, the catalyst is very active and selective to compound **1**, achieving 100 % conversion with 98% selectivity in 10 h reaction time (entry 4, Table 1). Moreover for comparison purposes the reaction was performed using a commercial 5%Pd/C (entry 5, Table 1). As can be observed, the commercial Pd/C catalyst resulted also very selective to methyl 4-octyloxypentanoate (**1**) but the activity was considerably lower and only 50 % conversion could be achieved after 6h reaction time. The lower activity showed by the commercial catalyst can be related with the crystal size of the Pd nanoparticles, that in the case of the commercial 5%Pd/C is around 4 nm (see Figure S1) while the crystal size of the prepared 5%Pd/C is 17nm (see Figure S6). As we will show later, the crystal size of the Pd nanoparticle has an important role on activity. Moreover, using the prepared 5%Pd/C catalyst, the reaction rate was improved by working with a ML/octanol molar ratio of 0.5, (entry 6, Table 1) and so, we decided to follow the study using this molar ratio.

With respect to the nature of the intermediates, and in clear contrast with those observed in the reductive etherification of aldehydes and ketones, in the case of ML we do not detect the presence of acetal and/or enol ether intermediates in the reaction media.

Then, to check if the acetal could be the intermediate compound formed during the reaction, the 5%Pd/C sample, was tested in the reaction of acetalization of ML with octanol (i.e. under the same reaction conditions but substituting the

hydrogen in the process by nitrogen). After 4h of reaction only 13 % of ML was converted, being the transesterified ketoester, octyl levulinate (**2**), the only compound detected. Moreover, a control experiment in absence of catalyst and hydrogen, showed that the transesterified ketoester (11 % yield) was the only product detected after 4 h. These results indicate that under these reaction conditions, the support is not able to catalyze the formation of the acetal intermediate, nor the transesterification process. Considering the high reaction rate of formation of ether **1** observed when the reaction is performed in presence of hydrogen (see Table 1), it would appear that under our reaction conditions the reaction route via acetals may not occur. However this route cannot be completely ruled out if one takes into account that Pd has been reported to catalyze acetalizations under hydrogen atmosphere. [21, 25]

Optimization of the catalyst metal function: effect of the nanoparticles metal size on the catalytic activity

It is known that by changing the metal crystallite size one can change the relative ratio between the less saturated Pd atoms (located at the crystal corners) and the more saturated Pd atoms located on crystal faces. This ratio will be lower when higher is the crystal size. Since the electronic properties of the more saturated and less saturated Pd atoms should be different, if the hydrogenation of the intermediate (enol ether) is a metal structure sensitive process, the activity (as per turnover frequency) would be different on samples with different crystal sizes. The only precedent on the effect of Pd crystal size on the catalytic activity was reported by Bethmont et al. [26] in the reductive etherification of butanal with octanol using Pd/C at 40 bar of hydrogen. The authors found that the reductive

etherification goes through the formation of the enol ether intermediate followed by hydrogenation, being the activity of an in situ reduced sample with an average Pd crystal size of 18 nm higher than the activity of an ex situ reduced Pd/C sample with a metal crystal size of 10 nm. Then, since the metal component of the catalyst is playing the key role during the reductive etherification of ML, the design of the metal components of the catalyst is mandatory. Here, we have studied the effect of the metal nanoparticles size on the process. For doing that Pd/C samples have been prepared with different average Pd crystallite size, by synthesizing samples with different Pd loading.

Thus, Pd/C samples with 0.2, 0.5, 1.5, 2.5, 5 and 10 wt % of Pd were prepared and the distribution and average crystallite Pd sizes were obtained from by HRTEM (see HRTEM photographs and sizes distribution in Figures S2-S7). As can be observed in Figure 1 and Table 2 the TOF (calculated as initial reaction rate per mol of Pd on the surface measured by chemisorption of CO) first increases when increasing Pd crystal size from 5 to 10 nm (2.5 % Pd loading), and then the TOF values are practically maintained as the crystal size increases. Since the proportion of Pd located on crystal faces increases with the crystal size, these results indicate that the hydrogenation of the enol ether should preferentially occur on dense metal planes of the Pd and activity increases when increasing the crystal size up to 10 nm, showing that it is a process sensitive to structure (i.e. the activity per site of less saturated Pd atoms located at the crystal corners is lower than the more saturated Pd atoms located on crystal faces). A further increase of crystal size has very low influence on the TOF values, which are similar independently of the crystal size. These results are indicating that Pd atoms located at the metal planes have similar intrinsic activity. Using the

optimized catalyst with a crystal size of 10 nm, total conversion of ML was achieved in 2 h reaction with 98 % selectivity to the ether **1**.

At this point, we checked the catalytic activity of the samples of Pd/C with different crystal size (5, 7, 10, 17 and 22 nm) on the reductive etherification of pivaldehyde with octanol (see Scheme 4) as a test reaction. The reaction test was chosen because the pivaldehyde can not form the enol ether as intermediate, and its reductive etherification occurs by hydrogenolysis of hemiacetal/acetal intermediate (see Schemes 3 and 4). As can be observed in Figures S8-S12, the reductive etherification of this substrate goes through the formation of the acetal intermediate. Indeed the acetal appears as a primary and unstable product, while the corresponding ether is a secondary and stable product. When TOF was calculated for the different samples, it is possible to see that, contrary to the reductive etherification of ML, the reductive etherification of pivaldehyde gives the same TOF independently of the Pd crystal size (See Figure 2). These results indicate that the hydrogenolysis of acetal is not a process sensitive to the structure (i.e. the activity per site of less saturated Pd atoms located at the crystal corners and the more saturated Pd atoms located on crystal faces is similar), and confirms that the reductive etherification of ML does not occur through the hydrogenolysis of the acetal/hemiacetal and, most probably, takes place by hydrogenation of the enol ether intermediate as was said above.

Optimization of reaction conditions

In order to further optimize the reaction conditions using the 2.5 %Pd/C catalyst, temperature, flow of hydrogen and molar ratio of reactants were varied. As can be seen in Figure S13 when decreasing the temperature from 160 °C to 120 °C

the conversion of ML was lower (65%) after 6 h reaction and the corresponding ether was obtained in 96 % selectivity. Additionally, an increase of the flow rate of hydrogen from 3.5 mL/min to 4.5 mL/min no modify the rate of conversion of ML indicating that the flow rate of 3.5 mL/min provide a desirable concentration of hydrogen in our reaction conditions, however, a decrease of the flow rate to 1.0 mL/min) decrease considerably the reaction rate (see Figure S14) and 5 h were required to achieve total conversion.

We also optimized the molar ratio of reactants and found that already with 1:1 molar ratio (entry 3, Table S1) a reasonable yield of the desired ether (82%) with 94% selectivity was obtained. When the proportion of octanol was increased the conversion of ML increased (entries 2 and 4, Table S1), being the molar ratio ML:Oct 2:1 the optimum ratio that allow obtaining excellent conversion (98 %) and selectivity (98%) to the ether **1** in only 2 h reaction time (entry 2, Table S1). However, when the proportion of ML was increased a decrease of reaction rate was observed (entries 1 and 3).

Scope of the reaction

The scope of the reductive etherification of methyl levulinate using 2.5%Pd/C as catalysts was explored using different available fatty alcohols with alkyl chain lengths of C8 to C16. As can be observed in Table 3 (Figures S15-S20) the corresponding methyl alkoxy-pentanoates were obtained in good yields and excellent selectivities. As can be seen, the etherification rate depends on the size of the alcohol. Thus the catalytic activity decreases when the alkyl chain of alcohol increases and longer reaction times were required to achieve total conversion. This behavior can be attributed to the existence of steric hindrance

for hydrogenation when the size of the alkyl chain of the alcohol increases. This was evidenced when a long chain secondary alcohol such as 2-decyl-1-tetradecanol was used (Table 3, entry 6).

On the other hand, Jadhav et al. [23] recently reported the production of automotive biolubricants by reductive etherification of different carbonyl compounds with alcohols that can be sourced from biomass. The optimum catalytic system was a commercial 5%Pd/C and silica supported 4-ethylbenzenesulfonic acid as co-catalyst that yielded 50-90 % of ethers working at 120 °C and 10 bar of hydrogen. Then, considering the superior properties of these lubricants with respect to conventional lubricants produced from petroleum, we thought that it would be interesting to test our catalytic system for producing biolubricants using building blocks from biomass. Thus, the reductive etherification in the presence of 2.5%Pd/C was also extended to the etherification of aliphatic and cyclic ketones and aldehydes that can be produced from biomass sources. As can be observed in Table 4 good yields and excellent selectivities to the corresponding ethers were obtained in all cases in short reaction times.

Stability and Reusability of the Pd/C catalyst

To check if the process was truly heterogeneous, the reductive etherification of ML with octanol using 2.5 %Pd/C was stopped after 30 min and the catalyst was filtered off in hot and the reaction was continued for 5 h. No further conversion was detected indicating that Pd leaching does not take place during the reaction (see Figure S21).

To study the reusability of 2.5%Pd/C catalyst, after reaction, it was filtered, and washed with dichloromethane in a Soxhlet system, and then used in a second

cycle. The results showed that after 2h, 85 % yield of ether **1** (98% selectivity) could be achieved, indicating a loss of activity of the catalyst.

The used catalyst was characterized by XRD and compared with the XRD patterns of the fresh catalyst. As can be seen in Figure S22, a signal corresponding to oxidized Pd species (PdO) are detected in the fresh catalyst which proportion increases during the reaction (see Figure S22b). These results agree with the XPS analysis where a component of PdO species is detected in the fresh catalyst, and which proportion increases in the used catalyst (Figure S23). However, the Pd crystal size analyzed by HRTEM of fresh and used catalyst (Figures S5-S24) as well EDS mapping (Figures S25) showed that in both cases, crystal size and dispersion of Pd is maintained after use. Therefore, the loss of activity can be attributable to the partial oxidation of the Pd⁰ during the reaction. Indeed, when the catalyst was reused, previous reduction under H₂ stream at 250°C, in a second and a third reaction cycle, the initial catalytic activity was practically recovered (see Figure 3).

Surfactant properties of 4-alkoxypentanoic acid sodium salts

As commented in the introduction, the 4-alkoxypentanoic acid methyl esters can be converted into surfactant molecules by saponification with bases obtaining the corresponding 4-alkoxypentanoic acid metal salts. Then in order to estimate the surfactant properties of these derivatives, we performed the saponification of 4-octyloxypentanoic acid methyl ester with NaOH. The effect of the 4-octyloxypentanoic acid sodium salt obtained on the surface tension of water was compared with that of a commercial surfactant such as the sodium myristate (sodium tetradecanoate). We have measured the surface tension in water

solutions of the corresponding 4-octyloxypentanoic acid sodium salt at different surfactant concentrations and the results in Figure 6 show that the surface tension of 4-octyloxypentanoic acid sodium salt was lower than for the commercial surfactant, while the critical micellar concentration of 4-octyloxypentanoic acid sodium salt resulted one order of magnitude lower than that of the commercial sample, i.e. $5 \cdot 10^{-3}$ and $2 \cdot 10^{-2}$ respectively. These results indicate that 4-alkoxypentanoic acid sodium salts have superior surfactant properties than conventional soaps with similar alkyl chain length.

Conclusions

Biomass derived surfactants of excellent properties have been obtained by converting methyl levulinate into methyl 4-alkoxypentanoates through a reductive etherification with fatty alcohols. A bifunctional catalysts based on Pd/C gives full conversion and selectivity when the metal crystal size was optimized.

The reaction occurs through the formation of the enol ether intermediate followed by hydrogenation.

The Pd/C catalyst and the reductive etherification with aliphatic alcohols can be extended to other aliphatic and cyclic ketones and aldehydes that can be obtained from biomass with excellent results.

The surfactant properties of 4-alkoxypentanoic acid sodium salt (surface tension and critical micellar concentration) have been measured and compete very favorable with conventional soaps.

Experimental Section

Reactants

Methyl levulinate ($\geq 99\%$), n-octanol ($\geq 99\%$), n-decanol ($\geq 98\%$), n-dodecanol ($\geq 98\%$), n-hexadecanol ($\geq 99\%$), n-octadecanol ($\geq 96\%$), 2-pentanone ($\geq 98\%$), cyclopentanone ($\geq 99\%$), 2-heptanone ($\geq 98\%$), pivaldehyde ($\geq 96\%$), 2-ethylhexanal ($\geq 96\%$), 2-decyl-1-tetradecanol ($\geq 97\%$), Palladium (II) acetylacetonate ($\geq 99\%$) and commercial 5%Pd/C, were purchased from Sigma-Aldrich. Carbon NORIT® RX 3 extra was purchased from NORIT.

Catalysts preparation and characterization

The different catalysts: 5%Pd/Al₂O₃, 5%Pd/TiO₂, 5 %Pd/CeO₂ and (0.2, 0.5, 1.5, 2.5 ,5 and 10%) Pd/C were prepared through a deposition-precipitation method by mixing the appropriate amount of support powder with the appropriate amount of solution of palladium (II) acetylacetonate in 10mL of toluene.^[27] After overnight stirring at room temperature, the solvent was evaporated and the catalyst dried at 100°C in oven, followed by reduction under H₂ stream (50mL/min) at 250°C for 3h.^[27] The physicochemical characteristic of the catalysts are presented in Tables S2 and Table S3.

The temperature required to reduce the catalyst was determined by TPR (temperature-programmed reduction). As can be seen in Figure S26, the metal starts to reduce at 120 °C and at 250 °C for the total reduction is practically achieved.

EDS mapping and HRTEM images were recorded using a JEM 2100F transmission electron microscopy operated at 200 kV.

The XPS spectra were recorded with a SPECS spectrometer equipped with a Phoibos 150 MCD-9 multichannel analyzer, using a nonmonochromatic AlK α (1486.6 eV) X-ray source. The spectra were recorded with an X-ray power of 100 W, pass energy of 30 eV, and under an operating pressure of 10⁻⁹ mbar. The XPS spectra were referenced to C 1s peak (284.5 eV), and spectra treatment was performed using the CASA XPS software.

Reaction procedure

Catalytic experiments were performed in absence of solvent. The correspondent carbonyl compound (2 mmol) and alcohol (4 mmol) were placed in a 10 mL round-bottom flask connected to a Dean-stark system and condenser and heated at 160 °C using a system equipped with a silicone bath, and magnetic stirrer. Then, the corresponding amount of catalyst (0.5 mol % of palladium) was added and a H₂ flow (3.5 mL/min) was bubbled in the reaction mixture. The reaction was followed taking samples at regular periods that were analyzed by gas chromatography using a flame ionization detector and a capillary column (HP5, 30 m x 0.25 mm x 0.25 mm), using nonane as external standard. The initial reaction rates r^0 [mol h⁻¹] were calculated in all cases for a conversion of the corresponding carbonyl compound below 20%.

To avoid the control by external diffusion the reductive etherification was carried under different stirring speed (300, 600, 1000, 1400 rpm). It was found that working at stirring speeds between 1000 and 1200 rpm there is not influence on the initial reaction rates. Thus, all the experiments were carried out at 1000 rpm. When the reaction was finished, the catalyst was filtered off and the mixture was analyzed by GC-MS chromatography. GC-MS analyses were performed with an

Agilent 6890N equipped with the same column as for GC. Purification of the final product was carried out by flash chromatography using mixtures of hexane/ethyl acetate as eluent, and their characterization was performed by ^1H NMR and ^{13}C NMR and UPLC-MS (see Supporting Information).

The dispersion of palladium in Pd/catalysts was estimated from CO adsorption using the double isotherm method on a Quantachrome Autosorb-1C equipment (Table S3). The samples were diluted with silica to make the tablet (60:40, sample:SiO₂). Prior to adsorption, the samples (300 mg with a pellet size of 0.8-1.1 mm) were reduced in situ in flowing pure hydrogen (25 mL/min) at the same reduction temperature applied before catalysis that is 250°C for 3 h (10 °C/min rate). After reduction the samples were degassed at 1333×10^{-3} Pa for 2 h at the reduction temperature, and then temperature lowered at 25°C (1 hour for cooling down the sample to adsorption temperature). Then, pure CO was admitted and the first adsorption isotherm (i.e. the total CO uptake) was measured. After evacuation at 25°C, the second isotherm (i.e. the reversible CO uptake) was taken. The amount of chemisorbed CO was then obtained by subtracting the two isotherms. The pressure range studied was $0.5\text{-}11 \times 10^4$ Pa. The dispersion of Pd (D) was calculated from the amount of irreversibly adsorbed CO assuming a stoichiometry of Pd/CO=1 as was used by other authors [28-31]. The mean Pd⁰ diameter (d) was determined from chemisorption data assuming spherical geometry for the metal particle according to the procedure described by Anderson [32]. Equations used for metal dispersion and metal diameter determination are shown below.

$$D (\%) = \frac{Nm * F_s * M * 100}{L} * 100$$

Nm: chemisorption uptake expressed in mol of CO per gram of sample

F_s: adsorption stoichiometry

M: molecular weight of the supported metal

L: percent loading of the supported metal

$$d = \frac{L * 6}{ASA * Z * 100}$$

d: mean metal diameter (m)

Z: density of the supported metal (g/m³)

ASA: active surface area (m²/g_{sample}) calculated from the following equation:

$$ASA = N_m * F_s * A_m * N_A$$

A_m: cross-sectional area occupied by each active surface atom

N_A: Avogadro's number

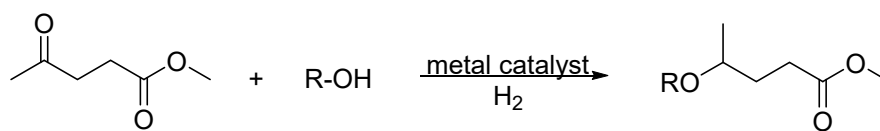
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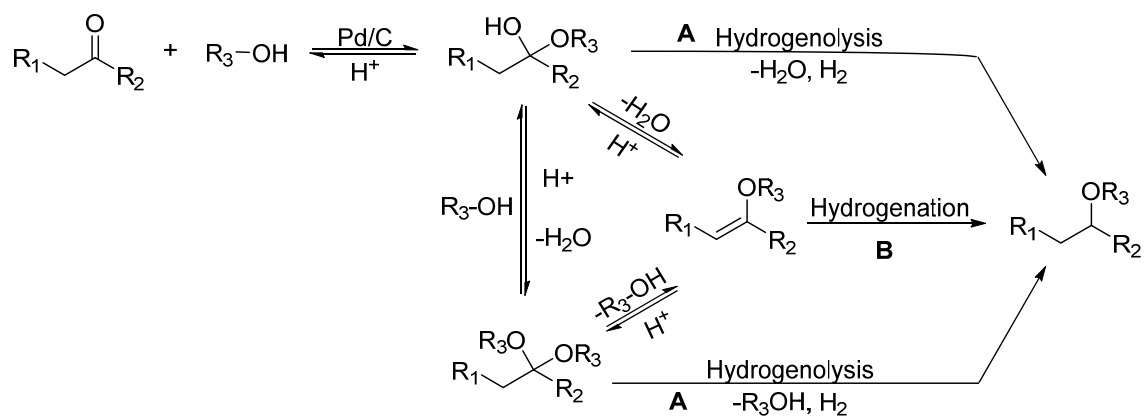
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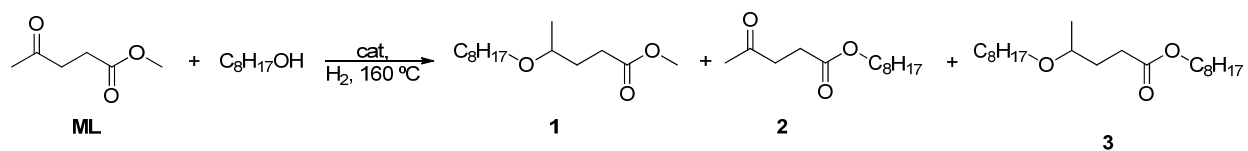
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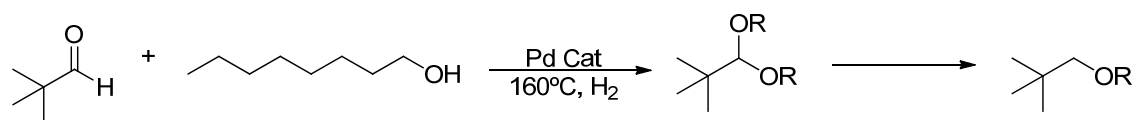
Scheme 1. Reductive etherification of methyl levulinate with aliphatic alcohols



Scheme 2. Mechanism proposed for the reductive etherification of carbonyl compounds with alcohols



Scheme 3. Reductive etherification of methyl levulinate with n-octanol



Scheme 4. Reductive etherification of pivaldehyde with octanol

Table 1. Results of the reductive etherification of methyl levulinate with 1-octanol using different Pd supported catalysts.^a

Entry	Cat	Conv (%)	Yield 1 (%)	Yield 2 (%)	Yield 3(%)	Sel.1 (%)
1	5%Pd/TiO ₂	91	7	84	-	8
2	5%Pd/CeO ₂	12	-	12	-	0
3	5%Pd/Al ₂ O ₃	12	4	8	-	33
4	5%Pd/C	80 (100)	79 (98)	-	1(2)	99(98)
5	5%Pd/C ^b	50	49	1	-	98
6	5%Pd/C ^c	100	98	-	2	98

[a] Reaction conditions: ML(2 mmol), 1-octanol (1 mmol), H₂ flow rate = 3.5 mL/min at atmospheric pressure, molar ratio 1-octanol/Pd=200, 160°C, 6 h. [b] Commercial 5 % Pd/C [c] using ML (1 mmol), 1-octanol (2 mmol) 5 h, molar ratio ML/Pd = 200. In brackets results at 10h.

Table 2. Results of the reductive etherification of ML with octanol using Pd/C samples with different Pd crystal size.^a

Entry	cat	Nanoparticle size (nm)	r^0	Time (h)	Conv. ML (%)	Yield 1 (%)	Yield 3 (%)	Sel. 1 (%)	TOF ^b (s ⁻¹)
1	0.2% Pd/C	2	0.6	6	95	49	41	50	n.m.
2	0.5% Pd/C	5	0.4	6	97	47	36	49	0.2
3	1.5% Pd/C	7	1.3	6	95	88	7	93	0.6
4	2.5% Pd/C	10	2	2	100	98	2	98	1.8
5	5% Pd/C	17	0.9	5	100	98	2	98	1.6
6	10% Pd/C	22	0.3	6	66	66	-	100	1.5

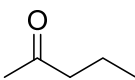
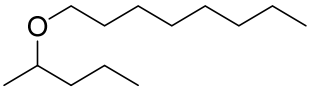
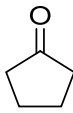
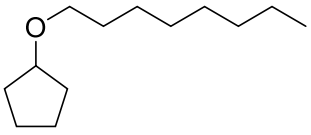
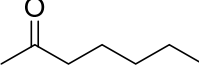
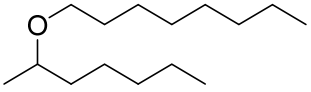
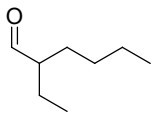
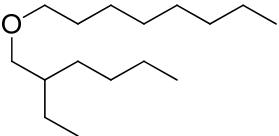
[a] Reaction conditions: 160°C, ML/octanol 1:2, ML/Pd=200; r^0 [mol h⁻¹] 10³. [b] initial reaction rate per mol of Pd in surface (calculated by CO chemisorption)

Table 3. Reductive etherification of methyl levulinate with different fatty alcohols.^a

Entry	R-OH	$r^{0[b]}$	t (h)	Conv. 1 (%)	Yield ether (%)	Selec. ether (%)
1	(CH ₂) ₇ CH ₃	2.0	2	100	98	98
2	(CH ₂) ₉ CH ₃	1.9	2	100	100	100
3	(CH ₂) ₁₁ CH ₃	1.8	2	100	100	100
4	(CH ₂) ₁₅ CH ₃	1.7	2	100	100	100
5	(CH ₂) ₁₇ CH ₃	0.9	3	100	100	100
6	2-decyl-1-tetradecanol	0.3	6	100	100	100

[a] Reaction conditions: alcohol/ML = 2, molar ratio ML/Pd=200, at 160 °C under H₂ flow (3.5mL/min).[b] [mol h⁻¹] 10^3

Table 4. Scope of the reductive etherification of biomass derived carbonyl compounds with n-octanol using 2.5%Pd/C as catalyst

Entry	ketone	product	t (h)	Conv. (%)	Yield ether (%)	Selec. ether (%)
1			3	100	100	100
2			2	100	100	100
3			3	100	100	100
4			3	100	100	100

Reaction conditions: molar ratio alcohol/carbonyl compound = 2, molar ratio carbonyl compound/Pd=200, at 160 °C under H₂ flow (3.5mL/min)

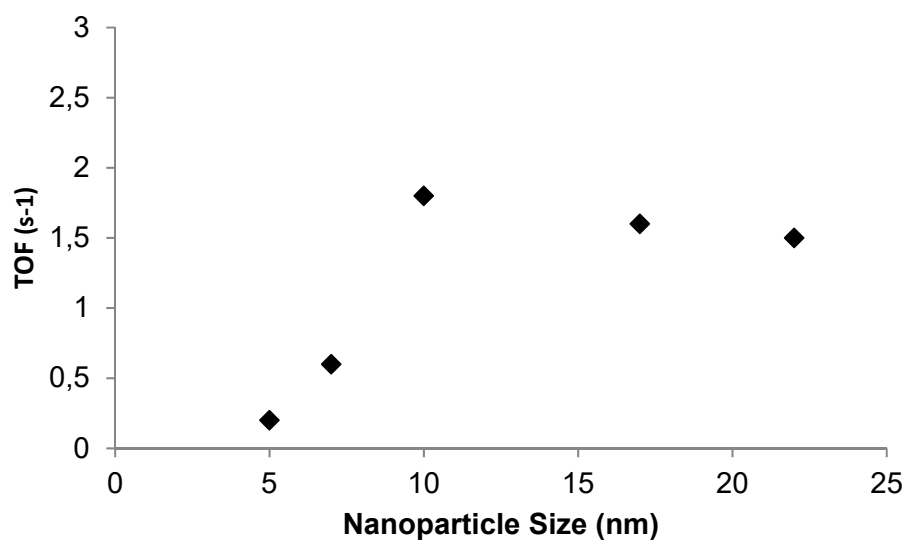


Figure 1. TOF values (initial reaction rate per mol of Pd in surface calculated by CO chemisorption) versus Pd crystal size in the reductive etherification of methyl levulinate with n-octanol using Pd/C samples as catalysts.

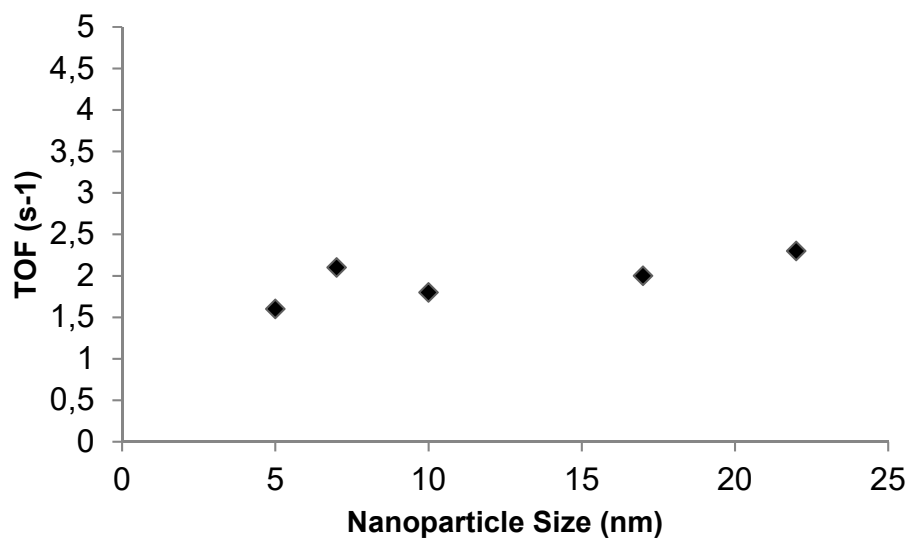


Figure 2. TOF values (initial reaction rate per mol of Pd in surface calculated by CO chemisorption) versus Pd crystal size in the reductive etherification of pivaldehyde with n-octanol using Pd/C samples as catalysts.

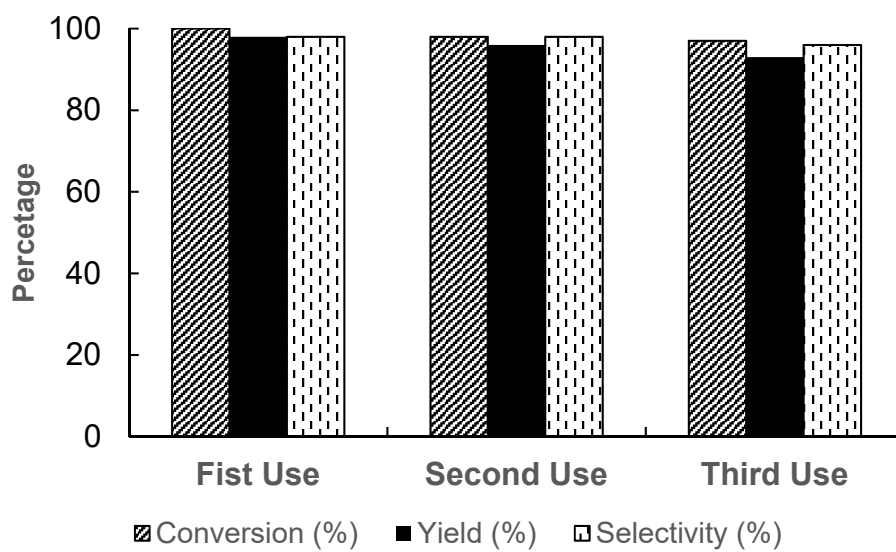


Figure 3. Reusability of 2.5% Pd/C in the reductive etherification of methyl levulinate with n-octanol at 2 h reaction time.

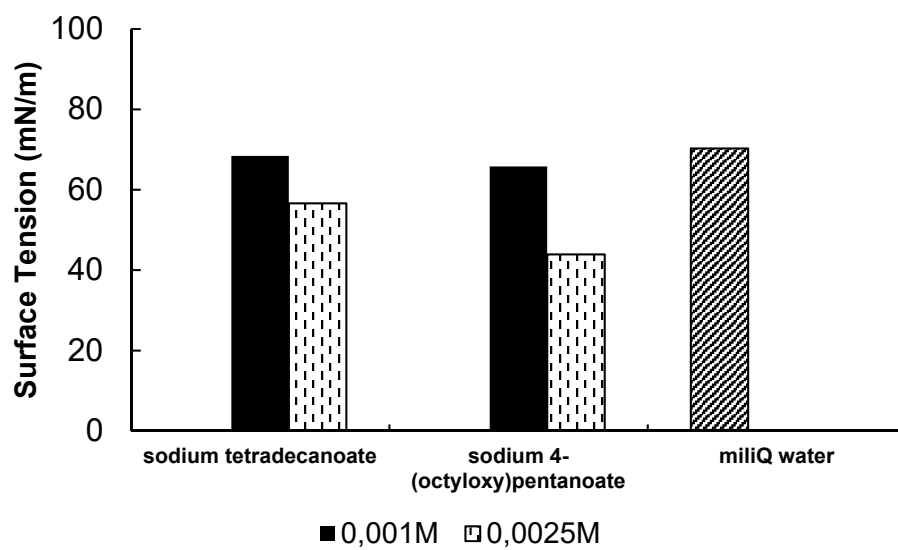


Figure 4. Surface tension of sodium tetradecanoate, sodium 4-(octyloxy)pentanoate and milliQ water.