Highly dispersed Pt nanoparticles supported on carbon nanotubes produced by atomic layer deposition for hydrogen generation from hydrolysis of ammonia borane

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Synthesis and characterization of supported Pd complex on carbon nanofibers for the selective decarbonylation of stearic acid to 1-heptadecene: the importance of subnanometric Pd dispersion

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Production of linear α-olefins from renewable sources is gaining increasing attention because it allows the transition from the current petrochemical synthesis route to a more sustainable scenario. In this work, we describe the synthesis and characterization of an innovative catalyst based on a di-µ-chloro-Bis[palladium(II) anthranilate] complex highly dispersed by incipient wetness impregnation over acyl chlorinated carbon nanofibers. Subnanometric dispersion of the metal complex allowed higher catalytic efficiency for the selective decarbonylation of stearic acid to 1-heptadecene as compared to the reference homogenous catalyst. The best catalytic performance (90 mol% selectivity, 71 mol% conversion, TON= 484) was achieved under mild reaction conditions (atmospheric pressure, 140 ºC) with a Pd loading in solution of 0.14 mol%. The post-mortem catalyst characterization and the recyclability tests evidenced the high stability of the catalyst. The highly dispersed catalyst developed in this work provides new opportunities in the rational design of more efficient catalytic systems for the sustainable transformation of fatty acids.

Introduction

Linear α-olefins represent an important class of commodity alkenes used for manufacturing basic industrial and consumer goods, such as detergents, oil-soluble surfactants, synthetic lubricants and olefin-based polymers as polyethylene. α-olefins represent an important class of commodity alkenes used for manufacturing basic industrial and consumer goods, such as detergents, oil-soluble surfactants, synthetic lubricants and olefin-based polymers as polyethylene. Currently, this kind of olefins are produced almost exclusively from fossil carbon sources via ethylene oligomerization or Fischer-Tropsch process from syngas. However, due to the global depletion of fossil fuel reservoirs and the environmental problems arising from the petrochemical industry, the development of more sustainable routes for obtaining α-olefins has become increasingly necessary. Fatty acids, which are abundantly available in vegetable oils and animal fats, represent an attractive renewable feedstock, since their selective decarbonylation can give access to high-value linear α-olefins.

Several transition metals including palladium, rhodium, iridium, and to a lesser extent nickel and iron, have been studied as catalytic systems for such decarbonylation reaction, mainly via homogeneous catalysis. Among them, homogeneous palladium-based catalysts have demonstrated the highest catalytic activity, yielding fatty acids conversion around 60-75 mol% and selectivity values higher than 97 mol%, with catalyst loadings as low as 0.01 mol% in solution. Nevertheless, these systems operate at high reaction temperatures (230-250 °C) and the olefin product must be continuously distilled to avoid the double bond isomerization, thereby maintaining the high selectivity. In this respect, some works have succeeded in reducing the reaction temperature to 110 ºC, reaching moderate α-olefin productivity (turnover number (TON) <33, turnover frequency (TOF) ~2 h⁻¹, α-selectivity>97 mol%), albeit at the expense of increasing the catalyst loading in solution (3 mol%).

Despite advances in the homogeneously catalysed conversion of fatty acids, recovering the catalyst remains a crucial challenge nowadays and, therefore, the industrial implementation of these homogeneous catalysts is still limited. Even though heterogeneous catalysts, which are easier to separate from reaction products and exhibit higher thermal stability, they have so far scarcely been explored in the production of α-olefins. In such heterogeneous catalytic systems, the α-selectivity (<30 mol%) is typically hindered by the H₂ required to inhibit catalyst deactivation, and most of the formed alkenes are transformed into saturated hydrocarbons, ketones, and paraffins. For instance, Davis and co-workers observed a rapid α-olefin isomerization during the decarbonylation of heptanoic acid over carbon-supported palladium and platinum nanoparticles, recording low TOF values (<19 h⁻¹) and low α-selectivity (<15 mol%) in the liquid phase. Similarly, Stern and Hillion obtained α-olefins by using a nickel catalyst promoted by either tin, germanium, or lead at 200–400 °C, but only TON=3...
could be obtained. Metal-free heterogeneous acid catalysts in water at 400–500 °C have been also evaluated on the production of linear α-olefins (selectivity >90 mol%, TOF <6 h⁻¹) ¹³. However, the catalytic process is limited to the use of unsaturated carboxylic acids and lactones as starting substrates. Most recently, Chatterjee and Jensen¹⁴ reported both high activity (TOF= 420 h⁻¹) and α-selectivity (>95 mol%) for a commercial 10 wt.% Pd/activated carbon catalyst in presence of phosphine ligands. Although, in situ distillation of the olefin product was not required, the reaction was conducted under high reaction temperatures (250–300 °C) and high catalyst loading in solution (1 mol%).

On this issue, immobilization of homogeneous catalysts over solid supports emerges as an alternative to bridge the advantages of both the homogeneous catalysts (high conversion, high selectivity, low mass transfer limitations) and those of their heterogeneous counterparts (easy to recover and reuse, low catalyst losses, high-temperature resistance). Highly dispersed metal catalysts,¹⁵–¹⁷ either of metal atom species or metal clusters, on nanostructured supports provide an attractive platform for immobilizing homogeneous catalysts with high catalytic performance.¹⁸,¹⁹ This novel class of catalysts presents better catalytic activity and selectivity than those based on conventional supported metal nanoparticles because all metal atoms can be available to participate in the catalytic process. Consequently, the utilization efficiency of the metal catalyst can be greatly improved, and the selectivity towards a desired product molecule can be modulated by finely adjusting the adsorption/desorption of active species.²⁰ Furthermore, the atomic metal dispersion can not only provide an understanding of the catalytic reactions at the atomic scale but also can contribute to the design of novel industrial catalysts and explore new mechanisms.

Nevertheless, when the metal particles size is reduced to the atomic level, the resulting metal atoms tend to aggregate due to their high surface energy. As a result, the density of the active sites in the catalyst is decreased and therefore its catalytic performance is hindered.²¹ In this regard, great efforts have been devoted to preserve the dispersion of the active metal species and to prevent their inherent aggregation. Typically, reducing the metal loading to an extremely low level, favours both the metal dispersion and the cost of the catalyst, however, in order to increase the number of active sites, a high metal content is desired. In practice, wet chemistry methods result in metal loadings from 0.1 to 1.0 wt.%,²²–²⁴ while metal contents above 1.0 wt.% have been challenging to satisfy, mainly due to the inherent aggregation of such metal atoms.²⁵

Preparation of supported catalysts with a remarkable dispersion of ultra-small metal nanoparticles and narrow particle size distribution, have been achieved by a strong electrostatic adsorption (SEA) approach over a wide variety of oxides and carbon substrates.²⁶–²⁸ In this method, the surface charge of the support is modulated as a function of pH relative to its point of zero charge (PZC), in order to attain the maximum electrostatic interaction with the metal precursor (often a metal complex). Once the pH of strongest interaction is optimized, the oppositely charged metal precursor adsorbs in a well-dispersed monolayer over the support and the high dispersion can be retained even after the precursor is reduced to the metallic state. Strong metal–support interaction is crucial to prevent aggregation of isolated single atoms. Metal complexation with organic ligands has become a valuable strategy to stabilize metal atoms without affecting their oxidation state.²⁹,³⁰ Such organic ligands not only prevent metals aggregation by steric hindrance but also can serve as binding agents to anchor the metals to the substrate.³¹ Moreover, organic ligands can steer the catalysis towards a desirable product molecule thereby tuning both the activity and selectivity of the metal-based catalyst. In particular, phosphine-based ligands like DPEphos, PPh₃ and Xantphos have been widely explored in the decarboxylative dehydrogenation of fatty acids to obtain α-olefins.³²–³⁵ When considering the material support for immobilizing highly dispersed metal complexes, carbonaceous nanomaterials such as graphene, carbon nanotubes and carbon nanofibers seem to be promising candidates.²⁹–³¹ Recently, several works have focused on the atomic metal dispersion over carbon substrates, rather than on conventional metal oxides, since the deactivation of the catalytic metal species due to direct covalent bonding with the support can be avoided.²⁵,³²,³³ Specially, functionalized carbon nanofibers (CNFs) have been found to provide both a fine and very high dispersion of anchoring sites, which allows a good dispersion of the catalytic metal species.³⁴,³⁵ In addition, the low atomic weight of carbon substrates favours the electron microscopy observation of metallic atoms having higher atomic weight.

In this work we describe the successful synthesis and characterization of an innovative catalytic system based on a highly dispersed palladium complex on CNFs. For this, active palladium species were first stabilized by complexation with anthracenilic acid as organic ligand and then the resulting [Pd₂An₂Cl₂] complex was immobilized on acyl chlorinated CNFs by incipient wetness impregnation using ethanol (EOH) or N,N-dimethyl formamide (DMF) as a solvent. Once the [Pd₂An₂Cl₂] complex is obtained, its immobilization over CNFs is a standard protocol to chemically anchor organometallic complexes on carbon substrates without affecting their electronic structure.³⁶,³⁷ This provides a strong amide bonding between the metal complex and the CNF support and allows a better stability of the complex. The catalytic performance of the obtained catalysts was further evaluated in the selective decarboxylation of stearic acid to 1-heptadecene under mild reaction conditions (atmospheric pressure, 110–220 °C) with a low catalyst loading in solution (0.14 mol% Pd).

**Experimental**

**Preparation of supported [Pd₂An₂Cl₂] complex catalysts**

All chemical reagents used were analytical grade and purchased from Sigma-Aldrich® corporation. Highly dispersed palladium on carbon nanofibers catalysts were prepared by incipient wetness impregnation of a [Pd₂(An)₂Cl₂], using ethanol or N,N-dimethyl formamide (DMF) as solvent.
Prior to the impregnation, \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex was synthesized using \(\text{PdCl}_2\) as metal precursor and arcanilic acid (AA) as a ligand. For this, 0.5 g of AA was melted at 150 °C and then 0.7 g of \(\text{PdCl}_2\) were added in equimolar ratio \(\text{PdCl}_2\):AA under \(\text{N}_2\) atmosphere to avoid the palladium oxidation. After mixing, the molten solid was dissolved in 50 ml of EtOH:H\(_2\)O (2:1 vol.) and the solution was stirred at 94 °C during 48 h, maintaining the \(\text{N}_2\) atmosphere. The resulting greenish compound was recovered by filtration and washed sequentially with copious amounts of EtOH:H\(_2\)O (2:1 vol.). Later, the solid \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex was dried in a vacuum oven at 60 °C overnight.

CNFs were prepared by catalytic decomposition of synthetic biogas (CH\(_2\)\(_3\):CO\(_2\) 50:50 v/v) over a Ni:Co:Al catalyst (33.3:33.3:33; wt.%) in a rotatory bed reactor at 650 °C using a weight hourly space velocity WHSV=30 L/(gcat-h).\(^{38}\) As-produced CNFs were purified by sonication with HCl (37%) at 60 °C during 4 h, washed with deionized water and dried overnight at 60 °C. The purified CNFs were subsequently functionalized with acyl chloride (-COCl) groups to serve as anchor sites for the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex. As shown in Scheme 1, carboxylic groups (-COOH) were first incorporated on the CNFs surface by refluxing in HNO\(_3\)/H\(_2\)SO\(_4\) (1:1 vol.) at 120 °C for 1 h. The treated CNF-COOH was recovered by filtration, washed with MQ-water until pH=7 and dried in a vacuum oven at 120 °C for 1 h. Afterward, the surface CNF-COOH was further transformed into acyl chloride groups by reaction with thionyl chloride (SOCl\(_2\)) in a rotatory bed reactor according to the procedure described by Le Nôtre and co-workers.\(^{9}\) Once the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex was dissolved in EtOH or DMF and then added dropwise to the modified CNF-COCl, in order to obtain a final Pd content of 1.5 wt.%, a relatively high metal loading considering the catalyst weight.\(^{22-25}\) The Pd amount (mol% Pd) loaded into the reactor was calculated regarding the number moles of starting stearic acid as follow:

\[
mol \text{ %Pd} = \frac{\text{wt. % Pd} \times g \text{ catalyst} / \mu_{\text{Pd}}}{n_{\text{SA}}} \times 100 (1)
\]

Where, wt. % Pd is the Pd content of the catalyst measured by ICP-OES spectroscopy, \(\mu_{\text{Pd}}\) stands for the molar mass of Pd and \(n_{\text{SA}}\) corresponds to the starting number of moles of stearic acid.
Quantification and identification of the liquid products were conducted in a CLARUS 580 (Perkin Elmer) gas chromatograph (GC) equipped with an FID detector (330 °C) and a 30 m length/250 µm diameter Elite-S column (CrossbondTM: 5% diphenyl-95% dimethylpolysiloxane). Due to the high polarity of the unreacted SA, a previous derivatization procedure was carried out to prevent its retention in the GC column. For this, the as-resultant liquid product was heated at 60 °C during 1 h under a N₂ stream to evaporate the AcOH formed during the decarbonylation reaction. Then, N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) was added in a ratio of 0.270 mL/mL liquid product, and the mixture was heated again at 60 °C during 1 h. This procedure allows the reaction between the hydroxyl group of the stearic acid and the BSTFA to form trimethylsilyl stearate, which is a less polar compound and elutes more easily through the column. Finally, the catalyst was removed by a 0.22 µm syringe filter and the amber coloured liquid was placed into a vial for GC analysis.

Chemical identification of the products was performed by matching the GC retention times with known standards, whereas the quantitative analysis was carried out using calibration curves of each compound. Due to the low solubility of the unreacted stearic acid at room temperature in DMPU, its calibration curves of each component were used to quantify the amount of the compound in moles. Selectivity towards 1-heptadecene and 2-heptadecene as reaction products (Gas chromatography—mass spectrometry, Varian GC 3800/Saturn 2200 MS), the SA conversion was calculated as the sum of yields to both products as shown in Eq. (2):

\[
\text{Yield (mol %)} = \frac{\sum a \cdot n_{\text{Product}}}{n_{\text{SAfeed}}}
\]

Where \(a\) stands for the stoichiometric coefficient and \(n\) is the amount of the compound in moles. Selectivity towards 1-heptadecene was calculated as the molar ratio between the obtained amount of 1-heptadecane and the sum of 1-heptadecane (1-hept) and 2-heptadecane (2-hept), as follows:

\[
\text{Selectivity}_{1-\text{hept}} \quad (\text{mol %}) = \frac{n_{\text{1-hept}}}{n_{\text{1-hept}} + n_{\text{2-hept}}}
\]

The catalytic activity of the prepared catalysts was calculated by the turnover number (TON) to the total of products, as shown in Eq. (4):

\[
\text{TON} = \frac{\text{Conversion}_{n_{\text{Pd}}} \times n_{\text{SAfeed}}}{n_{\text{Pd}}}
\]

Herein, the total number of moles of palladium in the catalyst (\(n_{\text{Pd}}\)) was calculated by inductively coupled plasma optical emission spectrometry (ICP-OES), since it is assumed that all the Pd species are accessible active sites.

**Materials characterization**

Elemental analysis (EA) of C, N, H, O was measured in a Thermo Flash 1112 furnace with a detection limit of 0.05 wt.%. Pd content was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Spectroblue (AMETEK) analyser, using the sodium peroxide fusion procedure to dilute the samples.

Chemical surface composition was characterized by X-Ray photoelectron spectroscopy (XPS) in an ESCAPlus (OMICROM) spectrometer using non-monochromatized MgKa radiation (hν = 1486.7 eV). All the spectra were analysed in the CASA® XPS software by applying a Shirley-type background.

Crystalline phase identification was carried out by powder x-ray diffraction (XRD) in a Bruker D8 Advance diffractometer operated with Ni-filtered CuKa radiation (λ = 1.5406 Å). XRD patterns were recorded from 10° to 80° 28 degrees with a step size of 0.05° and were analysed in the DIFRAC Plus EVA 8.0 software. Crystallite size calculations were performed by fitting the XRD patterns in TOPAS® software applying Rietveld analysis (LVol-IB, volume averaged column height calculated from the integral breadth).

Porosity and specific surface areas were obtained from N₂-physisorption at 77 K using a Micrometrics ASAP2020 instrument. Prior to the analysis, the samples were degassed at 150 °C for 5 h. Specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) equation in the p/p₀ range of 0.01–0.10. Micropore volume was estimated by the t-plot method using the Harkins y Hura thickness equation. Total pore volume was obtained at the maximum relative pressure reached by the adsorption branch (p/p₀ > 0.989).

Chemical bonds identification was performed by Fourier transform infrared (FTIR) and Raman spectroscopies. FTIR spectra were collected in a VERTEX 70 (Bruker) spectrometer from 400 to 4000 cm⁻¹ with a resolution of 1.9 cm⁻¹. Raman spectra were recorded using a Horiba Jobin-Yvon HR8800 UV confocal microscope, with a 532 nm laser excitation beam.

Nuclear magnetic resonance (NMR) spectroscopy was used to elucidate the molecular structure of the [Pd₂(An)₂Cl₄] complex synthesized. ¹H NMR spectra of both the [Pd₂(An)₂Cl₄] complex and the free anthranilic acid were recorded in acetone-\(d₆\) on a Bruker Avance 400 MHz instrument, by using the standard reference SiMe₄ (δH). Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively and the signal assignments were based on ¹H-¹H COSY experiments.

High-resolution scanning transmission electron microscopy (HR-STEM) was used to determine the morphology, size and dispersion of the palladium species impregnated over the CNFs. Micrographs images were taken in a FEI Titan Low-Base 60–300 STEM microscope (Advanced Microscopy Laboratory-LMA, INA) equipped with a Cs-probe corrector (CESCO-0.09 nm spatial resolution, CEOS GmbH) and a high-angle annular dark-field imaging (HAADF) detector. Before imaging, samples were dispersed on amorphous carbon-coated copper grids and then...
exposed to an electron beam shower during 20 min in order to remove any organic contamination. In some cases, an additional plasma cleaning for 1.5 seconds was used. In addition, energy-dispersive x-ray (EDX) spectroscopy was used to obtain qualitative information about the chemical composition of the particles identified.

Recyclability and leaching tests

Catalyst stability and its utilization efficiency were evaluated by recovering the catalyst and reusing it several times in the SA decarbonylation reaction at 140 °C. To facilitate the recycling of the catalyst, the reaction was scaled up to 40 mg catalyst. Immediately the reaction was finished, a small portion of the resultant liquid product was saved for GC-MS analysis. The other portion was mixed with an equal volume of anhydrous toluene (99.8%, Sigma-Aldrich) to dissolve the unreacted SA and then the solid catalyst was separated and recovered by centrifugation at 9500 rpm during 2 h at 20 °C. After supernatant removal, the catalyst was washed with anhydrous toluene and dried overnight at 60 °C in a vacuum oven. The as-recovered catalyst was repeatedly used in the SA decarbonylation reaction, without introducing fresh catalyst to the reactive liquid medium. The proportion of the reactants SA, groups from the anthranilate ligand forming two six-membered chelate rings bridged by two chloride atoms.

Results and discussion

[Pd2(An)2Cl4] complex characterization

Chemical structure of the synthesized di-µ-chloro-Bis[palladium(II) anthranilate] complex was investigated by a large set of analysis techniques including 1H-NMR, FTIR, Raman spectroscopy, X-ray diffraction and XPS spectroscopy. Scheme 3 presents the chemical structure of the [Pd2(An)2Cl4] complex suggested by the characterisation results detailed hereafter, which is consistent with similar compounds reported in the literature.40 Accordingly, this binuclear the palladium complex involves the coordination with the amino and carboxylate groups from the anthranilate ligand forming two six-membered chelate rings bridged by two chlorine atoms.

Further information about the chemical bonding in the palladium complex was obtained by IR spectroscopy. Fig. 2 presents the near- and mid-infrared spectra of the free anthranilic acid and the [Pd2(An)2Cl4] complex. Anthranilic acid exhibited a very rich set of signals in the infrared range evaluated. The characteristic stretching frequencies of ν(C=O) and ν(C–O) were detected at 1670 cm⁻¹ and 1370 cm⁻¹, respectively. Interestingly, the ν(OH) stretching and δ(OH) bending vibrations from the carboxylic acid (-COOH) were identified at 2534 cm⁻¹ and 935 cm⁻¹.41 However, upon palladium complexation, these signals disappeared and two new peaks corresponding to the νas(COO⁻) antisymmetric and the νs(COO⁻) symmetric stretching vibrations emerged at 1610 and 1419 cm⁻¹, respectively.42 This suggests that the ionized carboxylate group (COO⁻) might be involved in the coordination of the palladium centre by deprotonation of the -COOH from the anthranilic acid.43 According to Nakamoto,44 the separation between νas(COO⁻) and νs(COO⁻) vibrations (denoted as ∆νas-s) gives information about the interaction between the COO⁻ group and the metal atom. When ∆νas-s-Values are larger than those of the ionic form of the free ligand, a monodentate coordination mode occurs as in the case of the [Pd2(An)2Cl4] complex synthesized in this work (∆νas-s-Pd complex=191 > ∆νas-s Sodium anthranilate=135).45 The δ(NH2) bending and ν(C-}

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After complexation of palladium with anthranilic acid, the former peaks became less intense and more symmetrical, which is related to the shortening of such Pd-Cl chains.\(^{48}\) In the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) spectrum, besides the Pd–Cl vibration, the Pd–O,\(^{49}\) \(v_\text{Pd–N}\),\(^{50}\) \(\delta_\text{Pd–NH}\),\(^{50}\) and \(v_{\text{as}(\text{COO})}\)\(^{51}\) modes were also identified at 426, 628, 1048 and 1571 cm\(^{-1}\), respectively. These vibration modes agree with those observed in the FTIR analysis and support the proposed chemical structure of the metal complex depicted in Scheme 3.

### Table 1: Chemical analysis of the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex.

| Elemental Analysis (wt. %)* | ICP-OES (wt. %) | XPS (at. %) |
|-----------------------------|-----------------|-------------|
| C  21.2                      | 1.7             | 55.9        |
| H  3.4                       | 3.4             | 10.3        |
| N  50.0                      | 4.9             | 4.1         |
| Pd 50.0                      | 38.3            | 6.97        |
| Cl  1.7                      | 5.0             | 8.9         |

*In parenthesis the wt.% calculated from the molar mass (Mw= 556 g/mol) of the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex is indicated.

Chemical analysis data of the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex conducted by elemental analysis, ICP-OES and XPS are summarized in Table 1. Interestingly, the relative content of C, H and N was lower than that calculated from the chemical formula of the complex, whereas the palladium content resulted to be higher. This result can be due to the anthranilic acid was partially displaced from the Pd coordination sphere by the EtOH:H\(_2\)O mixture used during the washing process. As a result, in addition to the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex, some non-coordinated Pd particles could be retained in the filter while the anthranilic acid passed through it. This fact was corroborated by elemental analysis of the yellow-colored filtrate in which some traces of anthranilic acid were identified (43.6 wt.% C, 3.95 wt.% H, 9.78 wt.% N). The formation of Pd particles might be also due to after synthesis the anthranilate ligand was oxidized by contact with air, promoting the palladium reduction.\(^{42}\)

XPS spectrum in Fig. 4 shows the Pd 3d\(_{5/2}\), 3d\(_{3/2}\) doublet of the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex with a spin-orbital splitting of 5.3 eV and an intensity ratio \(I_{3d_{5/2}}/I_{3d_{3/2}}=1.5\). Upon deconvolution of the 3d doublet, three different Pd species could be detected. Besides

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**Journal Name**

**Fig. 3** Raman spectra of \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex and its basic constituents, anthranilic acid and PdCl\(_2\).

**Fig. 4** XPS spectrum of Pd 3d\(_{5/2}\), 3d\(_{3/2}\) for the synthesized \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex.

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For comparison purposes, Fig. 3 shows the Raman spectra of the \([\text{Pd}(\text{An})_2\text{Cl}]_2\) complex and its basic constituents, anthranilic acid and PdCl\(_2\). The free anthranilic acid exhibited sharp and high-intensity peaks along the recorded spectrum. Besides its characteristic Raman frequencies, a strong peak related to the lattice vibration was observed at 142 cm\(^{-1}\) indicating its crystalline nature.\(^{47}\) PdCl\(_2\) showed an intense band comprised by two peaks at 265 cm\(^{-1}\) and 310 cm\(^{-1}\), corresponding to the symmetric and antisymmetric stretching of Pd–Cl bonds, respectively.\(^{47}\) The low-intensity \(\delta_\text{Pd–Cl}\) mode was also observed at 144 cm\(^{-1}\), which is due to the restrained number of terminal Pd–Cl stretches in the “infinite” chain configuration of the pure a-PdCl\(_2\).\(^{48}\)

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**6 | J. Name., 2012, 00, 1-3**

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the low intensity metallic Pd\textsuperscript{0} 3d\textsubscript{5/2} band, centred at 334.1 eV, two signals corresponding to the Pd\textsuperscript{2+} state were identified at 337.1 eV and 338.5 eV, respectively. The first one was associated with the Pd–Cl bond\textsuperscript{52,53} while the second one was ascribed to the Pd–N bond contribution\textsuperscript{54,55}.

Catalysts characterization
AnPd/CNF catalysts prepared either with EtOH or DMF were characterized in order to determine their physical and chemical surface properties. Table 2 summarizes the chemical analysis composition of the prepared materials, performed by EA, ICP-OES and XPS. Both catalysts impregnated with DMF and EtOH exhibited a palladium content around 1.5 wt.\%, which is consistent with the nominal amount incorporated. Upon impregnation, the relative content of C, H and N in the CNF-COCI support was not greatly affected due to the low amount of [Pd\textsubscript{2}(An)\textsubscript{2}Cl\textsubscript{2}] complex incorporated. Nevertheless, some differences in the surface chemical composition of the catalysts were observed by XPS. The AnPd/CNF (EtOH) exhibited a higher surface Pd content and lower atomic percentages of C, O and N than AnPd/CNF (DMF). This result can be attributed to the anthranilic acid was partially displaced from the complex coordination sphere during impregnation, thereby leaving some non-coordinated Pd particles over the CNF-COCI support.

![XPS spectra of impregnated catalysts](image)

**Fig. 6** Pd 3d XPS spectra of the impregnated catalysts, (a) AnPd/CNF (EtOH) and (b) AnPd/CNF (DMF).

**Table 2** Chemical analysis of the prepared materials.

| Sample        | Elemental Analysis (wt.%) | ICP-OES (wt.%) | XPS (at.%) |
|---------------|---------------------------|----------------|------------|
|               | % C % H % N | % Pd % C % O % N % Cl % Pd |               |
| CNF-COCI support | 92.6 0.4 0.8 | 0.00 92.3 7.0 0.4 0.38 0.00 |               |
| AnPd/CNF (DMF)  | 92.8 0.5 0.9 | 1.50 88.6 8.4 1.2 1.43 0.42 |               |
| AnPd/CNF (EtOH) | 93.1 0.4 0.6 | 1.49 89.8 7.7 0.6 0.55 1.34 |               |
Fig. 7 Powder XRD patterns of the AnPd/CNF catalysts and the CNF-COCl support.

XRD patterns of the AnPd/CNF catalysts and the CNF-COCl support are shown in Fig. 7. All patterns showed a high intense peak at 26° and two weak peaks at 43° and 45° 2θ degrees, assigned to the (002), (100) and (101) reflections of the graphitic carbon (PDF file 75-2078), respectively. Additionally, the reflections peaks of the face-centred cubic crystal structure of Pd(0) (PDF file 88-2335) were also present in the pattern of the impregnated catalysts. The mean crystallite size of such Pd(0) particles calculated by applying Rietveld analysis (LVol-IB, TOPAS® software) was 9.3 nm for the AnPd/CNF (EtOH) and 12.1 nm for the AnPd/CNF (DMF) catalyst. These nanoparticles could have been formed either during the impregnation of CNF-COCl or during the synthesis of the [Pd₂(An)₂Cl₂] complex, as discussed before.

Further information about the chemical interaction between the [Pd₂(An)₂Cl₂] complex and the catalysts was obtained from the FTIR spectra shown in Fig. 8. Either the CNF-COCl support or the impregnated catalysts exhibited two weak bands at 1760 cm⁻¹ and 660 cm⁻¹ corresponding to the acetyl chloride ν(-COCl) and the νas (C-Cl) stretching vibrations, respectively. After complex impregnation, a new broad band emerged at 1190 cm⁻¹, which is due to C-N stretching of the amide group. This suggests that [Pd₂(An)₂Cl₂] complex is anchored to the CNF-COCl support through amide bonding as shown in Scheme 4.

Fig. 8 FTIR spectra of the synthesized materials.

Accordingly, acyl chloride (-COCl) groups serve as anchor sites, which form amide linkages with the [Pd₂(An)₂Cl₂] complex through a nucleophilic addition/elimination reaction during the impregnation process.

HR-STEM was used to determine the size, morphology, and dispersion of the palladium species impregnated over the CNFs. Fig. 10 shows the HAADF-STEM images of the AnPd/CNF catalysts at different magnifications. Particle counting measurements of different areas allowed to estimate the average size of the Pd particles observed as bright spots in the HAADF-STEM images. Three different groups of particles were observed, Pd sub-nanometric nanoparticles (yellow circles), Pd clusters (blue circles) and large Pd aggregates (red circles). AnPd/CNF (DMF) showed a well dispersed Pd sub-nanometric particles of ca. 0.7 nm and a high number of Pd clusters about 1.1 nm. A few amounts of Pd aggregates comprising primary particles of ca. 21.7 nm was also observed. Conversely, AnPd/CNF (EtOH) presented a lower dispersion of both Pd sub-nanometric particles and Pd clusters than AnPd/CNF (DMF), resulting in CNFs with large naked areas and bulky Pd aggregates with primary particles around 33.6 nm. In this catalyst, only a small amount of ca. 0.2 nm Pd sub-nanometric particles and Pd clusters of about 1.3 nm could be observed.
(up) Anchoring between the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex and the CNF-COCI support and (down) Nucleophilic addition/elimination in the reaction between acyl chlorides and amines.

Anchoring between the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex and the CNF-COCI support and nucleophilic addition/elimination in the reaction between acyl chlorides and amines.

Scheme 4

Here, a better dispersion of subnanometric particles was related to a higher population of \([\text{Pd}_2\text{An}_2\text{Cl}_2]\) species, instead of the large aggregates in which Pd crystals were identified (Fig. S4† and S5†). The bigger particle size obtained by STEM compared with XRD crystallite size might due to the presence of large palladium aggregates with different crystallite sizes.

In line with the characterization results, the differences observed in the dispersion of the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex may be attributed to a solvent effect. The EtOH, which is a polar protic solvent, might de-coordinate the Pd centre by displacing the anthranilic acid ligand, as well as, it might react with the acyl chloride (-COCl) groups on the CNF-COCI surface by a nucleophilic addition/elimination reaction (Scheme 5), blocking the anchoring sites for the complex impregnation thereby restraining its dispersion.

Additionally, the materials were analysed by Raman spectroscopy, as is shown in Fig. 9. Both the catalysts and the bare CNF-COCI support exhibited the characteristic strong G (1576 cm\(^{-1}\)) and D (1345 cm\(^{-1}\)) bands, attributed to the in-plane vibration of the sp\(^2\) bonds and the disorder degree in the sp\(^3\)-hybridized structure, respectively. Others less intense bands were also detected from 2350 to 3000 cm\(^{-1}\), which are related to the overtones and combinations among the D, G, and D’ modes.\(^5\)\(^9\) The relative intensity between the D and G band (I\(_D\)/I\(_G\)) is often associated with the density of defects occurring due to sp\(^3\) hybridization of the carbonaceous framework. Since Raman scattering is strongly sensitive to the electronic structure of the CNFs, a change in the I\(_D\)/I\(_G\) ratio can be related with structural modifications derived from the complex immobilization.\(^6\)\(^0\) After impregnation with \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex, the relative intensity of the D band was increased in both catalysts, which reflects the chemical interaction between the complex and the CNF-COCI support. Interestingly, the I\(_D\)/I\(_G\) ratio of AnPd/CNF (DMF) was slightly higher than that of the AnPd/CNF (EtOH) catalyst, which suggests that, when impregnating with DMF, the functionalization degree of the AnPd/CNF (DMF) could be higher than when EtOH was used as a solvent.
Selective decarbonylation of stearic acid to 1-heptadecene

Highly dispersed AnPd/CNF catalysts were tested in the selective decarbonylation of stearic acid to produce 1-heptadecene. The influence of the impregnation solvent and the reaction temperature on the catalytic performance of the prepared materials is summarized in Table 4. For comparison purposes, a homogeneous reaction was performed using the unsupported \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex with a Pd loading of 5 mol% under the same reaction conditions (entry 1). The AnPd/CNF catalyst prepared with EtOH exhibited the lowest catalytic performance with a selectivity to 1-heptadecene of 54 mol%, a yield of 0.5 mol% and a TON=4 (entry 2). However, when the aprotic solvent DMF was used for the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex impregnation, the activity and selectivity were notably increased to TON=18 and 87 mol%, respectively, achieving values close to the unsupported \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex catalysed reaction with a yield of 2.6 mol% (entry 3). This enhancement in the catalytic performance can be attributed to the high palladium dispersion in the AnPd/CNF (DMF) catalyst. Since the \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex was more homogeneously dispersed in AnPd/CNF (DMF) than in the case of AnPd/CNF (EtOH) (Fig. 10), this catalyst may contain a higher number of active palladium atoms on the surface available to participate in the catalytic process.

Table 4 Comparison among the palladium-based catalytic systems for the decarbonylation of stearic acid to 1-heptadecene used in this work and some similar ones reported in the literature.

| Entry | Palladium catalyst | Catalytic system | Pd loading (mol %) | T (°C) | yield (mol %) | 1-hept select. (mol %) | TON | TOF (h\(^{-1}\)) | Reference |
|-------|---------------------|------------------|-------------------|-------|--------------|----------------------|-----|----------------|-----------|
| 1     | \([\text{Pd}_2(\text{An})_2\text{Cl}_2]\) complex | Homogeneous precatalyst | 5.00 | 110 | 90 | 97 | 18 | 1.0 | This work \(\text{d}\) |
| 2     | AnPd/CNF (EtOH) | Homogeneous precatalyst supported on CNFs | 0.14 | 110 | 0.5 | 54 | 4 | 0.2 | This work \(\text{d}\) |
| 3     | AnPd/CNF (DMF) | Homogeneous precatalyst supported on CNFs | 0.14 | 110 | 2.6 | 87 | 18 | 1.0 | This work \(\text{d}\) |
| 4     | CNF-COCI support | --- | 0 | 110 | 0.1 | 75 | 0 | 0 | This work \(\text{d}\) |
| 5     | AnPd/CNF (DMF) | Homogeneous precatalyst supported on CNFs | 0.14 | 125 | 3.4 | 86 | 23 | 1.3 | This work \(\text{d}\) |
| 6     | AnPd/CNF (DMF) | Homogeneous precatalyst supported on CNFs | 0.14 | 140 | 71 | 90 | 484 | 26.9 | This work \(\text{d}\) |
| 7     | AnPd/CNF (DMF) | Homogeneous precatalyst supported on CNFs | 0.14 | 180 | 72 | 92 | 495 | 27.5 | This work \(\text{d}\) |
| 8     | AnPd/CNF (DMF) | Homogeneous precatalyst supported on CNFs | 0.14 | 220 | 61 | 89 | 423 | 23.5 | This work \(\text{d}\) |
Regarding the CNF-COCl support, it was observed that it does not have any catalytic activity for the decarbonylation reaction (entry 4). Aiming to improve the catalytic performance of the AnPd/CNF (DMF) catalyst in the decarbonylation of SA, the reaction temperature was varied from 110 °C to 220 °C. Both the yield and the catalytic activity were improved by increasing the reaction temperature, while the selectivity to 1-heptadecene was ranged from 86 mol% to 92 mol%, without significant variations (entries 3, 5–8). A prominent enhancement in the yield and TON was registered at 140 °C, reaching values as high as 71 mol% and 484, respectively (entry 6), even much higher than those obtained during the homogenous catalysis with the unsupported \( \text{Pd}_2(\text{An})_3\text{Cl}_3 \) complex at 110 °C (entry 1). A further increasing of 35 °C in the reaction temperature caused only a slight increase of 11 units in the TON (entry 7). However, when the temperature was raised to 220 °C, the yield and the TON were decreased to 61 mol% and 423 (entry 8). This can be due to thermal degradation of the \( \text{Pd}_2(\text{An})_3\text{Cl}_3 \) complex or formation of off-cycle species that reduce the AnPd/CNF (DMF) catalyst activity.\(^6,\(^6\)\(^3\)\)

In order to elucidate the catalytic activity of the Pd aggregates observed in the catalysts, the decarbonylation reaction was carried out at 180 °C using a previously reported heterogeneous catalyst comprised of 0.6 wt.% Pd nanoparticles of around 2.5 nm supported on a carboxylated CNF-COOH (Fig. S6\(^\text{f}\)).\(^6\)\(^4\) The prepared 0.6%Pd/CNF catalyst exhibited an extremely low yield of 7.6 mol% (entry 9) when compared with the supported AnPd/CNF (DMF) catalyst (72 mol% of SA conversion yield) under the same reaction conditions (entry 7). This result demonstrates that Pd(0) nanoparticles have a low contribution to the catalytic process while the dispersed \( \text{Pd}_2(\text{An}_2\text{Cl})_3 \) complex is the most active phase responsible for the decarbonylation reaction.

In a similar homogeneous \( \text{PdCl}_2(\text{triphenylphosphine})_2 \) catalysed decarbonylation reaction, Liu and co-workers\(^5\) achieved a surprising TON= 1338 under very low Pd loading (0.05 mol%), with close values of yield and selectivity (entry 11). Nevertheless, in order to promote the reactivity and to ensure the \( \alpha \)-selectivity, this reaction required acidic additives like (t-Bu)\(_2\)biphenol and a portion-wise addition of AcOH every 30 min with sequential distillation of the formed AcOH, making the process certainly laborious.

On the other hand, the extraordinary performance of the AnPd/CNF (DMF) catalyst developed in this work is an interesting achievement since the decarbonylation reaction was performed under relatively mild operation conditions (atmospheric pressure and 140 °C) with very low Pd loadings in solution (0.14 mol%). For instance, this catalyst attained an activity (TON=484, TOF=26.9) almost three times higher than a homogeneous precursor comprising of \( \text{Pd}-(\text{cinnamyl})\text{Cl} \) (DPEPhos) (entry 12). Even more, when comparing with a heterogeneous 10 wt.% Pd/C catalyst, evaluated under the same reaction strategy and reactants, we could obtain a superior TON= 484, with similar values of yield and \( \alpha \)-selectivity using an 85 mol% lower palladium loading in solution (entry 13). This result highlights the exceptional catalytic performance of such catalysts containing the active phase in a subnanometric dispersion state, compared to conventional homogeneous and heterogeneous catalysts.
The widely accepted reaction mechanism for the fatty acid decarbonylation to linear \( \alpha \)-olefins via palladium-based catalysts is depicted in Scheme 6.\textsuperscript{4, 14} The reaction is presumed to start with the formation of a mixed anhydride between the carboxylic group of the fatty acid and the sacrificial anhydride (Ac\(_2\)O). This mixed anhydride leads to the oxidation of the active Pd(0) centres by oxidative addition, giving Pd(II) carboxylate species (i). Next, the carboxylate ligand undergoes decarbonylation to generate alkylpalladium(II) releasing carbon monoxide (ii). Finally, the catalytic cycle is completed by the \( \beta \)-hydride elimination of the alkyl ligand to deliver the olefin product (iii) and the subsequent regeneration of the active Pd(0) catalyst (iv).

In order to determine the stability and utilization efficiency of the catalysts developed in this work, AnPd/CNF (DMF) was selected for leaching and recyclability studies due to its high catalytic performance. The catalyst was separated from the liquid product by centrifugation at 9500 rpm during 2h at 20 °C, resulting in a recovery efficiency of about 80% with respect to the initial amount of catalyst incorporated. The recovered catalyst was evaluated again in the SA decarbonylation reaction at 140 °C. Table 5 summarizes the performance of the AnPd/CNF-DI (DMF) catalyst after four reutilization tests. The yield was maintained up to the 3\textsuperscript{rd} cycle (ca. 17%) although a 18% yield decrease was observed after the 4\textsuperscript{th} cycle involving a TON decrease from 129 (TOF=7.2 h\(^{-1}\)) to 86.9 (TOF=4.8 h\(^{-1}\)). Interestingly, the selectivity to 1-heptadecene was maintained in ca. 90 mol% in all cycles. It is important to point out that, aiming to facilitate the recovering of the catalyst, the amount of reactants in the recyclability tests was 4-fold scaled regarding the standard experiments summarized in Table 4. However, although the reaction was scaled up, the molar proportion of each component was retained and the yield of the fresh catalyst in the first cycle of the recycling tests (cycle 1, Table 5) was about 1/4 of that of the standard test (entry 6, Table 4), under the same operating conditions (140 °C, 18 h). This fact may be tentatively assigned to diffusion problems due to the limited dimension of the reaction tube. Temperature gradients along
the reactor cannot be discarded. More efforts should be done in order to improve the reaction in larger-scale reactors, although the results presented inhere evidence the high stability of the catalyst.

Table 5 Recyclability test of the AnPd/CNF-DI (DMF) catalyst for the SA decarbonylation reaction at 140 °C.

| Entry | AnPd/CNF-DI (DMF) catalyst | yield (mol%) | 1-hept select. (mol%) | TON | TOF (h⁻¹) |
|-------|-----------------------------|--------------|-----------------------|-----|-----------|
| 1    | Cycle 1: Fresh catalyst     | 16.8         | 92                    | 129 | 7.2       |
| 2    | Cycle 2: recovered catalyst | 17.0         | 90                    | 129 | 7.2       |
| 3    | Cycle 3: recovered catalyst | 17.3         | 92                    | 131 | 7.3       |
| 4    | Cycle 4: recovered catalyst | 12.0         | 90                    | 87  | 4.8       |

Conditions: 40 mg AnPd/CNF catalyst (1.5 wt.% Pd), 4 mmol stearic acid, 8 mmol Ac₂O, 16 mL DMPU, 0.36 mmol DPE-phosphine, 4 mmol Et₃N, Final volume of reaction= 18 mL. 18 h reaction time, 140 °C.

The heterogeneity of the catalytic system was evaluated by measuring the leaching of Pd species from the recovered AnPd/CNF (DMF) catalyst after the first reutilization cycle. Table 6 summarizes the chemical composition of the AnPd/CNF (DMF) catalyst before and after reaction.

Table 6 Chemical analysis of the AnPd/CNF (DMF) catalyst before and after reaction.

| Sample            | Elemental Analysis (wt.%) | ICP-ES (wt.%) | XPS (at.%) |
|-------------------|---------------------------|---------------|------------|
|                   | % C  | % H  | % N  | % Pd | % C  | % O  | % N  | % Cl  | % Pd |
| Fresh AnPd/CNF (DMF) | 92.8 | 0.5  | 0.9  | 1.50 | 88.6 | 8.4  | 1.2  | 1.4   | 0.4  |
| Used AnPd/CNF (DMF)  | 92.3 | 0.3  | 0.6  | 1.30 | 85.1 | 11.5 | 0.5  | 0.5   | 1.3  |

Fig. 11 Pd 3d XPS spectra of the AnPd/CNF (DMF) catalyst, (a) before and (b) after decarbonylation reaction.

Fig. 12 Powder XRD patterns of the AnPd/CNF (DMF) catalyst before and after decarbonylation reaction.
Similarly, Raman spectrum of the AnPd/CNF (DMF) catalyst was preserved upon decarbonylation reaction, and only a slight decreasing in the I_D/I_G ratio from 1.13 to 1.02 was recorded (Fig. 13). The reduction in the I_D/I_G ratio implies a decrease in the defect degree of the carbonaceous structure of the catalyst support. Considering the mild reaction conditions used during the SA decarbonylation and that the graphitization of the CNF support was nor largely affected (Fig. 12), it can be inferred that this slight reduction in the I_D/I_G ratio was caused by a decrease in the functionalization degree after the leaching of the [Pd_2(An)Cl_2] complex.

Further information about the chemical bonds in the AnPd/CNF (DMF) catalysts was obtained by FTIR spectroscopy (Fig. 14). In order to compare the relative content of functional groups in the catalysts and considering that the graphitic carbon structure of the CNF support was preserved upon reaction (Fig. 12 and 13), the signals were normalized to obtain C=C equal transmittance (1582 cm⁻¹). Upon decarbonylation reaction, the intensity of the peak centred at 3500 cm⁻¹ (related to ν(O–H) and ν(N–H) vibrations) was decreased, while the two peaks centred at 2921 cm⁻¹ and 2850 cm⁻¹ (ascribed to the ν(C–H) vibrations) were increased. Moreover, a notable increase in the intensity of the COOH peak was observed at 1380 cm⁻¹. These results suggest the transformation of the amide anchoring sites –C≡(O)NH–R of the catalyst support into –COOH groups as a result of the [Pd_2(An)_2Cl_2] complex leaching.

On the other hand, the ν(C–N) peak at 1195 cm⁻¹ suffered a splitting into three differenced peaks centred at 1155 cm⁻¹, 1116 cm⁻¹ and 1000 cm⁻¹. This splitting in the ν(C–N) vibration can be related to a change in the electronegativity of the bonding neighbourhood during decarbonylation reaction, in which the closely overlapped bands provide different relative intensity contributions. Particularly, FTIR spectrum of the spent AnPd/CNF (DMF) catalyst shows the generation of several peaks in the region 3500–4000 cm⁻¹. According to Hooke’s law these groups should be related to small atoms strongly bonded. The creation of such strongly bonded functionalities has a high degree of uncertainty, however, they might appear due to adsorption of new functional groups from product remnants moieties on the catalyst surface during reaction.

**Conclusions**

In this work a di-µ-chloro-Bis[palladium(II) anthranilate] complex was successfully synthesized and highly dispersed over acyl chlorinated CNFs by incipient wetness impregnation with different solvents. The use of EtOH as impregnation solvent decreased the palladium dispersion on the AnPd/CNF (EtOH) catalyst, resulting in a material with large naked areas and bulky palladium aggregates. This fact was attributed to the ability of EtOH to displace the anthranilate ligand from the Pd centre and occupy the chlorine anchor sites on the functionalized CNF-COCI support. Consequently, this material exhibited a low catalytic activity during the selective decarbonylation of stearic acid to 1-heptadecene. In contrast, the use of DMF as an impregnation solvent allowed a better dispersion of the palladium species and, therefore, the AnPd/CNF (DMF) catalyst exhibited a better catalytic performance with a selectivity to 1-heptadecene of 87 mol%, a yield of 2.6 mol% and a TON=18 at 110 °C. Interestingly, the increase of the reaction temperature up to 140 °C resulted in a prominent enhancement of the AnPd/CNF (DMF) catalyst activity without a detriment of α-selectivity. The best catalytic performance (90 mol% selectivity, 71 mol% SA conversion, TON=484) was achieved operating the decarbonylation reaction at 140 °C with a very low palladium loading in solution (0.14 mol%). The post-mortem catalyst characterization and the recyclability tests evidenced the high stability of the catalyst. The mild reaction conditions used in this work and the high activity of the developed catalyst represent a step forward for energy and cost savings in the sustainable transformation of fatty acids into valuable chemicals such as linear α-olefins.

**Conflicts of interest**

There are no conflicts to declare.

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