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Tuning Zirconia-Supported Metal Catalysts for Selective One-Step Hydrogenation of Levoglucosenone

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Abstract

Levoglucosenone, directly produced from cellulose-containing residual biomass via pyrolysis treatments, is believed to be a promising bio-renewable platform for both fine and commodity chemicals. In this work, the possibilities given by tuneable catalysts based on Pd and Pt supported on metallic oxides to produce the desired product in the one-pot hydrogenation of levoglucosenone are evaluated. Particularly, the excellent catalytic performance of Pd/ZrO_2 and Pt/ZrO_2 type materials for the synthesis of dihydrolevoglucosenone (or Cyrene) and levoglucosanol, respectively, during the mild hydrogenation of levoglucosenone is demonstrated. In the Cyrene synthesis, the $Pd/t-ZrO_2$ material showed the best catalytic activity compared to other Pd-supported on metallic oxides. This catalyst achieved near 95% yields of Cyrene by working under mild reaction conditions, with very low catalyst loadings ($\approx$3wt%) and using water as solvent. On the other hand, the one-pot hydrogenation of levoglucosenone to levoglucosanol is reported for the first time with a Pt-based heterogenous catalyst (Pt/ZrO_2-mix, yield $\approx$90%), by working at low temperatures and mild H_2 pressures with water as solvent. Comparison of the results attained with other Pt-supported metallic oxides let us to conclude that the metal crystal facets (specifically the 100 facet) play an important role during hydrogenation process to give selectively levoglucosanol. In addition, the stability and re-usability of both catalysts under operation conditions are also evaluated. Finally, catalytic tests including the use of crude bio-liquids obtained from reached-cellulose biomass pyrolysis and containing $\approx$66wt% of levoglucosenone are also assayed, thus demonstrating the possibility of scaling-up the process over these metals supported on zirconia catalysts.

Introduction

Over the last decades, the increasing use of fossil resources has led to their depletion along with an increment in the levels of greenhouse gases (GHG). Therefore, the conversion of alternative, clean and renewable raw materials into fuels and chemicals has become a very interesting way of dealing with global warming and contributing to the diversity of energy sources. Among the many resources being nowadays tested to replace petroleum and natural gas, lignocellulosic biomass stands out as a very promising alternative, especially as the only one which could be used as a source of organic carbon to produce chemicals.[1-3]

Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose, Scheme 1), is believed to be a promising bio-renewable platform for both fine and commodity chemical industries, being especially interesting the new insight provided by Huber and co-workers[4,5] into how to transform this molecule into different high added value products, such as α,ω-diols useful as monomers for the production of polyesters and polyurethanes. Levoglucosenone can be directly produced from cellulose-containing urban and industrial residual materials such as waste paper by means of thermal pyrolysis of acid pre-treated cellulose,[6] microwave assisted pyrolysis,[7] ionic liquid assisted pyrolysis[8-10] and, more recently, heterogenous catalytic pyrolysis.[11,12] Nonetheless, it was not until the Australian company Circa developed the Furacell™ technology, a continuous process to convert a wide range of cellulosic biomass into levoglucosenone,[13] that it gained real commercial interest to produce commodity chemicals. Besides its more recent use as a platform molecule for the production of α,ω-diols, its highly functionalized structure makes it an attractive chiral synthon which has been used in the last decade for the synthesis of a wide variety of natural and non-natural compounds.[14] Regarding the bicyclic structure, the 1,6-anhydro bridge locks the conformation and sterically hinders one face of the molecule providing it with an excellent facial selectivity. Levoglucosenone has been proved to be an excellent chiral scaffold for the preparation of useful organic compounds due to the large number of works demonstrating its application as starting material for the synthesis of bioactive compounds, disaccharides and chiral inductors for asymmetric synthesis.[15-18]

In this work, the spotlight has been put on the hydrogenation opportunities that heterogeneous catalysts based on supported metals could offer for levoglucosenone, with the aims of continuing opening new research lines for the valorisation of this compound and giving new tools for organic chemists in its use as a raw material for complex organic synthesis involving multiple steps.

Levoglucosenone presents two different functionalities susceptible to be hydrogenated, the carbonyl group in position C-2 and the double bond in position C-3 (Scheme 1). On one hand, selective carbon-carbon double bond hydrogenation affords dihydrolevoglucosenone (Cyrene™),

a saturated compound, which preserves the carbonyl group at C-2. This ketone is difficult to obtain without concomitant partial hydrogenation of the C=O to C-OH, thus generating the saturated alcohol or levoglucosanol (Scheme 1). On the other hand, the selective reduction of the carbonyl function at C-2 leads to the corresponding allylic alcohol (Scheme 1).

Regarding homogenous catalysis, reactions to obtain the simplest products resulting from levoglucosenone reduction have been already described, such as the treatment with lithium aluminium hydride or sodium borohydride to produce the corresponding saturated alcohol,[19] as well as its combination with another previous step by means of which the double bond is hydrogenated by using Pd/C.[20] Both of them are already well-known processes. As purely heterogeneous catalysis is concerned, some previous studies have been carried out by Dupont[21,22] in order to obtain selectively 1,6-hexanediol from levoglucosenone by using a $Pt/W/TiO_2$ catalyst, among others, at temperatures between 60 and 180 °C and H_2 pressures of 55 bar. The process implies the ring opening of the intramolecular acetal group, reduction of the carbonyl group, hydrogenolysis of the secondary carbinol groups and hydrogenation of the double bond. Recently, Huber and co-workers reported the use of Pd supported on carbon, alumina and silica-alumina to obtain a variety of products via hydrogenation (i.e. dihydrolevoglucosenone and levoglucosanol) and hydrogenolysis (i.e. tetrahydrofurandimethanol (THFDM) and 1,6-hexanediol precursors).[23] Besides that, they have reported and studied the kinetics of the hydrogenolysis of levoglucosanol over bifunctional platinum catalysts supported on silica−alumina in tetrahydrofuran.[24] Nonetheless, the use of quite elevated hydrogen pressures (>30 bars), high loads of catalysts, highly diluted solutions of levoglucosenone in organic solvents (i.e. THF), as well as a clear catalytic deactivation during the process remain as important disadvantages.
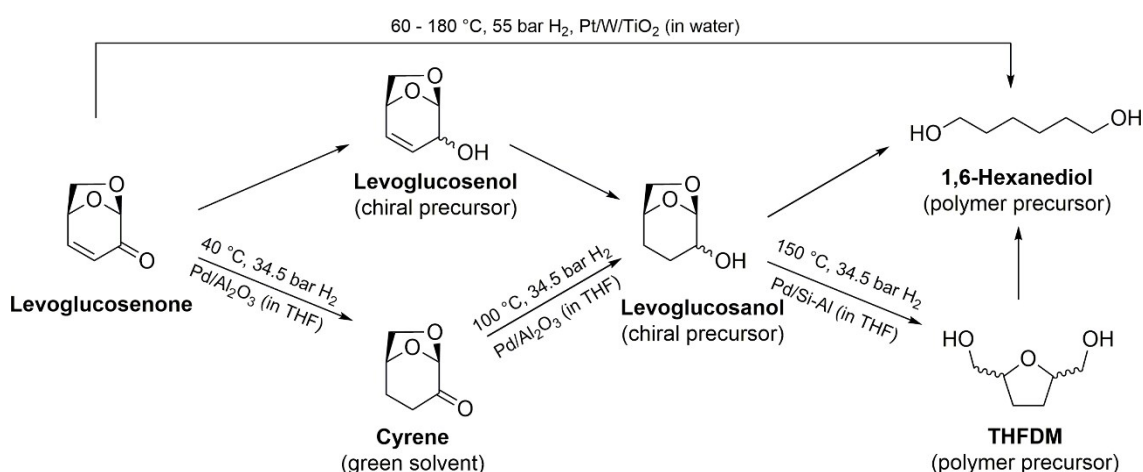
Scheme 1. Levoglucosenone and its hydrogenated derivatives. Reaction conditions are also indicated for those processes working with an already described heterogeneous catalyst.[21-23,25,26]

Up to now, the ability of Pd to hydrogenate the double bound of levoglucosenone has been evaluated at lower temperatures thanks to the work of Huber and co-workers.[23] They also claimed that, by means of increasing the temperature, the simplest hydrogenation products can be transformed into some hydrogenolysis products with the same Pd-based catalysts.[23] Clark and co-workers have also proved that it is possible to hydrogenate levoglucosenone to Cyrene in the absence of solvent by either increasing the pressure or by lengthening the chemical reaction time[25]. However, the selective catalytic production of Cyrene under operational conditions scalable at industrial level are still a considerable challenge. More importantly, the synthesis of the saturated alcohol (levoglucosanol) from levoglucosenone by using only one catalyst in a selective one-pot process has not been achieved yet.

Following this idea, the work presented herein is focused on establishing one-pot processes for the selective reduction of levoglucosenone under moderate hydrogenation conditions. Based on preliminary results attained with commercial Pd, Pt and Ru supported on carbon catalysts under moderate conditions, the study and application of supported Pd and Pt metals which showed selectivity towards one specific hydrogenated product was extended to the use of different metal oxides as supports. Thus, a combination of the specific metallic species with the adequate support selection allowed tuning the catalytic properties of the solid materials to produce the desired hydrogenated product in a one-pot process. Particularly, the excellent catalytic performance of Pd/ZrO_2 and Pt/ZrO_2 type materials for the synthesis of dihydrolevoglucosenone (or Cyrene) and levoglucosanol, respectively, during the hydrogenation of levoglucosenone under mild reaction conditions will be demonstrated. Modulating the amount of (111), (100) metal surface facets allows to tune the selectivity to the target product. The stability and re-usability of both catalysts under operation conditions were also evaluated. In addition, catalytic tests including the use of crude bio-liquids obtained from reached-cellulose biomass pyrolysis and containing ≈66wt% of levoglucosenone were also assayed, thus demonstrating the possibility of scaling-up the process offered by these metals supported on zirconia catalysts.

Experimental

Materials and supports

Pure levoglucosenone (95%) used in this study was supplied by Carbosynth. In addition, a distilled fraction obtained from reached-cellulose biomass pyrolysis containing at least 98% of levoglucosenone was also used in some experiments. Cyrene (99.5%) was supplied by Sigma-Aldrich and used as standard. Acetonitrile (Scharlau, analytical grade, 99.5%) and H_2O (milliQ, Millipore) were used as solvents in the reactions. Additionally, a solution of chlorobenzene

(Sigma-Aldrich, 99.90%) in acetonitrile was used to dilute the samples and as an internal standard. The hydrogen used (99.999%) was purchased from Abelló Linde S.A. On the other hand, a mixture containing ≈66wt% of levoglucosenone (determined by GC analysis) obtained through thermal pyrolysis of microcrystalline cellulose in IQUIR laboratory (Rosario, Argentine) was used as the feed for some hydrogenation catalytic systems already proved to be efficient in certain levoglucosenone hydrogenation processes.

As far as the catalysts are concerned, γ-Al_2O_3 nanopowder (Sigma-Aldrich, 99.0%), TiO_2 nanoactive (NanoScale Corporation, 99%), SiO_2 (Chempure, 99%) and different polymorphous of ZrO_2: tetragonal, (Chempure, 99%) and monoclinic (Chempure, 99%) were used as supports in powder form. In addition, a mixture of both polymorphous of ZrO_2, namely ZrO_2-mix (and containing a monoclinic/tetragonal mass ratio of around 60/40) was prepared in the laboratory and used as support. The precursor used for the synthesis of the mixed zirconia was $ZrOCl_2.8H_2O$ (Sigma-Aldrich, 99.5%) with ammonia solution (Sigma-Aldrich, 25 %vol.) as precipitant agent, and the preparation was performed by following the procedure described by Zhang et al.[27] $Pt(NH_3)_4(NO_3)_2$ (Sigma-Aldrich, 99.995%) and $Pd(NH_3)_4Cl_2 \cdot H_2O$ (Sigma-Aldrich, 99.00%) were chosen as metallic precursors. 5wt% Pd/C, 5wt% Pt/C and 5wt%Ru/C were also purchased from Sigma-Aldrich for comparative purposes.

Preparation of supported Pd and Pt catalysts

The catalytic materials based on either supported Pd or supported Pt were prepared by incorporating the metal (≈2wt% with respect to the support used) by incipient wetness-impregnation method with different metal oxides as supports and using an aqueous solution of either $Pd(NH_3)_4Cl_2 \cdot 6H_2O$ or $Pt(NH_3)_4(NO_3)_2$. The supports used were all commercial except for the ZrO_2 mix (mixture of tetragonal and monoclinic phases), being this one prepared as afore-described. The solid samples were oven-dried at 100 °C overnight, and then calcined at 400 °C under air atmosphere. The obtained catalytic materials were activated under a H_2 flow (100 mL/min) at 400 °C during 4 h before using them in catalytic tests.

Catalyst characterization

The presence of the crystalline phases corresponding to each catalyst were determined by X-ray diffraction (XRD) in a PANalitical Cubix Pro diffractometer equipped with a PW3050 goniometer (CuKα radiation), provided with a variable divergence slit and working in fixed irradiated area mode. By means of this XRD analysis the amount of tetragonal and monoclinic phase present in the ZrO_2 mixture was estimated by comparing the areas of the characteristic

peaks (monoclinic phase 2θ≈28º, tetragonal phase 2θ≈30º). Percentages were calculated from the Gaussian areas h x w, being h the height and w the half-width of the characteristic peak. Surface areas of the solid samples (200 mg) were calculated by the BET method by carrying out liquid nitrogen adsorption experiments at 77 K, in a Micromeritics flowsorb apparatus. Chemical composition was determined by using an inductively coupled plasma emission spectrophotometer (ICP) Varian 715-ES. The organic matter deposition after using the catalysts was checked by means of thermogravimetric analyses (TG) carried out in a Mettler Toledo TGA/SDTA 851 apparatus, using a heating rate of 10 ºC/min in an air stream until 800 ºC was reached. Elemental analyses (EA) were carried out in a Fisons EA1108CHN-S apparatus. The reduction behaviour of the most effective catalysts was studied by temperature-programmed reduction (TPR) in a Micromeritics Autochem 2910 equipment. About 30 mg of the calcined catalyst were initially flushed with 30 cm^3/min of Ar at room temperature for 30 min, and then a mixture of 10vol% of H_2 in Ar was passed through the catalyst at a total flow rate of 50 cm^3/min while the temperature was increased up to 1273 K at a heating rate of 10 K/min. The H_2 consumption rate was monitored in a thermal conductivity detector (TCD) previously calibrated using the reduction of CuO as reference. The strength and nature of the acidic sites present in the main catalysts tested were evaluated in an infrared spectrophotometer FT-IR Nicolet, Is-10 Thermo with pyridine as a probe molecule. Quantification of acid sites has been done using the extinction coefficients of ref. [28]. Textural characterization of solids was performed by high-definition transmission electron microscopy (HR-TEM) on a Jeol JEM-2100F equipment, working at a voltage of 200 kV. Pd/ZrO$_2$ materials were analysed by CO chemisorption isotherms at 308 K in an ASAP 2010C equipment; before starting the adsorption, the samples (ca. 0.5 g) were pre-treated in H_2 at 623 K and vacuum for 30 min. The stoichiometry of CO:Pd was assumed as 1:1.

IR spectra of CO adsorption were done on reduced samples prior and after *"ex situ"* levoglucosanone adsorption, using a Bruker "Vertex 70" spectrometer and a DRIFT catalytic cell. The samples have been reduced *"ex situ"* at 400 ºC for 4h. For the IR-CO titration prior to levoglucosanone adsorption, the reduced samples have been treated *"in situ"* in a H_2 flow (10 ml/min) for 1h at 200 ºC, and cooled down to 25 ºC in a flow of N_2. At 25 ºC, the N_2 has been switched to a flow of 4% CO/Ar (10ml/min). Spectra have been acquired at 25 ºC after 15 min gas flow. For the IR-CO titration of the samples after levoglucosanone adsorption, levoglucosanone has been adsorbed *"ex situ"* following a wet impregnation method. For that, the sample has been reduced *"in situ"* in the glass vessel, (at 200 ºC for 1h), and then a solution 0.5M of levoglucosenone in acetonitrile has been added at room temperature and stirred for 30 min. Afterwards, the sample has been dried (rota-evaporated) and transferred in a N_2 -box to the DRIFT cell. In the DRIFT cell, the sample has been initially flushed with N_2 at 25 ºC during 45 min followed by switching to a 4% CO/Ar flow. Spectra has been acquired after 15 min gas flow.

Deconvolution was done by using Origin software and examples of deconvoluted spectra can be found in the ESI (Figure S29).

For the IR-KBr analysis, the samples after levoglucosanone adsorption has been diluted in KBr and pressed into IR transparent wafers. IR spectra have been acquired after 1h evacuation at 10^{-5} mbar.

Catalytic experiments

Hydrogenation reactions of levoglucosenone with metal supported solid catalysts were carried out in a 6 mL batch glass micro-reactor equipped with a probe for sampling and a pressure gauge for pressure measurement. In general, 0.126 g of levoglucosenone (1 mmol), either 15.5 mg (when having 5wt% of metal) or 30.0 mg (when having 2wt% of metal) of solid catalyst and 0.500 g of solvent (acetonitrile or water) were added in the standard experiments. The reactor was sealed and pressurized with a range from 10 to 21 bars of H_2. For a few experiments, the pressure was increased above 21 bars of H_2; in these cases reactions were performed in a 12 mL stainless steel autoclave-type reactor with PEEK (polyether-ethyl-ketone) interior, equipped with a magnetic bar, pressure control and a valve for liquid sample extraction. In both cases, the corresponding reactor was rapidly heated to the reaction temperature (45 – 100 °C) and maintained with vigorous stirring throughout the reaction (between 2.5 and 7 h). In all cases, the pressure of H_2 in the system remained constant at the selected value. Liquid aliquot (≈50-100 μL) were taken off at different time intervals, and then diluted in a solution of 2wt% chlorobenzene in acetonitrile (internal standard) for their corresponding chromatographic analysis.

Analysis of the reaction mixtures were carried out by means of two different GC instruments: a 3900-Varian GC equipped with a FID detector and a capillary column (HP-5, 30 m length) and a Bruker 430 GC equipped with a FID detector and a capillary column (TRB-624, 60 m length). In the first case, the HP-5 capillary column provided us with a first separation between the two simplest hydrogenation products i.e. Cyrene and 1,6-anhydro-3,4-dideoxy-β-D-gluco-hexopyranose (levoglucosanol) and the rest of products. In the second case, the TRB-624 column was able to make a better separation between these two referred hydrogenated compounds. Products identification was done by GC–MS (Agilent 6890N GC System coupled with an Agilent 5973N mass detector), and nuclear magnetic resonance spectroscopy (NMR) recorded with Bruker Avance instrument operating at ^1H Larmor frequency of 300 MHz. Chemical shifts are given in ppm and relative to TMS for ^1H and ^{13}C.

Conversion was calculated by comparing the amount of levoglucosenone added at the beginning of the experiment with that determined by the GC measurement of the final mixture:

$$C(mol.\%) = \frac{n^0_{levoglucosenone} - n^f_{levoglucosenone}}{n^0_{levoglucosenone}} \cdot 100 \quad \text{(eq. 1)}$$

Selectivity was calculated for each of the different products of the reaction, and it was defined as a function of the total amount of products quantified by GC analysis:

$$S(mol.\%) = \frac{n^f_{desired\ product}}{\sum n^f_{total\ products}} \cdot 100 \quad \text{(eq. 2)}$$

The yield was defined as the quotient between the amount of the desired product and the amount of levoglucosenone present in the initial mixture:

$$Y(mol.\%) = \frac{n^f_{desired\ product}}{n^0_{levoglucosenone}} \cdot 100 \quad \text{(eq. 3)}$$

TON (Turnover number) was also calculated as the mol of levoglucosenone consumed per mol of metal present in the solid catalyst calculated by ICP:

$$TON = \frac{n^0_{levoglucosenone} - n^f_{levoglucosenone}}{n^0_{METAL}} \quad \text{(eq. 4)}$$

Finally, carbon balances were calculated for each reaction, taking into account the total amount of products detected by our analysis by GC, along with the remnant levoglucosenone:

$$CB(mol.\%) = \frac{\left[(n^0_{levoglucosenone} - n^f_{levoglucosenone}) \cdot 6\ C\ atoms\right] + \sum(n^f_{product} \cdot X\ C\ atoms)}{n^0_{levoglucosenone} \ x\ 6\ C\ atoms} \cdot 100 \text{ (eq. 6)}$$

Being X de total number of C atoms in the molecules corresponding to the different by-products.

Reusability tests

Pd/ZrO$_2$ and Pt/ZrO$_2$ were the catalysts that gave the best results and were initially recovered from the reaction mixture by filtration, then thoroughly washed for 20 minutes with either water or a mixture of water/EtOH (1:1 in weight), and finally tested again in a levoglucosenone hydrogenation reaction. In the case of Pd/ZrO$_2$ material, after being used, the catalyst was regenerated under the same conditions employed for its first activation (400 ºC, under H$_2$ flow during 4 h), and then reused in the levoglucosenone hydrogenation under the same reaction conditions.

Results and discussion

Compositional, structural and textural characterization of Pd and Pt based catalysts

Main compositional, structural and textural data obtained from Pd- and Pt-based catalysts are summarized in Tables 1 and 2, respectively.

The ICP analysis of both Pd and Pt catalytic samples confirmed a good incorporation of the metals onto the supports in the range of 1.5-2.5wt% (see Tables 1 and 2). The Pd supported materials showed surface area values ranging from 83 to 139 m^2/g, except in the case of the SiO_2-based material (surf. Area = 207 m^2/g). Similarly, Pt supported materials also presented surface values in the range of 86 and 146 m^2/g, with the same exception in the case of silica-based sample. In any case, the values of surface area were either close to or above 100 m^2/g and similar to those observed for materials of common application in catalysis.

Table 1. Main textural and physico-chemical properties of Pd-based materials using different metal oxides as supports.

| Catalyst	Pd (wt %)[a]	Support	Surface area (m^2/g)[b]	Pore vol. (cm^3/g)	Metal particle size (nm)[c]
Pd/C	5.0*	Amorphous C	696	0.61	4
Pd/SiO$_2$	1.9	Amorphous silica	207	0.67	5
Pd/TiO$_2$	2.4	Anatase	120	0.32	3
Pd/Al$_2$O$_3$	2.1	γ-alumina	139	0.52	3
Pd/ZrO$_2$-mix	2.5	Monoclinic and tetragonal zirconia (60:40 wt)	88	0.13	5 (8)[d]
Pd/*m*-ZrO$_2$	2.1	Monoclinic zirconia	83	0.23	n.d. (5)[d]
Pd/*t*-ZrO$_2$	1.9	Tetragonal zirconia	133	0.18	4 (5)[d]

a: Pd content and chemical composition measured by ICP. b: Values calculated from N_2 adsorption isotherms by applying the BET method. c: Average diameter of Pd nano-particles calculated from TEM measurements of, at least, 150 particles. d: Average diameter of Pd nano-particles evaluated by CO chemisorption, being the stoichiometry Pd:CO = 1:1. * Value provided by Sigma-Aldrich.

Table 2. Main textural and physico-chemical properties of Pt-based materials using different metal oxides as supports.

Catalyst	Pt (wt %)[a]	Support	Surface area (m^2/g)[b]	Pore vol. (cm^3/g)	Metal particle size (nm)[c]
Pt/C	5.0*	Amorphous C	963	0.75	2
Pt/SiO$_2$	1.8	Amorphous silica	211	0.64	4
Pt/TiO$_2$	2.1	Anatase	122	0.33	2
Pt/Al$_2$O$_3$	2.0	γ-alumina	138	0.50	3
Pt/ZrO$_2$-mix	1.5	Monoclinic and tetragonal zirconia (60:40 wt)	86	0.12	2
Pt/m-ZrO$_2$	1.6	Monoclinic zirconia	92	0.23	n.d.
Pt/t-ZrO$_2$	1.4	Tetragonal zirconia	146	0.18	n.d

a: Pt content and chemical composition measured by ICP. b: Values calculated from N_2 adsorption isotherms by applying the BET method. c: Average diameter of Pt nano-particles calculated from TEM measurements. * Value provided by Sigma-Aldrich.

As can be seen in Figure 1, the X-ray diffractogram of the Pd supported on ZrO_2-mix shows some peaks that can be associated with the presence of the tetragonal phase of ZrO_2 and others corresponding to the monoclinic phase. This was expected, since this material was a mixture containing, 60% monoclinic phase and 40% tetragonal phase. The diffractogram of the Pd/Al$_2$O$_3$ material corresponds to aluminium oxide with very low crystallinity, while the Pd/TiO$_2$ material showed predominantly anatase phase. Likewise, the signals corresponding to crystallographic planes of metallic palladium (Pd^0) can be difficultly distinguished in the Pd/ZrO$_2$-mix, Pd/TiO$_2$, and Pd/Al$_2$O$_3$. These observations can be taken as evidence of a good metallic dispersion of Pd^0 species onto the corresponding supports. Only in the case of Pd/SiO$_2$, the metallic phase can be clearly differentiated from the support.

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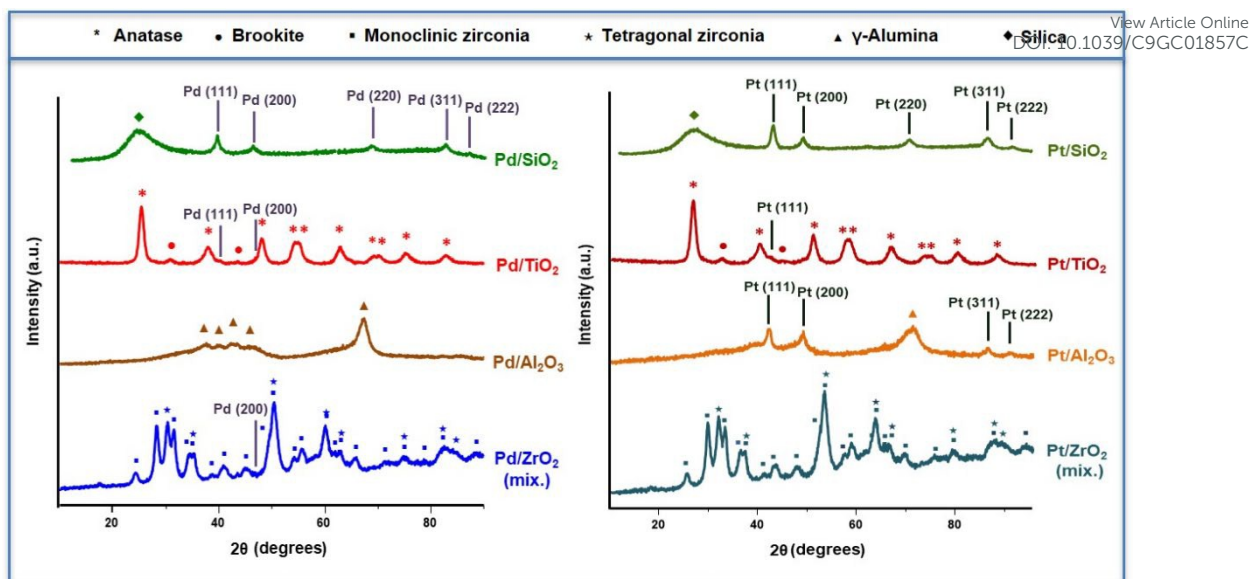
Figure 1. X-ray diffractograms of materials based on Pd (left) and Pt (right) supported on SiO_2, TiO_2, Al_2O_3 and ZrO_2-mix.

X-ray diffraction data of the most representative Pt-supported catalytic samples here prepared (Pt/SiO_2, Pt/TiO_2, Pt/Al_2O_3, and Pt/ZrO_2-mix) are presented in Figure 1(right). Similar to that observed with Pd-supported samples, the crystalline phases corresponding to the alumina (aluminium oxide), titania (mainly anatase) and mixed zirconia (monoclinic and tetragonal) were ascertained. In addition, the presence of signals corresponding to Pt metallic species (Pt^0) was very difficult to distinguish in Pt/ZrO_2-mix and Pt/TiO_2 materials, mainly due to the high dispersion of Pt onto these supports. Nevertheless, the diffraction peaks assigned to Pt^0 species clearly appeared in the cases of Pt/Al_2O_3 and Pt/SiO_2 sample, probably due to lack of signals of amorphous alumina and silica supports.

It is known that zirconium oxide can occur mainly in two different crystalline phases at room temperature; tetragonal (t-ZrO_2) and monoclinic (m-ZrO_2), both presenting different acid-base properties and, therefore, different catalytic properties.[29,30] Thus, Pd and Pt supported materials were also prepared on these different zirconia polymorphous (X-ray diffraction patterns shown in Figure S1, SI) with the aim of evaluating their specific catalytic properties.

Pd- and Pt-supported materials were also analysed by means of HR-TEM measurements, the images obtained for different selected catalysts are shown in Figures 2 and 3, respectively.

In the case of Pd-supported materials, the presence of metallic Pd nanoparticles can be appreciated in all of them, having quite similar average sizes and below 10 nm in all cases, regardless of the type of support used. The metal particle size distributions were found centred around 2.5-4.0 nm in the case of Pd/SiO$_2$, Pd/TiO$_2$, Pd/Al$_2$O$_3$, Pd/ZrO$_2$-mix and Pd/t-ZrO$_2$. All particle size distributions were narrow, especially in the case of Pd/TiO$_2$. Nonetheless, a small fraction of particles bigger than 10 nm could be found in all the materials (see Figure S2, in SI).

With regard to Pt-supported materials, Pt nanoparticles were clearly distinguished for all of them, the average sizes being very similar (≤4nm), regardless of the type of support used. Particle size distributions for Pt/TiO$_2$ and Pt/ZrO$_2$ were very narrow, with most of the particles located in the area between 1 and 3 nm. The particle size distribution width for Pt/Al$_2$O$_3$ was wider, ranging from 1 to 6 nm. Last, Pt/SiO$_2$ had the widest distribution observed with a particle size distribution centred in ≈2nm (see Figure S3, in SI).
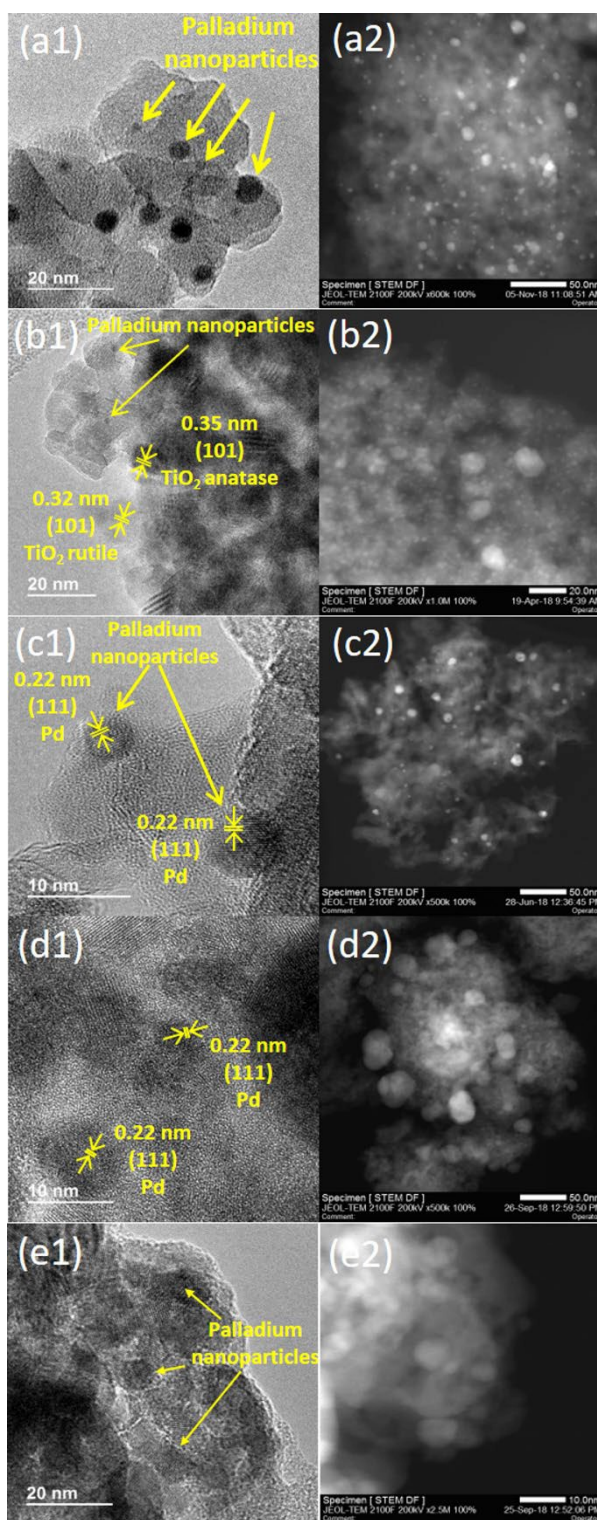
Figure 2. Micrographs of samples of a) Pd/SiO$_2$, b) Pd/TiO$_2$, c) Pd/Al$_2$O$_3$, d) Pd/ZrO$_2$-mix, e) Pd/t-ZrO$_2$ obtained by measurements of HR-TEM.
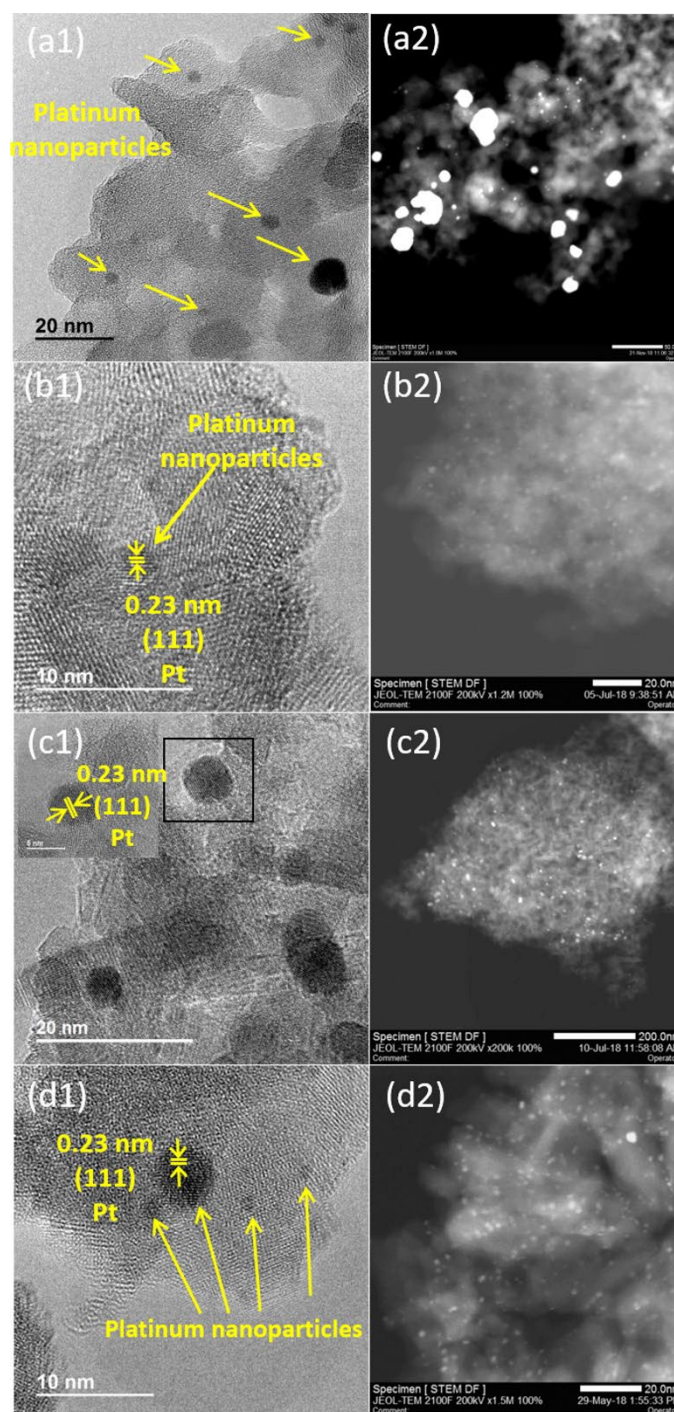
Figure 3. Micrographs of samples of a) Pt/SiO$_2$, b) Pt/TiO$_2$, c) Pt/Al$_2$O$_3$, and d) Pt/ZrO$_2$-mix obtained by measurements of HR-TEM.

Acid properties of Pd and Pt based catalysts

With the aim of establishing relations between the chemical properties of the main catalysts and their catalytic behaviour, a study of their acidic properties was carried out through pyridine (probe molecule) adsorption and desorption at different temperatures monitored by FT-IR spectroscopy.

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For both palladium-containing and platinum-containing materials, mainly Lewis-type acid centres were found. The results of acidity measurements of Table 3 show important differences between the different materials used in both cases, allowing us to order the catalysts in terms of their acidity depending of the type of support as follows: $TiO_2 > Al_2O_3 > ZrO_2 > SiO_2$, for both Pd and Pt-supported materials. As can be seen, while acid sites offered by silica supported samples are practically negligible, titania and alumina-based materials possess higher acidity, the strength of half of these acid sites being from moderate to strong. In the case of ZrO_2-based materials, a reasonable amount of Lewis acid sites is observed, these sites presenting mainly week to moderate acid strength. These observations could have some influence on the catalytic properties of the different materials in the hydrogenation reaction of interest. This fact will be discussed in the next sections.

Table 3. Lewis acid centres distribution for Pd- and Pt-supported catalysts measured by FT-IR with pyridine adsorption-desorption at 150, 250 and 350 °C. Molar extinction coefficients from Ref. [28].

Catalyst	Lewis Acid sites (µmol/g)		
	150 °C	250 °C	350 °C
Pd/SiO₂	6	-	-
Pd/TiO₂	284	111	98
Pd/Al₂O₃	222	131	88
Pd/ZrO₂-mix	98	53	66
Pt/SiO₂	9	-	-
Pt/TiO₂	283	108	56
Pt/Al₂O₃	179	110	70
Pt/ZrO₂-mix	102	39	47

Effect of the type of metal used in levoglucosenone hydrogenation

With the aim to check what type of products could be obtained by hydrogenating levoglucosenone under moderate reaction conditions (see Scheme 1), preliminary catalytic experiments were carried out with 5wt%Pd/C, 5wt%Pt/C or 5wt%Ru/C commercial catalysts at two different temperatures (80 and 100 °C) and levoglucosenone (0.126 g) diluted in acetonitrile (0.500 g) as solvent during 5 h of reaction (see Experimental Part). Results depicted in Table 4 clearly show that total conversions (100%) of levoglucosenone are achieved in all cases. However, the

distribution of products obtained in each case differs according to the type of metal used. Thus, with 5wt%Ru/C it was not possible to achieve good yields of any product. 5wt%Pd/C catalyst showed a high selectivity (between 65% and 82%) towards the hydrogenation of the C=C group, dihydrolevoglucosenone (Cyrene) being obtained as the main product. Finally, the 5wt%Pt/C material succeeded in hydrogenating both the carbon-carbon double bond and the carbonyl group of levoglucosenone, thus affording the saturated alcohol levoglucosanol with a selectivity of ≈50%. These last two results have been confirmed, not only by GC measurements, but also through ^{1}H-NMR analysis of the final reaction mixtures (see Figures S8, S9 for dihydrolevoglucosenone and Figures S10, S11 for levoglucosanol in SI).

Table 4. Catalytic results obtained in the selective hydrogenation of levoglucosenone with different metals supported on carbon commercial catalysts.

Catalyst	Conversion (mol. %)	Selectivity to CYRENE (mol. %)	Selectivity to LEVOGLUCOSANOL (mol. %)	Selectivity to Others[c] (mol. %)	Carbon balance (%)
Ru/C[a]	100	0	8	92	60
Pd/C[a]	100	82	0	18	98
Pt/C[a]	100	50	10	40	92
Ru/C[b]	100	31	6	63	92
Pd/C[b]	100	65	0	35	88
Pt/C[b]	100	0	50	50	98

Reaction conditions: 0.126 g levoglusenone, 0.500 g acetonitrile, 12.5wt% catalyst, at 10 bar H_2 pressure during 5 h, and at two temperatures: a) 100 ºC and b) 80 ºC; c) Others = Dimeric species derived from levoglucosenone, small number of products resulting from the solvent reacting with the reactant, and other unidentified by-products.

Considering the good yields to dihydrolevoglucosenone (Cyrene, >80%) and levoglusanol (≈50%) obtained with Pd and Pt supported on carbon commercial catalysts, respectively, the study was focused on the employment of Pd or Pt based materials supported on different metal oxides as supports for the one-pot selective hydrogenations of levoglucosenone. The effect of operational conditions and reaction media on the catalytic performance, as well as the stability of the different metal-supported materials used are described in next sections.

Selective hydrogenation of levoglucosenone over Pd supported on different metal oxides

Taking into account that the best yield to dihydrolevoglucosenone (Cyrene, which has already been considered as a green solvent[25,26]), was achieved by using 5wt%Pd/C under moderate reaction conditions (at 100 ºC and P_{H2} =10 bar), different Pd-based catalysts were prepared by incipient wetness-impregnation of the Pd precursor onto different metal oxides as supports (i.e. SiO_2, TiO_2, Al_2O_3, ZrO_2, see Experimental part). The catalytic results attained for levoglucosenone hydrogenation are summarized in Table 5.

Table 5. Catalytic results in the selective hydrogenation of levoglucosenone over Pd supported on different metal oxides.

Catalyst	Pd (wt%)[a]	Conversion (mol. %)	Selectivity to CYRENE (mol. %)	TON	Carbon balance (%)
Pd/C	5.0*	100	82	134	98
Pd/SiO₂	1.9	100	92	160	98
Pd/TiO₂	2.4	100	73	133	90
Pd/Al₂O₃	2.1	100	95	146	99
Pd/ZrO₂-mix	2.5	100	84	119	87

Reaction conditions: 0.126 g levoglucosenone, 0.500 g acetonitrile, 25.0wt% catalyst *(except for Pd/C, 12.5wt%), at 10 bar H_2 pressure and 100 ºC during 5 h. a) Measured by ICP.

The outcome of the four catalysts tested Pd/Al₂O₃, Pd/SiO₂, Pd/ZrO₂-mix, and Pd/TiO₂, affording 95, 92 84, and 73% yield of dihydrolevoglucosenone (Cyrene), respectively, demonstrated that they are promising materials for the selective production of this interesting compound considered as green solvent and building block. Therefore, the possibility of turning the reaction towards a more sustainable process was studied by optimizing reaction conditions with these catalysts. In a first attempt, temperature was lowered by working at 80 ºC, carrying out experiments by taking sample out from the reactor at 2.5 and 5 h of reaction. Figure 4 makes clear how, when working with Pd/ZrO₂-mix under these reaction conditions, the yield of dihydrolevoglucosenone (Cyrene) is almost quantitative (98 mol.% calculated by GC analysis), with a TON of 145 and a Carbon balance of 96%, both calculated at 5 h of reaction. The ¹H and ¹³C NMR of the reaction mixture at the final time (5 h) (Figures S12, S13 in SI), together with its GC-MS spectra (Figure S21 in SI), corroborate the presence of dihydrolevoglucosenone (Cyrene) as the main product of the reaction with a very high purity with small traces of levoglucosenone and levoglucosanol, among

other compounds. This result places the Pd supported on mixed zirconium oxide (along with Pd/SiO$_2$ and Pd/Al$_2$O$_3$, the last already described by Huber and co-workers[23]) as a very promising heterogeneous catalyst to yield dihydrolevoglucosenone (Cyrene) through almost a quantitative reaction from levoglucosenone by using moderate reaction conditions.
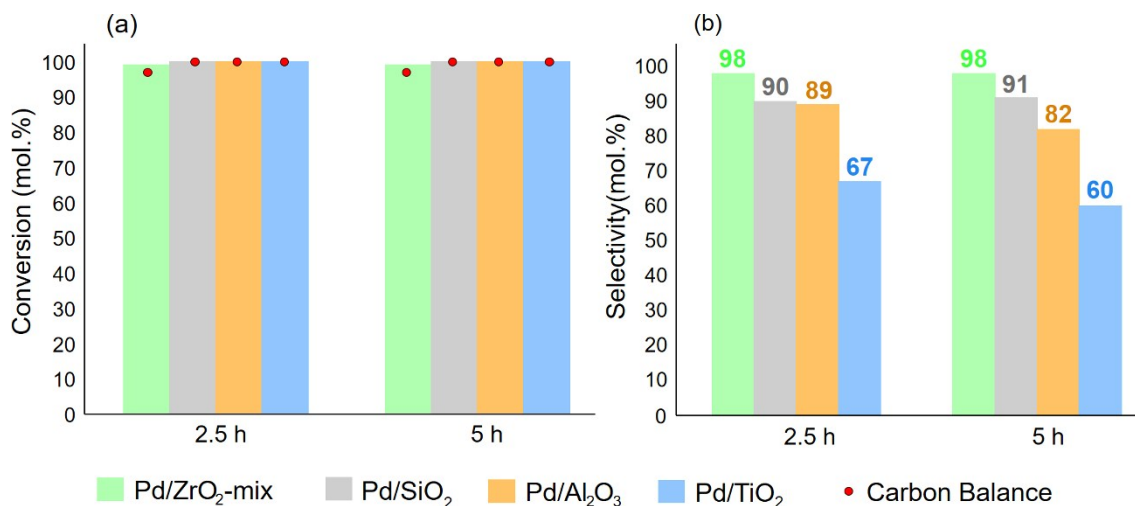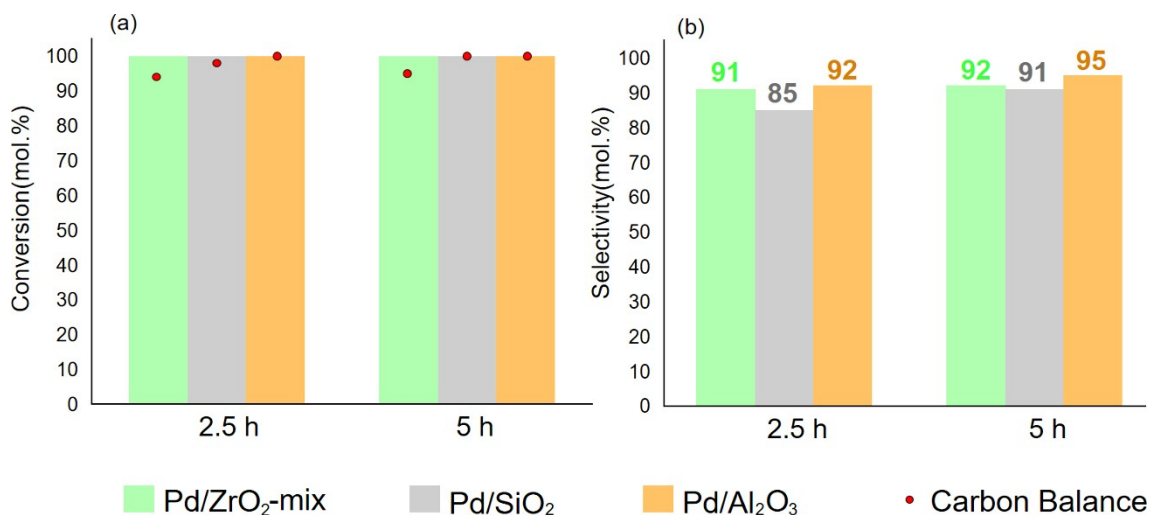

Figure 4. Reactant conversion (a) and selectivity to dihydrolevoglucosenone (Cyrene) (b) for different Pd-based catalysts in the selective hydrogenation of levoglucosenone at different reaction times. Reaction conditions: 0.126 g levoglucosenone, 0.500 g acetonitrile, 25.0wt% catalyst, at 10 bar H$_2$ pressure and 80 ºC during 5 h.

Although the catalytic activity observed is quite similar for all the Pd-based catalysts tested, some differences appeared in the selectivity values, this may be due to differences in support properties. In this sense, the strength and nature of the acidic sites present in the Pd catalysts were analysed by infrared absorption spectroscopy using pyridine as probe molecule. Results already described in *Acid properties of Pd and Pt based catalysts* section (see also Figure S26, SI) show how, and excess of acid sites results in a decrease in selectivity to the desired dihydrolevoglucosenone (Cyrene). Thus, Pd/TiO$_2$ catalyst having the higher amount of Lewis acid sites gave lower selectivity, followed by Pd/Al$_2$O$_3$ and Pd/ZrO$_2$-mix, which yield the highest amounts of dihydrolevoglucosenone. Apparently, high contents of Lewis acid sites in the catalysts favoured the strong adsorption of reactant onto the support and the generation of by-products via secondary or consecutive reactions, thus lowering the final production of the desired dihydrolevoglucosenone (Cyrene).

Since Pd/SiO$_2$, Pd/Al$_2$O$_3$ and Pd/ZrO$_2$-mix catalysts were efficient when working at 80 °C, the effect of changing the reaction media from acetonitrile to water as solvent was evaluated, thereby making the process even more environmentally-friendly. Figure 5 shows that the presence of water did not have any significant effect on the dihydrolevoglucosenone (Cyrene) yield when

using mixed ZrO$_2$, while just a little decrease in selectivity is observed when using SiO$_2$ as support at 2.5 h. In the case of Pd/Al$_2$O$_3$ even a slight increase on the selectivity towards dihydrolevoglucosenone was observed when comparing water and acetonitrile usage, thus placing these three catalysts at the same level when working under these operational conditions (see Figure 5).
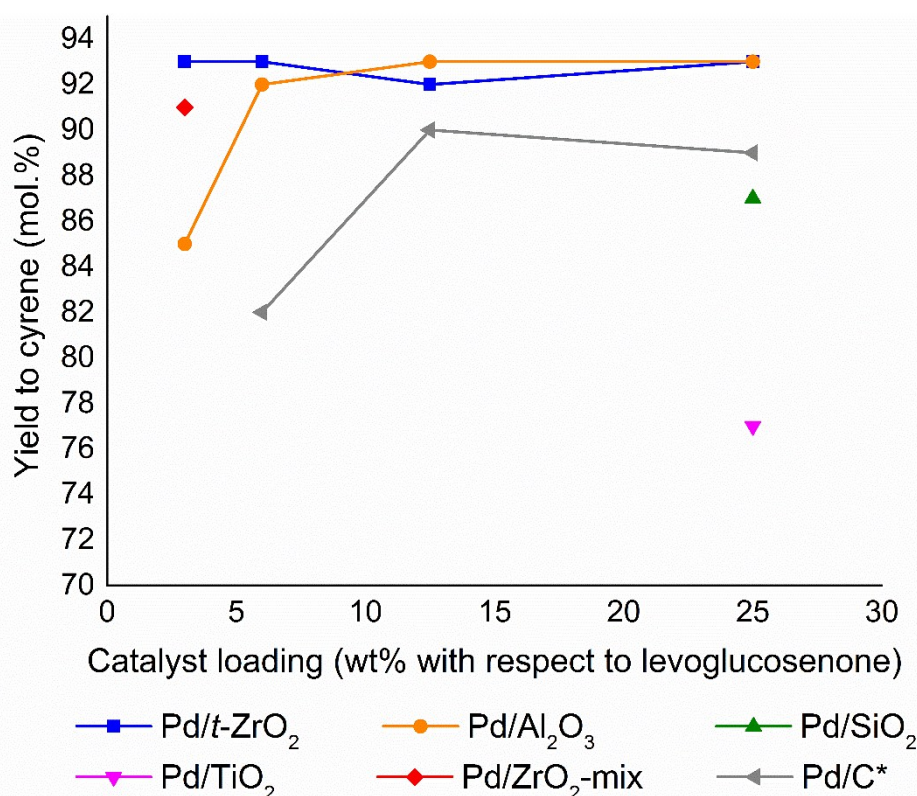

Figure 5. Reactant conversion (a) and selectivity to dihydrolevoglucosenone (Cyrene) for Pd/ZrO$_2$-mix, Pd/SiO$_2$ and Pd/Al$_2$O$_3$ catalysts in the selective hydrogenation of levoglucosenone with water as solvent. <u>Reaction conditions:</u> 0.126 g levoglucosenone, 0.500 g water, 25.0wt% catalyst, at 10 bar H$_2$ pressure and 80 °C during 5 h.

Once the optimal reaction conditions (80 °C, 10 bar H$_2$ pressure and water as solvent) were stablished, the effect of zirconia crystalline phase on the activity of Pd/ZrO$_2$ catalysts for the low temperature selective hydrogenation of levoglucosenone to dihydrolevoglucosenone (Cyrene) was investigated. For this purpose, catalysts based on Pd supported on ZrO$_2$ possessing tetragonal (Pd/*t*-ZrO$_2$) and monoclinic (Pd/*m*-ZrO$_2$) crystalline phases were prepared with similar Pd loading and dispersion as compared with Pd/ZrO$_2$-mix (see Table 1). The structural features of the Pd/ZrO$_2$ catalysts were characterized by X-ray powder diffraction, confirming the majority presence of tetragonal or monoclinic zirconium oxide phases in each case. In addition, HR-TEM and STEM-DF measurements performed for these materials show the presence of well-defined Pd nanoparticles (Diam. ≈3nm) homogeneously dispersed on the ZrO$_2$-type supports (see *Compositional, structural and textural characterization of Pd and Pt based catalysts* section). Figure S24 in SI shows that the three Pd supported on ZrO$_2$ catalysts prepared reached complete conversion of levoglucosenone at 2.5 h of reaction with high selectivity to dihydrolevoglucosenone (Cyrene, >90%) in all the cases. Although, apparently Pd/*t*-ZrO$_2$ showed slightly higher yield to dihydrolevoglucosenone (95%) than the other zirconia based materials,

repeated experiments (up to three times) providing the corresponding errors bars are helpful to evidence that the differences observed are not enough as to clearly distinguish between these three zirconia based catalysts.

In order to select the best catalyst between Pd/SiO$_2$, Pd/Al$_2$O$_3$, Pd/ZrO$_2$-mix., and Pd/t-ZrO$_2$ materials, and considering that all of them provide similar yields of dihydrolevoglucosenone or Cyrene (95% at 5 h reaction), the catalytic activity of these Pd-materials was studied more in detail. In this sense, a decrease in the catalyst loading for these Pd-catalysts was done and samples were taken out from the reactor at shorter times (30 min.). The attained results are depicted in Figure 6, showing that the Pd-catalyst with tetragonal phase of zirconia is intrinsically more active than the other Pd-based materials, also including 5wt%Pd/C commercial catalyst. Thus, Pd/t-ZrO$_2$ material can keep the maximum yield to Cyrene ($\approx$93%) even when decreasing the quantity of catalyst till having just 3.0wt%, unlike what happens with Pd on alumina and Pd on carbon catalysts, where dihydrolevoglucosenone yield goes down to $\approx$80% when reaching catalyst loading $\leq$5.0wt%. The situation is even worse when using Pd/SiO$_2$ and Pd/TiO$_2$ catalysts, where the yield to dihydrolevoglucosenone goes down even at higher loadings.

Figure 6. Yield to dihydrolevoglucosenone (Cyrene) in the selective hydrogenation of levoglucosenone over Pd/t-ZrO$_2$ and Pd/Al$_2$O$_3$ catalysts. *Pd/C loading was always half with respect to the other catalysts. <u>Reaction conditions:</u> 0.126 g levoglucosenone, 0.500 g water, at 10 bar H$_2$ pressure and 80 °C during 30 min.

Reusability tests of Pd-supported on tetragonal zirconia

Once the adequate Pd supported catalyst for the selective hydrogenation of levoglucosenone to dihydrolevoglucosenone (or Cyrene) was selected (Pd/*t*-ZrO$_2$), it was crucial to test the re-usability of the catalytic system. According to the work of Huber and co-workers,[23] catalysts described so far suffered from deactivation problems, mainly as a consequence of the carbonaceous matter deposition on the catalyst surface throughout the reaction. Hence, it was totally advisable to carefully test this catalytic feature. To address this issue, catalyst re-cycles were carried out by washing the catalyst used in the reaction with water (or water/ethanol mixture) and subsequently without any additional regeneration process, it was submitted to the same reaction conditions used for the fresh material (see Experimental part).
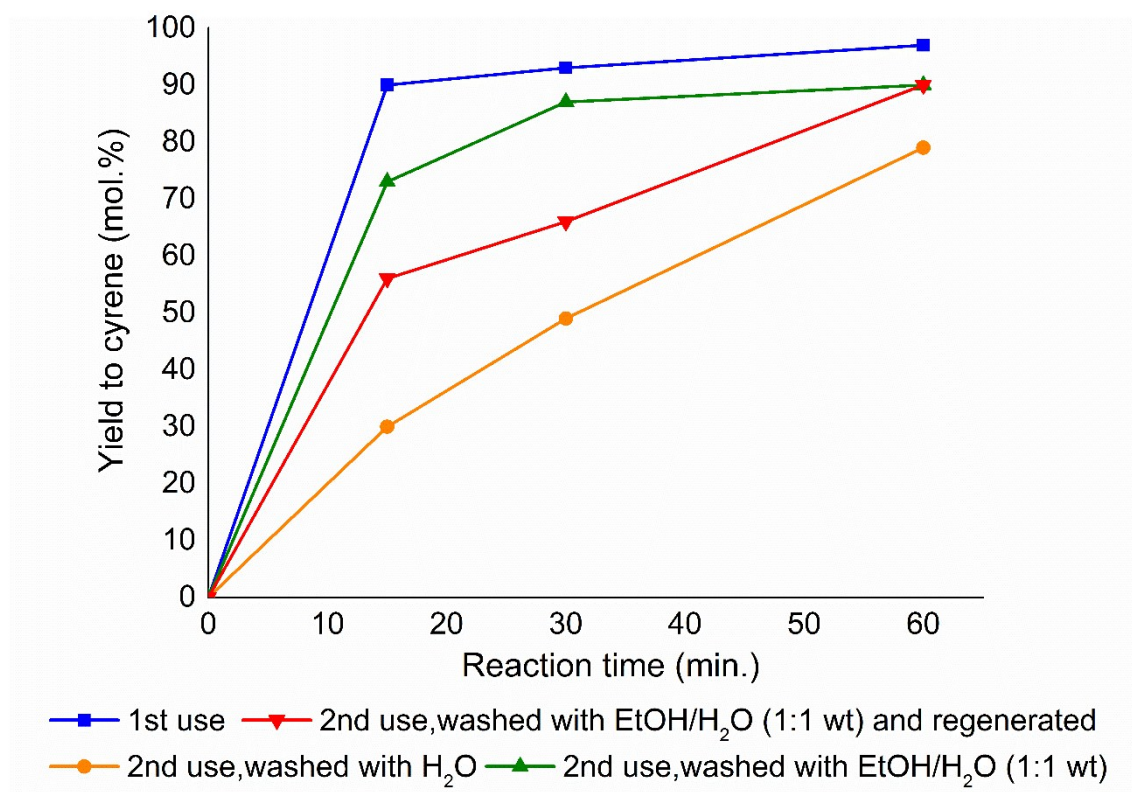
Figure 7. Yield of dihydrolevoglucosenone (Cyrene) in the selective hydrogenation of levoglucosenone over Pd/*t*-ZrO$_2$ after two consecutive catalytic cycles. <u>Reaction conditions:</u> 0.126 g levoglucosenone, 0.500 g of water, 3.0 wt% of Pd/*t*-ZrO$_2$ at 80 ºC and 10 bar H$_2$ pressure during 60 min.

Results of the recycling tests for levoglucosenone hydrogenation to obtain dihydrolevoglucosenone (Cyrene) over Pd/*t*-ZrO$_2$ depicted in Figure 7 unveil a decrease in the

catalytic performance during the first re-use (after washing with water) compared to the yield attained when using a fresh catalyst during the same reaction time. Elemental analysis (EA) of the catalysts after use and washing with water revealed the presence of organic mater containing at least 9.4wt% of carbon on Pd/t-ZrO$_2$ catalyst. As it was also previously reported,[23] these data point out the organic matter deposition as the main reason for blocking the Pd active sites and inhibiting hydrogenation capacity, therefore losing the catalytic activity of the catalyst. Apparently, washing with water is not effective enough to completely remove the cabonaceous deposits from the catalytic surface, resulting in lower yields of the desired product when the catalyst is re-used. In order to restablish the initial catalytic activity, the recovered catalyst was first adequately washed with a mixture of EtOH/water (1:1 in weight), and then regenerated by thermal treatment under H$_2$ flow (see Experimental part). Afterwards, the regenerated Pd/t-ZrO$_2$ sample was re-used in the selective hydrogenation of leglucosenone, thereby partially avoiding the deactivation and yielding ≈92% of dihydrolevoglucosenone (Cyrene) after 60 minutes, a result very similar to that obtained with the fresh catalyst in its first use (see Figure 7). This can be explained by considering that the washing with EtOH/water allows a better removal of the organic matter from the catalytic surface (see data of Table S1 in SI). However, results at shorter times also unveil that a slight deactivation of the catalyst still remains after this second reductive process. This fact was related to an increase in the metal particle size distributions attached in Figure S2E (see SI), which shows a broader distribution in the case of the regenerated catalyst, as well as an average size of nanoparticles considerably above the former one (≈12 nm for regenerated catalyst vs ≈5 nm for fresh catalyst by HR-TEM). Then, the decission was made of just washing the catalyst with the mixture EtOH/water (1:1 in weight) but avoiding the thermal regeneration process. The results show that by just washing with this mixture of solvents, the catalytic performance of the catalyst is practically restablished, even at reaction times shorter than 1 h, and any metallic leaching was observed either (see Table S1 in SI).

In conclusion, Pd/t-ZrO$_2$ material have proven to be an active and effective catalyst for the selective hydrogenation of levoglucosenone to obtain dihydrolevoglucosenone (Cyrene) in high yield (≥92%) under mild reactions conditions, its reusability being also demonstrated after making the appropiate choice of solvent (ethanol:water) for washing procedure and avoiding the need of thermal regeneration.

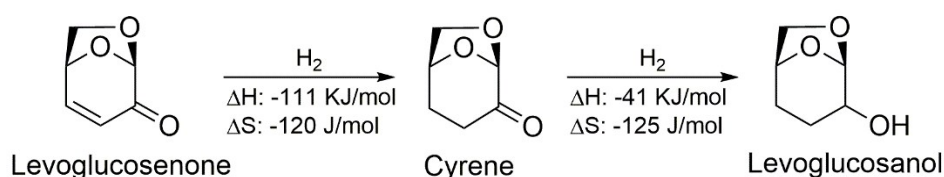### *One-pot selective hydrogenation of levoglucosenone over Pt supported on different metal oxides*

Taking into consideration the results obtained in our preliminary catalytic tests with different metal supported commercial catalysts, where 5wt%Pt/C produced levoglucosanol in

approximately 50% yield (see *Effect of the type of metal used in levoglucosenone hydrogenation* section, Table 4), an optimization of the reaction conditions to maximize the selectivity towards the saturated alcohol product was firstly done by varying the temperature and the H_2 pressure during reaction. In a second step, a catalytic screening with Pt supported on different metal oxides was carried out to select the best catalyst for a two steps reduction of levoglucosenone to levoglucosanol in one-pot. Interestingly, levoglucosanol is a product which still preserves chirality (also providing a new estereogenic center due to the alcoholic group formation), and it can also be further converted to tetrahydrofurandimethanol (THFDM) as Huber and co-workers have recently proved.[24] THFDM is an α,ω-diol that could potentially substitute existing α,ω-diols in organic synthesis and polymer industry.
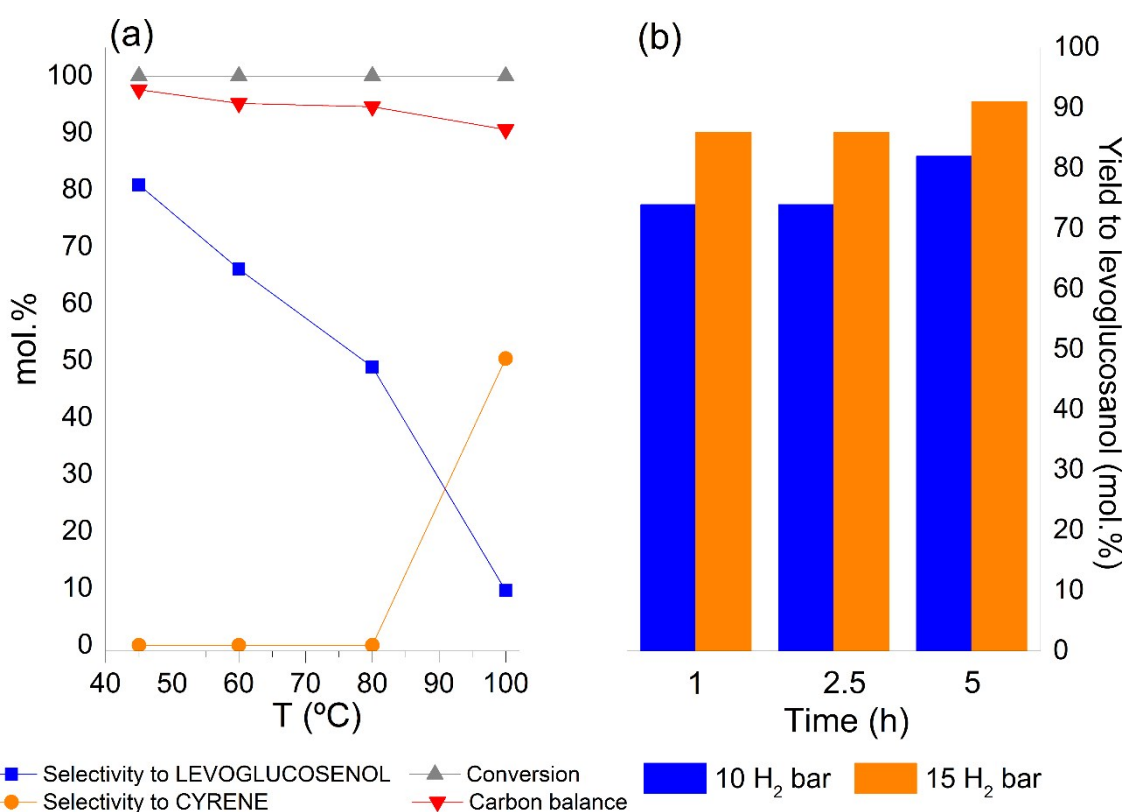
Figure 8. (a) Effect of temperature on the selective hydrogenation of levoglucosenone (at P_{H2} = 10 bars). (b) Effect of pressure on the selective hydrogenation of levoglucosenone to levoglucosanol (at 45 ºC). Reaction conditions: 0.126 g levoglucosenone, 0.500 g acetonitrile, 12.5wt% of 5wt%Pt/C during 5 h.

Scheme 2. Thermodynamics of levoglucosenone hydrogenation process (adapted from Ref.[23]).

The effect of reaction temperature on the selective hydrogenation of levoglucosenone with acetonitrile as solvent and using 5wt%Pt/C as catalyst was assessed. Results shown in Figure 8a demonstrate how the reaction moves towards the production of levoglucosanol when decreasing the temperature. This fact is not surprising if the results of Gaussian DFT calculations reported by Huber and co-workers are taken into consideration (see Scheme 2).[23] To produce dihydrolevoglucosenone (Cyrene), the enthalpic term is more important than the entropic one, with respect to what happens in the route of dihydrolevoglucosenone to levoglucosanol. Due to this, when raising the temperature, the thermodynamics of the system prevents us from achieving a complete hydrogenation.

In addition, after selecting the reaction temperature (45 °C), an increase in the H_2 pressure from 10 to 15 bar favours the complete hydrogenation reaction of levoglucosenone giving close to 90% selectivity to the corresponding saturated alcohol at 100% conversion (see Figure 8b).

With these results in mind, a catalytic screening was done by testing Pt supported on different metal oxides under these conditions (at 45 ºC and P_{H2} = 15 bar) with both acetonitrile and water as solvents, and the results are summarized in Table 6. As can be seen, complete levoglucosenone conversion was reached in all cases by using acetonitrile as solvent. Pt/C and Pt/ZrO$_2$-mix showed similar yields (87-88%) to the saturated alcohol (levoglucosanol), but TON calculated for the Pt/ZrO$_2$-mix (TON = 224) is practically twofold times higher than that achieved for Pt/C (TON = 132), it means that the catalytic activity per Pt center is quite higher in the case of Pt/ZrO$_2$-mix catalyst when comparing to the commercial Pt/C catalyst. Moreover, the yield of levoglucosanol obtained with Pt/Al$_2$O$_3$ material was lower (74%), and even much lower in the case of Pt/TiO$_2$ sample. This general trend is even more pronounced than that observed with Pd-supported materials, and also generally exhibited when replacing acetonitrile by water as reaction solvent. In this sense, when representing selectivity to levoglucosanol vs Lewis acid sites for different Pt-supported catalysts in the hydrogenation of levoglucosenone (see Figure S26, SI) an optimum value of Lewis acidity is observed for Pt/ZrO$_2$-mix, while an excess of Lewis acidity apparently results in a decrease in the selectivity to the desired levoglucosanol, in favour of Cyrene and other by-products. Nevertheless, these interesting observations are not enough to elucidate the catalytic behaviour of Pt-catalysts since, for example, it is difficult to explain why Pt/SiO$_2$ yields almost no levoglucosanol. Thus, further studies are needed to ascertain the interactions taking place between Pt nanoparticles and levoglucosenone during the hydrogenation process (see *FT-IR spectroscopic* studies section).

Table 6. Catalytic results in the selective hydrogenation of levoglucosenone with Pt supported on different metal oxides.

| Catalyst	Pt (wt%)[a]	Conversion (mol. %)	Selectivity to LEVOGLUCOSANOL (mol. %)	TON	Carbon balance (%)
		CH_3CN / H_2O	CH_3CN / H_2O	CH_3CN / H_2O	CH_3CN / H_2O
Pt/C	5.0*	100 / 97	87 / 21	132 / 128	96 / 98
Pt/SiO_2	1.8	94 / 96	8 / 6	169 / 179	100 / 100
Pt/TiO_2	2.1	100 / 98	24 / 30	146 / 149	92 / 93
Pt/Al_2O_3	2.0	100 / 96	74 / 33	176 / 166	97 / 99
Pt/ZrO_2-mix	1.5	100 / 97	89 / 59	224 / 214	97 / 92
Pt/t-ZrO_2	1.4	100 / 98	88 / 56	239 / 234	99 / 94

Reaction conditions: 0.126 g levoglucosenone, 0.500 g solvent, 25.0wt% of catalyst *(except for Pt/C, 12.5wt%), at 45 °C and 15 bar H_2 pressure during 2.5 h. a: measured by ICP.

From the above discussed results, it can clearly be concluded that Pt/ZrO_2-mix is the most adequate catalyst for the complete levoglucosenone hydrogenation process in both organic and aqueous media. In this sense, the influence of the presence of different crystalline phases of ZrO_2 in the Pt/ZrO_2 catalyst was also assessed. Results in Table 6 also show that practically similar levoglucosanol yields were attained by using Pt/t-ZrO_2 as catalyst. Thus, no significant effects have been observed when using different zirconia polymorphous in the direct production of levoglucosanol from levoglucosenone. The ^{1}H NMR and ^{13}C NMR analysis together with a GC-MS spectrum proved that levoglucosanol was, in fact, the main product of this reaction, detecting only some small quantities (<10 mol.%) of several unidentified products (see Figures S14, 15 and S22 in SI) when working with acetonitrile as solvent.

The effect of the use of water as solvent on the catalytic activity of Pt-catalysts during the direct (one-pot) hydrogenation of levoglucosenone to levoglucosanol was also assessed. As it can be seen (Table 6), the use of water leads to a strong decay in the selectivity to the saturated alcohol in all the cases. In the specific case of Pt/ZrO_2-mix, the use of water was found to be detrimental for the selective production of levoglucosanol, only reaching ≈50% yield of the desired alcohol after 5 h of reaction (see Figure S25). Nonetheless, these effects can be counteracted by working under higher H_2 pressures. As can be seen in Figure S25, approximately 90% levoglucosanol selectivities can be achieved by working with H_2 pressures ≥18 bar, even in the presence of water. Summarizing, the results up to now exposed in this section let us to conclude that it is possible to use Pt/ZrO_2-mix as a catalyst for the direct production of levoglucosanol from levoglucosenone under mild reaction conditions, and even using water as a solvent.

Reusability tests for Pt-supported on mixed zirconia

Similar reusability tests performed for Pd/*t*-ZrO$_2$ material were also carried out for the Pt/ZrO$_2$-mix catalyst in the selective hydrogenation of levoglucosenone to levoglucosanol under mild reaction conditions. As can be seen in Figure 9, the same detrimental effect in the catalytic activity can be observed for the reusability test of Pt/ZrO$_2$-mix when washing the catalyst only with water. Although it is a fact that some deactivation is occurring once again, it is not unreasonable to think about the possibility of using the same catalyst for one reaction and then, trying regenerating the material by introducing a more effective washing (EtOH/water, 1:1 in weight) in-between reuses, as it was previously performed for the Pd-supported on zirconia catalyst case. In the case of Pt/ZrO$_2$-mix material, after washing it with a mixture of EtOH and water (1:1 in weight), the catalyst was able to achieve the same result attained with the fresh catalyst in its first use, thus yielding >95% of levoglucosanol. More interestingly, the amount of carbon deposited on the Pt/ZrO$_2$-mix catalyst determined by elemental and thermogravimetric analysis was only 4.1wt%, it means that very low amounts of carbonaceous matter remain on the catalytic surface after uses. It is also necessary to mention that no leaching was observed (Table S1). All these results unveil the possibility of applying this catalyst on a large scale to obtain levoglucosanol from levoglucosenone, by re-cycling the solid material several times only by adequate washing of the catalyst and without the need of thermal regeneration treatments.
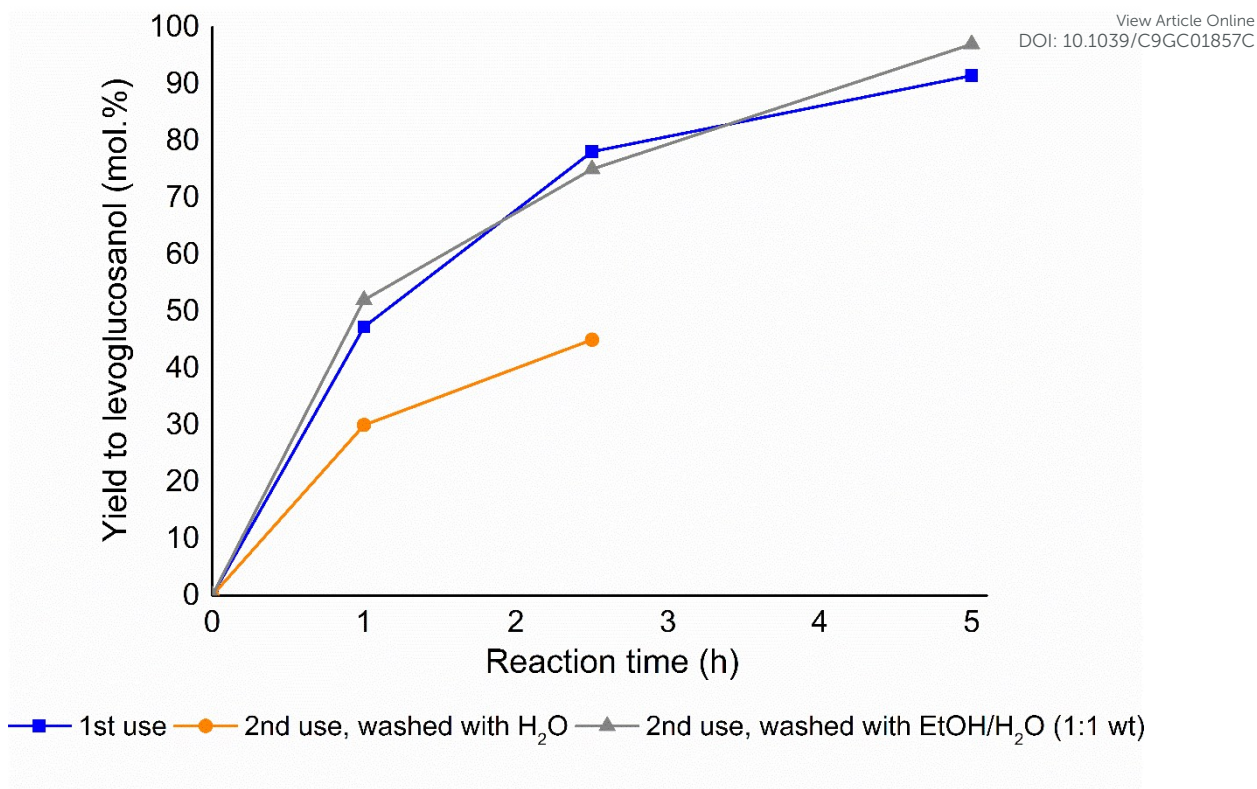
Figure 9. Yield to dihydrolevoglucosenone (Cyrene) in the selective hydrogenation of levoglucosenone over Pt/ZrO$_2$-mix over two consecutive catalytic cycles. <u>Reaction conditions:</u> 0.126 g levoglucosenone, 0.500 g of water, 25.0wt% of Pt/ZrO$_2$ (mixture) at 45 °C and 18 bar H$_2$ pressure during 5 h.

FT-IR spectroscopic studies

According to the previous discussion, the yield to products is influenced by the acid properties of the support, as for example in the Pd/TiO$_2$ catalyst, where an excess of Lewis acidity results in an strong adsorption of reactants and accordingly to the formation of by-products. This, while reasonable, does not explain the full catalytic data, as for instance, the practical absence of levoglucosanolon Pt/SiO$_2$ catalyst.

This result points towards the role of another parameter not yet considered. Hydrogenation of α,β-unsaturated aldehydes on Pt and Pd catalysts has been reported to be sensitive to the particle morphology, i.e exposed crystal facets, where both electronic effects and steric effects play an important role. Thus, double bonds adsorb in a π CC form on Pt (110), except in acrolein where it adsorbes in a di-σ CC mode on Pt(111). Unsaturated aldehydes adsorb preferentially in a planar η4 mode on Pt(100), while crotonaldehyde and cinamaldehyde adsorb in a σ CO mode on Pt(111).[31] These different adsorption modes on specific crystal faces influence the selective hydrogenation of the different functional groups.[31-33] Moreover, it has been shown that cleavage
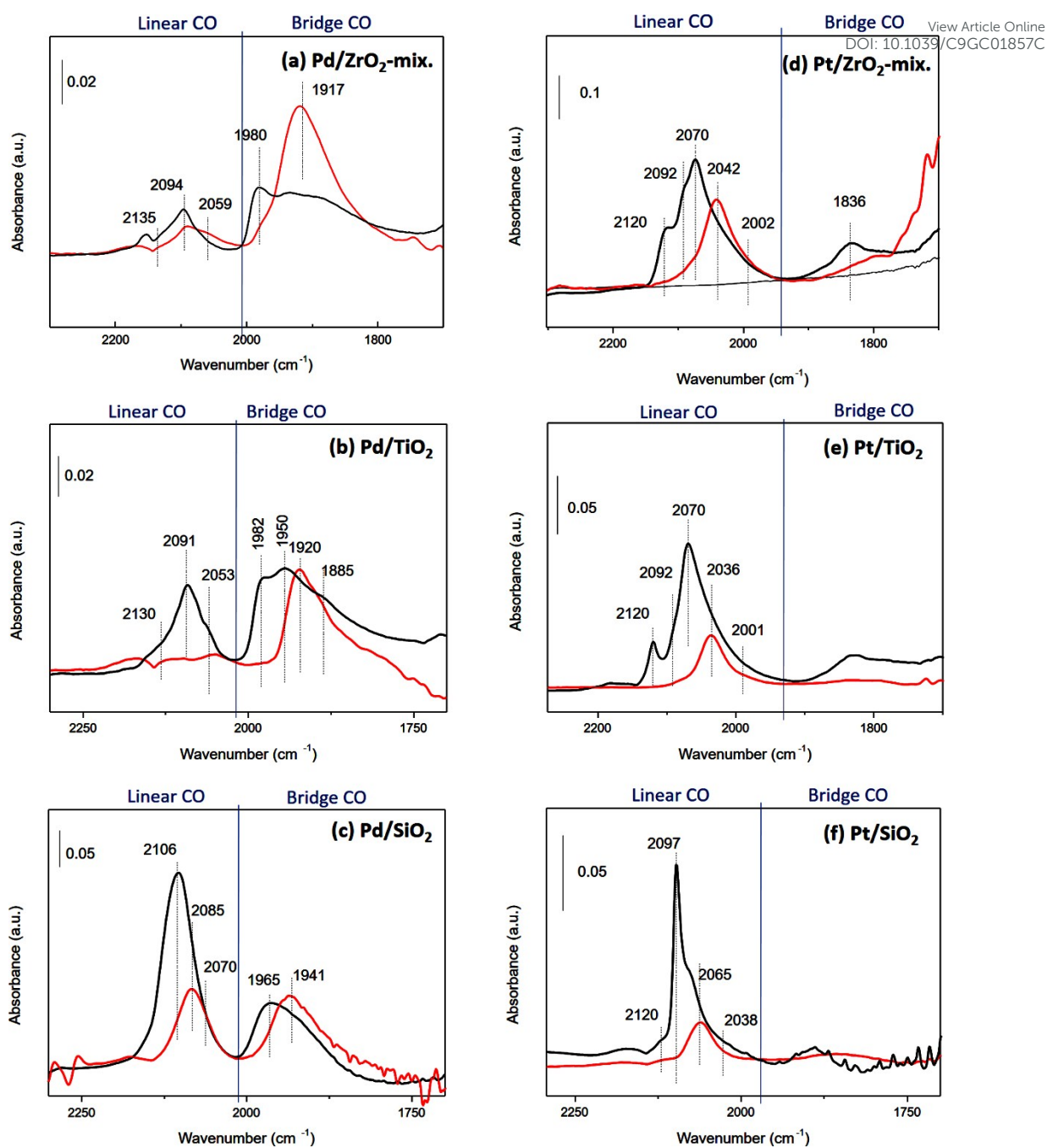
27

of C-O bond in ethers is also influenced by the Pt crystal facet, being enhanced on Pt(100).[34] Based on these precedents, the metal crystal facets of the Pt and Pd supported catalysts have been characterized by IR studies using CO as a probe molecule. As shown in Figure 10 (black line), several IR bands are observed; at 2121cm^{-1} corresponding to oxidated metal species, ~2090-2100 cm^{-1}, 2074-2069 cm^{-1} and 2058 cm^{-1}, due to CO linearly bonded on (111), (100) and (110) facets respectively[35], 2042-2030 cm^{-1}, assigned to CO bonded on atoms at steps and corners, and 1980-1900 and 1880-1800 cm^{-1} corresponding to bridged and tri-bonded CO, respectively.[36-38] Different band intensities can also be found for each one of the samples. This results in different crystal morphologies exposing different facets. Indeed, Pd catalysts show well ordered crystals exposing mainly (111) facets, while in the case of Pt catalysts, both (111) and (100) facets are primordially observed in the Pt/ZrO$_2$, and Pt/TiO$_2$ samples, whereas in the Pt/SiO$_2$ sample the main facet is the (111). If comparing these data with the catalytic data, it seems that the metal (111) facet is involved in C=C hydrogenation, while C=O hydrogenation takes place on (100) facets. This is in concordance with the general tendency observed throughout the article, where Pd-based materials hydrogenate only C=C (to give Cyrene), whereas Pt-based materials tend to hydrogenate both C=C and C=O (giving Levoglucosanol).

In this case, a greater amount of (100) facets (i.e. IR band intensity), as occurs in the Pt/ZrO$_2$ sample, would improve the selectivity to levoglucosanol, which is in perfect match with the catalytic results of Table 6. However, the reported IR results do not explain all the catalytic data, since for instance (100) facets are also observed (while in less extension) in Pd/SiO$_2$, exhibiting close to 100% cyrene selectivity. In order to explain that, the interaction of levoglucosenone with the surface sites of the catalyst needs to be considered. In this sense, IR spectra of levoglucosenone adsorption on the different samples has been studied by IR-KBr in combination with IR-CO titration experiments. The IR-KBr spectra (Figure S30) of levoglucosenone adsorbed on the bare support and on the corresponding Pt, Pd supported catalysts are quite similar, revealing that an important fraction of the reactant is adsorbed on the support. The lower adsorption observed on SiO$_2$ samples corresponds with their lower acidity. On the other hand, the IR-CO titration experiment unveils an important part of the metal being blocked by surface adsorbed species (Figure 10, red line), where those sites where levoglucosenone adsorption is either weak or absent remains "free" for CO titration. We can assume that these "free" sites (reactant no coordinated sites) are not involved in the catalytic process. According to Figure 10 (red line), those sites correspond clearly to steps and corners. On the other hand, it is seen that the (100) facets in the Pd/SiO$_2$ sample, while present, doesn't interact with levoglucosanone. This match with the catalytic study where no levogucosanol is formed. In addition the (110) facets (IR band at ~2058 cm^{-1}) seem not to interact with levoglucosanone, except in the Pd/TiO$_2$. In this sample, the formation of subproducts, as already discussed, can be related either to an excess of surface acid

sites or to bond cleavage on the less selective (110) facets. Table 7 summarizes the levoglucosenone interaction with the different metal facets thanks to an estimation based on comparing areas before and after levoglucosenone adsorption.

Table 7. Estimated levoglucosenone interaction by comparing areas before and after the adsorption of levoglucosenone on the reduced catalysts. (-): not detected facet.

| Catalyst	Estimated levoglucosenone interaction (area % covered by the molecule)				
	2121 (M^{x+})	2100-2090 (111)	2074-2069 (100)	2058 (110)	2042-2030 (steps&corners)
Pd/ZrO$_2$-mix.	100	57	Not observed	0	Not observed
Pd/TiO$_2$	100	100	-	100	-
Pd/SiO$_2$	-	100	0	-	0
Pt/ZrO$_2$-mix.	100	100	89	-	0
Pt/TiO$_2$	100	100	95	-	0
Pt/SiO$_2$	100	100	-	13	8

Figure 10. IR spectra of CO adsorption on Pd and Pt supported catalysts after a reduction treatment, prior (black) and after levoglucosenone (red) adsorption.

Hydrogenation experiments with real pyrolysis feed

To conclude the study of the two catalytic systems (Pd/t-ZrO$_2$ and Pt/ZrO$_2$-mix) already described for both, selective hydrogenation of levoglucosenone to dihydrolevoglucosenone (Cyrene) and direct hydrogenation of levoglucosenone to levoglucosanol, respectively, the biggest issue that should still be faced was the hydrogenation of levoglucosenone present in a real mixture coming

from reached-cellulose biomass pyrolysis. Thus, a crude bio-oil mixture containing ≈66wt% of levoglucosenone (see Experimental Part) was used as the feed for both hydrogenation catalytic systems, and the results appear in Figure 11. As can be seen in Figure 11a for the hydrogenation of levoglucosenone over Pd/*t*-ZrO$_2$, it is possible to achieve almost the same yields to dihydrolevoglucosenone (Cyrene, ≥92% at 1 h reaction) when using both pure levoglucosenone feed or by treating a real pyrolysis liquid containing levoglucosenone. This is a very promising result proving that it is possible to carry out this selective catalytic hydrogenation process for obtaining dihydrolevoglucosenone from levoglucosenone in high yields by using Pd/*t*-ZrO$_2$ catalyst, and more importantly, employing real feedstock from reached-cellulose biomass pyrolysis which possess high amount of water together with several bio-derived compounds.

However, when a similar study is made for Pt/ZrO$_2$-mix catalyst to perform the hydrogenation of levoglucosenone to levoglucosanol, the system is not able to carry out the complete hydrogenation to levoglucosanol when the catalyst faces the pyrolysis liquid. Nonetheless, if making the reaction conditions more drastic (this meaning higher H$_2$ pressure and more catalyst), it is possible to increase the yield to levoglucosanol (≈25%) by working with the real feedstock containing levoglucosenone. Nevertheless, these results are still lower when comparing to the levoglucosanol yield (≈90%) attained when pure levoglucosenone is used as feed (Figure 11b).
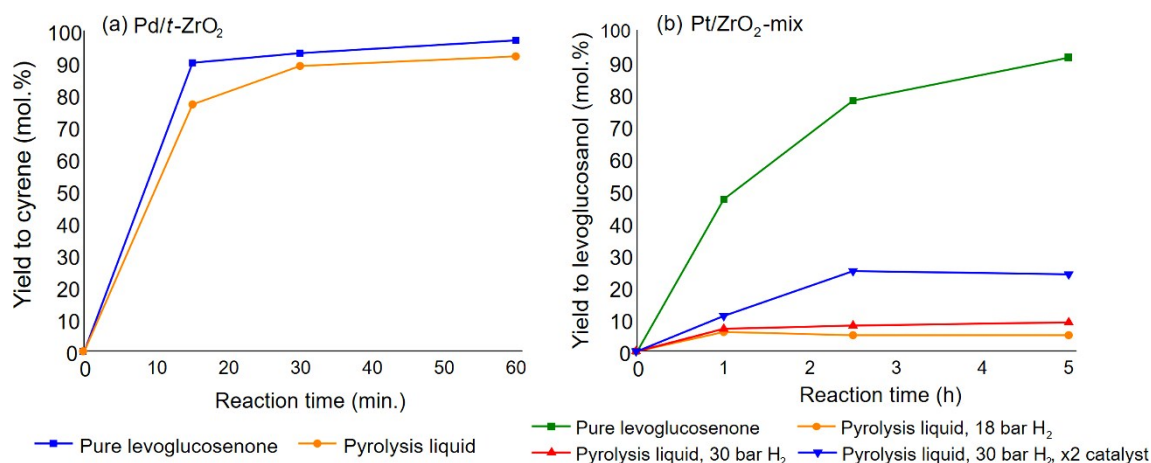
Figure 11. Comparison of the catalytic performance of (a) Pd/*t*-ZrO$_2$ and (b) Pt/ZrO$_2$-mix, when feeding the reactor with pure levoglucosenone or with a pyrolysis liquid containing levoglucosenone. <u>Reaction conditions:</u> (a) 0.126 g levoglucosenone, 0.500 g of water, 3.0wt% Pd/*t*-ZrO$_2$ at 80 ºC and 10 bar H$_2$ pressure during 60 min. (b) 0.126 g levoglucosenone, 0.500 g of water, 25wt% of Pt/ZrO$_2$-mix at 45 ºC and 18 H$_2$ pressure during 2.5 h.

It is worthing to note that the liquid mixture obtained through thermal pyrolysis of biomass containing 66wt% of levoglucosenone also possesses water and other bio-derived compounds as impurities. In order to identify the more relevant bio-compounds present in this pyrolysis liquid and with the aim of finding out what components of the crude could be responsible for the catalyst poisoning during levoglucosanol synthesis, some additional experiments were done. In this sense, GC, GG-MS and also NMR analysis (Figures S16, S17, S20 and S23) showed furfural (≈11wt% with respect to levoglucosenone) and other furan-derivatives (≈15wt% with respect to levoglucosenone) as the main by-products present in the crude. Therefore, experiments of direct hydrogenation of levoglucosenone to levoglucosanol over Pt/ZrO$_2$-mix by adding small quantities of furfural to pure levoglucosenone in water were carried out, results pointing out to the furfural as one of the possible catalyst poisoners, as the yield to levoglucosanol progressively decreases with the increase of this compound in the reaction mixture (Figure S27).

Conclusions

The results obtained in this work show that it is possible to carry out the hydrogenation of levoglucosenone to dihydrolevoglucosenone (Cyrene) in an efficient and highly selective way with Pd-based catalysts. From Pd-supported on different metallic oxides (i.e. TiO$_2$, Al$_2$O$_3$, and ZrO$_2$), the Pd/t-ZrO$_2$ catalyst has proven to have the best performance. In particular, this catalyst has been able to achieve near 95% yields of dihydrolevoglucosenone (Cyrene) by working under mild reaction conditions, with very low catalyst loadings (≈3wt%) and using water as solvent. In addition, the Pd/t-ZrO$_2$ system succeeded in approaching previously failed or not adressed issues such as reusability and real feed processing. In the case of reusability, after one use and adequate washing of the catalyst, almost the same results in terms of dihydrolevoglucosenone yield (≈90%) of fresh catalyst can be achieved. More interestingly, when treating a real pyrolysis mixture containing levoglucosenone with this Pd/t-ZrO$_2$ catalyst, identical results are attained when comparing to that reached with pure levoglucosenone.

On the other hand, the complete hydrogenation of levoglucosenone to the saturated alcohol or levoglucosanol has been reported for the first time in one-pot process with a Pt-based heterogenous catalyst (Pt/ZrO$_2$-mix, yield ≈90%), being a very interesting option to produce this levoglucosenone derivative, mainly due to the low temperatures and mild pressures here employed. Moreover, although Pt/ZrO$_2$-mix catalyst is clearly deactivated after the first catalytic cycle and it is unable to carry out the process when washing it with just water, this fact is again totally solved by washing the catalyst with an EtOH/water mixture. Nonetheless, when feeding the reactor with the real pyrolysis liquid containing levoglucosenone, the results attained in terms

of levoglucosanol yields were lower than expected in comparison to those obtained when pure levoglucosenone is fed. Further improvements could be attained by increasing either the H_2 pressure or the catalyst loading in the reaction media, but the best option in this case consists in the elimination (for example via distillation) of impurities like furfural and other furan derivatives, which could be in competition with levoglucosenone for the Lewis acid centers and apparently the main responsible of the catalyst deactivation. Spectroscopic data shows that the hydrogenation of levoglucosenone is surface sensitive, where the presence of (111) and (100) metal facets plays an important role in the selective formation of cyrene and levoglucosanol, respectively. Broadly speaking, Pd-catalysts show mainly (111) facets, whereas Pt-catalysts show a combination of both (111) and (100) facets, being possible to explain the different selectivity of each metal to either Cyrene (Pd) or levoglucosanol (Pt) based on this fact. The behavior observed with different supports can be also rationalized in terms of the ratio between the exposed metallic facets on each case together with their differences in the Lewis acidity, being an excess of Lewis acid sites detrimental for the selectivity to the desired hydrogenated product.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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