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Palladium nanoparticles stabilized by novel choline-based ionic liquids in glycerol applied in hydrogenation reactions.

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Abstract

Palladium nanoparticles stabilized by choline-based ionic liquids in glycerol were prepared from Pd(II) precursors by simply heating at 80 °C under argon; in this process, the water present in the ionic liquid was found to be the responsible for the reduction of Pd(II) into zero-valent palladium species. Palladium nanoparticles were fully characterized in both liquid phase and solid state. The as-prepared metal nanoparticles exhibited remarkable catalytic activity in hydrogenation processes for a significant variety of functional groups (alkenes, alkynes, nitro derivatives, benzaldehydes, aromatic ketones).

Highlights

- Palladium nanoparticles in glycerol stabilized by novel choline-based ionic liquids.
- Characterization of palladium nanoparticles both in solid and liquid phase.
- Palladium nanoparticles showing high catalytic activity in hydrogenation reactions.
- Selective hydrogenations for non-conjugated alkynes.
- Efficient reduction of carbonyl derivatives.

Keywords: palladium nanoparticles, choline-based ionic liquids, amino acid, glycerol, hydrogenation

1. Introduction

Palladium nanoparticles (PdNPs) due to their high efficiency, selectivity and their ability to perform various kinds of catalytic reactions have emerged as an important tool in organic synthesis. PdNPs are one of the most used and efficient catalysts to build C–C bonds and to perform other chemical transformations such as carbon-heteroatom bond formation, hydrogenation, carbonylation and oxidation processes [1]. Well-defined PdNPs are appropriate catalysts for hydrogen activation and hydrogen spillover [2,3]. However, the choice of the right type of stabilizer is a key parameter for the synthesis of PdNPs precluding agglomeration and leaching of metal [4]. For this purpose, stabilizers like surfactants, ligands, polymers and ionic liquids have been widely used [5] to tailor PdNPs size, composition and morphology, thereby tuning the reactivity and selectivity of these systems [6]. In this context, ionic liquids (ILs) have emerged as promising contenders for the stabilization of nanoparticles. As mentioned by Dupont *et al.*, ILs exhibit dispersive forces with polar and nonpolar nano-domains and can form extended networks of hydrogen bonds due to which they are to be considered as supramolecular fluids and not homogeneous solvents [7]. Imidazolium-based ionic liquids represent the most commonly used

molten salts applied in catalysis, in particular for the stabilization of metal-based nanoparticles [8]. Choline chloride, a quaternary ammonium salt, has also emerged as a popular choice for bio-sourced ILs and its use in synthesis of nanoparticles in the form of deep eutectic solvents (DESs) or otherwise have also been reported [9].

In our group, PdNPs stabilized by [BMI][PF₆] have been generated in previous studies leading to high catalytic activity in Suzuki cross-coupling reaction without palladium leaching up to ten cycles [10, 11]. In this frame, in particular, PdNPs stabilized by thioether-phosphine ligands had been used as catalytic precursors in Heck–Mizoroki cross-coupling and C=C hydrogenation reactions [12]. However, the above-mentioned ILs have environmental concerns, which consequently led to the search of an environmental friendly medium. In this context, our team has developed the synthesis of nanoparticles in glycerol medium [13-14]. Glycerol is produced in high amounts as waste in biodiesel production. Its properties like low-cost, non-toxicity, high boiling point (290 °C), negligible vapor pressure (< 1 mmHg at 293 K), high solubilizing ability for organic (except those completely apolar) and inorganic compounds, and low miscibility with other organic solvents such as ethers and alkanes, constitute striking properties that make it especially interesting for applications in catalysis. It plays an important role as support for the immobilization of PdNPs, permitting an easy recycling of the catalytic phase [13]. Our team has synthesized PdNPs in both solution and solid state, using naturally occurring cinchona-based alkaloids in neat glycerol and successfully applied in dihydrogen-based processes, such as hydrogenation of unsaturated functional groups (alkenes, alkynes, imines, and nitro-based substrates) and hydrodehalogenation of halo-aromatic compounds [14].

In order to extend our research in sustainable chemistry, we report here the synthesis of PdNPs using choline based ionic liquids in neat glycerol; the synthesized PdNPs were applied in hydrogenation reactions. Choline based ILs are environmentally friendly with good biocompatible properties and presenting interesting solvent properties: non-flammability, negligible vapor pressure at ambient conditions and high solubility [15]. Furthermore, we also avoid the plausible reactivity of ILs (such as in case of imidazolium-based ILs) with the metal surface [16].

2. Experimental

2.1. Materials and methods

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. All manipulations were performed using Schlenk techniques under argon atmosphere. Glycerol was dried under vacuum at 80 °C for 18 h prior to use. *N*-tosyl-alanine was prepared following previously reported methodology [17]. High-pressure reactions were carried out in a Top Industrie Autoclave. NMR spectra were recorded on a Bruker Advance 300 spectrometer at 293 K (300 MHz for ¹H NMR, 75.5 MHz for ¹³C NMR and 50.6 MHz for ¹⁵N). GC analyses were carried out on a GC Perkin Elmer Clarus 500 with ionization flame detector, using SGE BPX5 column composed by 5% phenylmethylsiloxane, coupled to a Perkin Elmer Clarus MS560 mass detector. TEM images of PdNPs dispersed in glycerol were obtained from a JEOL JEM 1400 instrument running at 120 kV. PdNPs size distributions and average diameters were determined from TEM images applying Image-J software associated to a Microsoft Excel macro. IR spectra were recorded in the range of 4000-400 cm⁻¹ on a Varian 640-IR FTIR Spectrometer. Powder X-ray diffraction analyses were collected on a XPert (Theta-Theta mode) Panalytical diffractometer with $\alpha(\text{Cu K}\alpha 1, \text{K}\alpha 2)=1.54060, 1.54443 \text{ \AA}$. Elemental and ICP-AES analyses were carried out at the “Service d’Analyse” of Laboratoire de Chimie de Coordination (Toulouse) using a Perkin Elmer 2400 series II analyser and an iCAP 6300 ICP Spectrometer. XPS measurements were performed at room temperature with a SPECS PHOIBOS 150 hemispherical analyzer (SPECS GmbH, Berlin, Germany) in a base pressure of 5x10⁻¹⁰ mbar using monochromatic Al K α radiation (1486.74 eV) as excitation source. Mass spectroscopy was done using

UPLC Xevo G2 Q TOF (Waters) by high-resolution electrospray technique. Viscosity was measured using the Rheometer AR2000Ex from TA Instruments.

2.2. Synthesis of choline *N*-tosylalaninate (**B**)

Choline hydroxide (103 mg, 0.85 mol, 46 wt.% in H₂O) was stirred with an aqueous solution of *N*-tosyl-alanine (206 mg, 0.85 mmol) at 60 °C for 12 h. After the ion exchange reaction, water was evaporated under vacuum at 80 °C, obtaining a brownish viscous oil (294.1 mg, 99.9%). **B** was obtained as a racemic mixture. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.72 – 7.61 (m, 2H), 7.35 – 7.22 (m, 2H), 4.08 – 3.96 (m, 2H), 3.69 – 3.60 (m, 1H), 3.50 – 3.44 (m, 2H), 3.19 – 3.12 (m, 9H), 2.29 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 172.6, 142.4, 137.8, 129.5, 126.6, 67.0, 67.0, 66.9, 55.1, 53.2, 53.1, 53.1, 52.1 20.9, 19.6. HR-MS (ESI+) for C₅H₁₄NO⁺: Theoretical = 104.1075, Experimental = 104.1072; HR-MS (ESI-) for C₁₀H₁₂NO₄S⁻: Theoretical = 242.0487, Experimental = 242.0483. IR (ATR, cm⁻¹) 3256, 3045, 2954, 2922. 2866, 2853, 2427, 1718, 1598, 1456, 1397, 1324, 1221, 1093, 958, 884, 816, 708, 662. Viscosity 3054 Pa.s at 25 °C and 2.973 Pa.s at 80 °C.

2.3. Synthesis of palladium nanoparticles stabilized by choline-based derivatives in glycerol

0.05 mmol (14.1 mg) of [PdCl₂(cod)] and 0.85 mmol of choline-based derivative [117 mg for choline chloride (**A**); 294.5 mg for choline *N*-tosylalaninate (**B**)] were dissolved in 5 mL of glycerol and stirred under argon in a Schlenk flask at 80 °C for 18 h. Then, the resulting solution was washed with dichloromethane (3x5 mL) in order to remove any insoluble IL from glycerol phase. A black colloidal solution was then obtained.

2.4. Synthesis of palladium nanoparticles stabilized by choline tosylalaninate at solid state, **PdB**

After synthesis, PdNPs in glycerol were transferred to a centrifugation tube and 2 mL of ethanol were added. Centrifugation was carried out at 4500 rpm for 1 h and then the solution was separated by decantation. This process was repeated 3 times until complete removal of glycerol. The remaining black powder was then dried under vacuum at 80 °C overnight. Elementary analysis (palladium content determined by ICP-AES) for **PdB**: Pd 84.0%, C 7.55%, N 0.30%, H 0.40%.

2.5. General procedure for Pd-catalyzed hydrogenation in glycerol

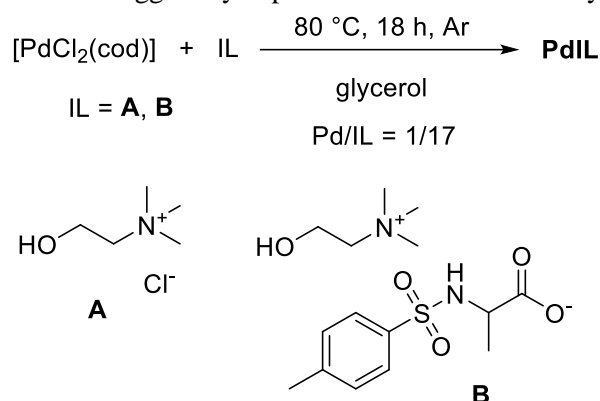
In a Fisher–Porter bottle (working from 1 to 3 bar total pressure) or an autoclave (working from 3 to 20 bar total pressure), the appropriate substrate (1 mmol for 1 mol% of catalyst or 10 mmol for 0.1 mol% of catalyst) was added to 1 mL of preformed nanoparticles (2.85 mg of Pd) in glycerol under argon. The reaction mixture was put under vacuum and then pressurized with H₂ at the convenient pressure, heated up at 80 °C and stirred for the appropriate time; then cooled down to room temperature before extraction. Organic products were extracted from glycerol by a biphasic methodology, adding dichloromethane (5 × 3 mL); organic phases were collected and solvent removed under vacuum. Conversion and yields were determined by GC using decane as internal standard. The obtained products were characterized by GC-MS data and ¹H and ¹³C NMR and compared to literature reports to confirm spectral identity (see Supplementary Material).

3. Results and discussion

3.1. Synthesis of palladium nanoparticles stabilized by choline-based ionic liquids in glycerol

Palladium nanoparticles (**PdA**, **PdB**) were prepared by thermal decomposition of [PdCl₂(cod)] (cod = 1,5-cyclooctadiene) in the presence of a choline-based ionic liquid [choline chloride (**A**); choline *N*-tosylalaninate (**B**)], using glycerol as solvent (Scheme 1). The ionic liquid **B** was prepared based on the reported methodology for the preparation of choline carboxylate ionic liquids (see above, Experimental section) [18]. In both cases, black colloidal solutions were obtained, constituted by spherical small nanoparticles (for **PdA**, 1.4 ± 0.6 nm; for **PdB**, 1.7 ± 0.6 nm), exhibiting a very well-dispersion mainly thanks to the supramolecular structure of glycerol which avoids agglomeration, as evidenced in our

previous works using ligands and polymers as stabilizers [13, 14, 19] (Fig. 1). It is important to highlight that these reaction conditions do not trigger any deprotection of choline *N*-tosylalaninate [20].



Scheme 1. Synthesis of palladium nanoparticles in glycerol using choline-based ionic liquids (**A**, **B**) as stabilizers.

Control tests proved that the water present on the IL (for **A**, 0.25%; for **B**, 1.70%; determined by Karl-Fischer titration) is the responsible of the reduction of Pd(II) into Pd(0); [PdCl₂(cod)] in dry glycerol under the same conditions used in the synthesis of PdNPs was stable and did not exhibit decomposition. This is in agreement with the work carried out by Hirai and coworkers, proving the unsuccessful synthesis of zero-valent rhodium nanoparticles in anhydrous alcohols [21].

When PdNPs were synthesized in the absence of any stabilizer using wet glycerol and different palladium precursors, Pd(0) agglomerates were formed [13(d)].

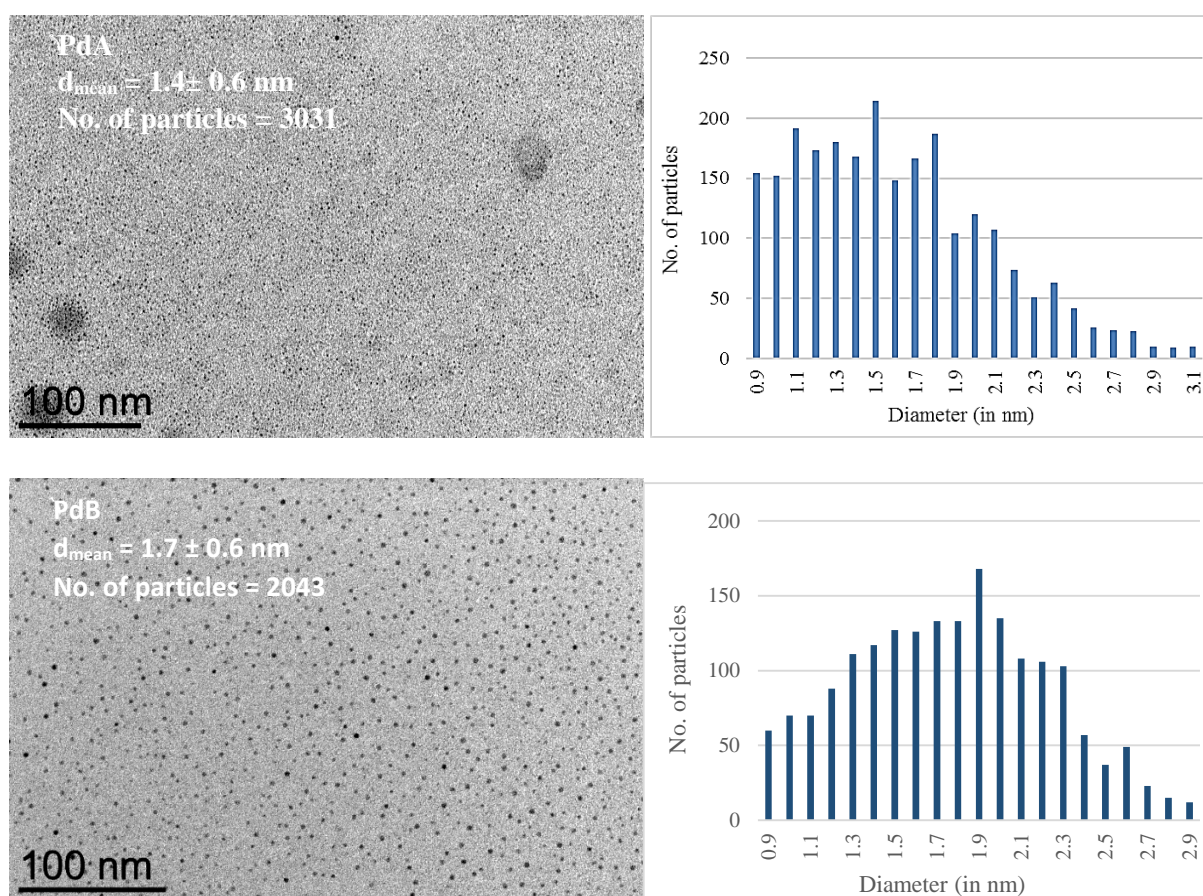


Figure 1. TEM images of **PdA** and **PdB** in glycerol with the corresponding size distribution diagrams.

Palladium acetate was also tested as starting metal precursor with the two choline derivatives, obtaining in both cases aggregates; for choline chloride, anisotropic nano-objects were observed probably due to the presence of halides at the metal surface (see Fig. S1 in the Supplementary material) [22]. We then added polyvinylpyrrolidone (mean molecular weight = 10000 g.mol⁻¹), in order to improve the dispersion, but in this case very few nanoparticles could be detected by TEM (see Fig. S2 in the Supplementary material). Curiously, when dihydrogen was used as reducing agent, an immediate precipitation of bulk palladium took place.

We envisaged the use of choline alaninate as stabilizer (see experimental part and Scheme S1 in the Supplementary Material) [23], instead of the protected anion *N*-tosylalaninate; however, choline alaninate became unstable under atmospheric conditions, due to its high reactivity with carbon dioxide, giving the corresponding carbamate (see Scheme S2 in the Supplementary Material) [24]. Moreover, we also studied the effect of the solvent on the synthesis of colloidal PdNPs, using water and ethanol instead of glycerol under the same conditions than those described in Scheme 1. In both cases, fast precipitation of black palladium was observed, proving that glycerol avoids the agglomeration of metal-based nanoparticles probably due to its supramolecular structure [13(a), 25, 26].

Given the better catalytic behavior of **PdB** (see below Table 1), this catalyst was selected for full characterization. Palladium nanoparticles at solid state were isolated by centrifugation. Powder X-ray diffraction (PXRD) analysis showed the presence of crystalline nanoparticles exhibiting face cubic center Pd(0) structure (Fig. 2). The crystallite size found from the X-ray diffraction peaks (calculated by the Scherrer equation) is *ca.* 3.7 nm; differences in size between TEM and XRD are frequently observed because the average crystallite size (PXRD) is not necessarily the same as the particle size (TEM)[27]. XPS analysis corroborated the absence of any oxidized palladium species (Fig. 3 and Fig. S3 in the Supplementary Material); XPS showed the presence of carbon, oxygen and nitrogen that confirms the presence of the ionic liquid even after isolation of nanoparticles; the presence of chloride probably comes from the metal precursor.

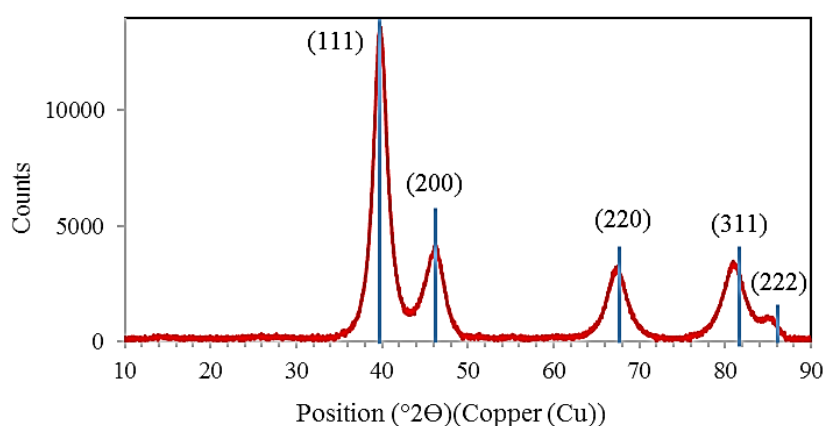


Figure 2. PXRD diffractogram of **PdB** at solid state (sharp blue lines correspond to the diffraction pattern of bulk fcc Pd(0)).

(a)

(b)

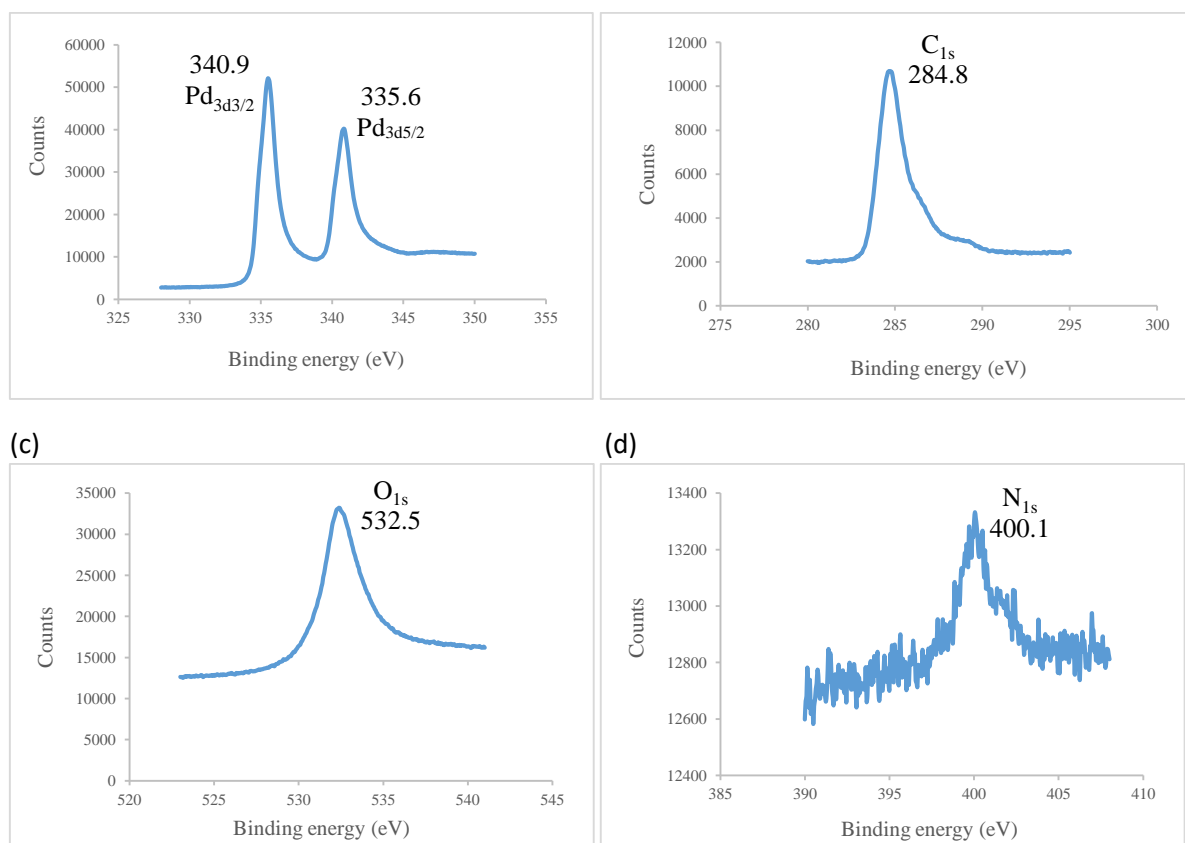


Figure 3. HR-XPS spectra of **PdB** at solid state for (a) Pd(0), (b) carbon, (c) oxygen and (d) nitrogen.

It is important to highlight that **PdB** at solid state could be re-dispersed in glycerol without formation of aggregates (see Fig. S4 in the Supplementary Material). This is in agreement with the XPS analysis that shows the presence of IL at the surface of PdNPs in solid state.

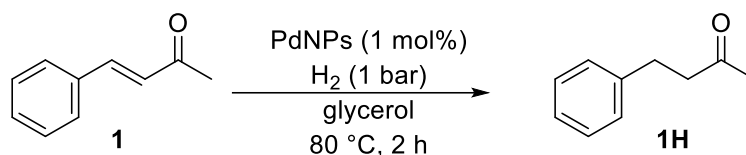
3.2. Pd-catalyzed hydrogenation reactions

The surface reactivity of palladium nanoparticles is very well known, in particular applied in hydrogenation processes involving different kinds of functions [28]. The morphology effect of PdNPs (size, shape) on reactivity is crucial [4]. PdNPs synthesized by wet methodologies contain stabilizers (salts, ligands, polymer, surfactants etc.) [29], which modify the surface state and in consequence their catalytic behavior [30]. In ionic liquid medium, many works have been reported in the literature, mainly focused on the hydrogenation of alkenes and alkynes [31], but only few of them concerning other functional groups such as carbonyls [32].

In the present study, we focused on sustainable ionic liquids from choline, due to the stabilization of PdNPs essentially by electrostatic effect, in glycerol, which helps to the dispersion of nanoparticles. We chose the hydrogenation of 4-phenylbut-3-en-2-one as benchmark reaction. Both catalysts, **PdA** and **PdB**, behave likewise, giving exclusively 4-phenylbutan-2-one (entries 1-2, Table 1), interesting skeleton present in fragrances [33]. Both systems were also highly active at low Pd load (0.1 mol%, entries 3-4, Table 1). However, at shorter times (1 h reaction), only **PdB** preserved the activity (entry 5 vs 6, Table 1), probably due to the non-innocent effect of the chloride anions present in **PdA**, which can trigger a poison effect due to the adsorption of chloride ions at the surface [32].

Table 1

Hydrogenation of 4-phenylbut-3-en-2-one catalyzed by PdNPs in glycerol stabilized by ChCl (**A**) and ChTsAla (**B**).^a



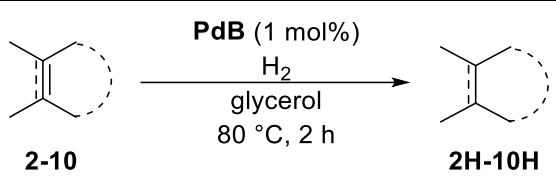
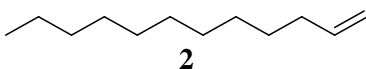
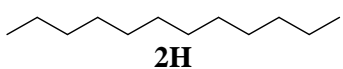
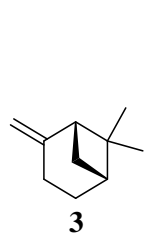
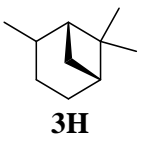
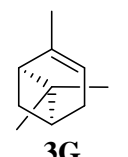
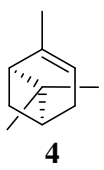
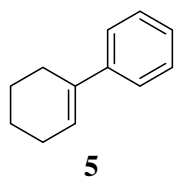
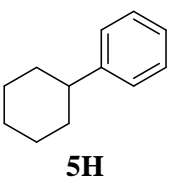
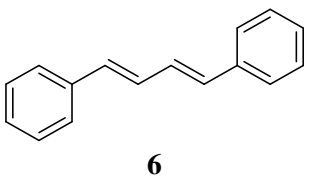
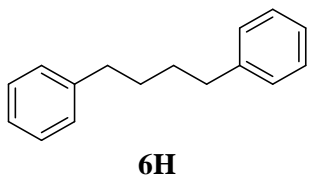
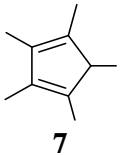
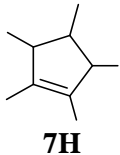
Entry	Catalyst	Conv. (yield) ^b (%)
1	PdA	100 (96)
2	PdB	100 (93)
3 ^c	PdA	50 (49)
4 ^c	PdB	100 (91)
5 ^{c,d}	PdB	96 (92)
6 ^{c,d}	PdA	55 (51)

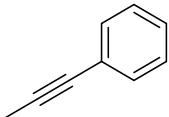
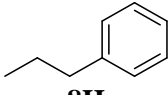
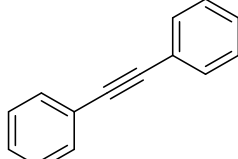
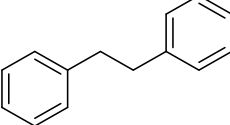
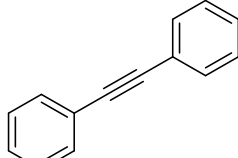
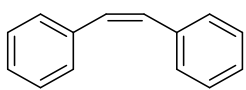
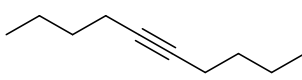
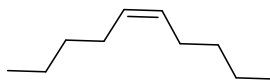
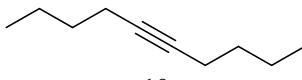
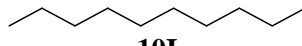
^a Results from duplicated experiments. Reaction conditions: 1 mmol of **1** and 1 mL of the corresponding catalytic glycerol solution of PdNPs (10^{-2} mol L⁻¹, 0.01 mmol of total Pd). ^b Determined by GC and GC/MS using decane as internal standard. ^c 0.1 mol% Pd load. ^d Reaction time 1 h.

With the aim of carrying out a scope related to functions to be reduced by **PdB** we firstly analyzed the behavior of **PdB** in the hydrogenation of alkenes and alkynes (Table 2). The terminal non-substituted alkene 1-dodecene (**2**) was converted into dodecane and internal alkenes in a ratio of 54/46 respectively under smooth conditions (3 bar H₂ and 2 h of reaction; entry 1, Table 2). Under harsher conditions (20 bar H₂, 18 h), (-)-β-pinene (**3**) was mainly isomerized, giving only 18% of hydrogenated product (entry 2, Table 2); **PdB** was not active enough to reduce (+)-α-pinene (entry 3, Table 2). However, for conjugated C=C bonds (alkene **5**), full conversion was achieved under 3 bar H₂ overnight (entry 4, Table 2). In agreement with this behavior, the extended conjugated substrate **6** was fully hydrogenated concerning the non-aromatic C=C bonds (entry 5, Table 2). The more sterically hindered conjugated substrate 1,2,3,4,5-pentamethylcyclopentadiene (**7**) allowed the selective reduction of one of the two endocyclic C=C bonds working at 20 bar of H₂ pressure (entry 6, Table 2).

Internal aromatic alkynes (**8**, **9**) were fully reduced obtaining the corresponding alkane derivatives (entries 7-8, Table 2). At lower H₂ pressure (entry 9, Table 2), only the formation of the corresponding *Z*-alkene was observed, giving up to *ca.* 50% yield; longer reaction times led to the formation of 1,2-diphenylethane. However, the internal alkyl-substituted alkyne, 5-decyne (**10**; entry 10, Table 2) gave mainly the corresponding internal alkene; at longer time (18 h), full hydrogenation was observed (entry 11, Table 2).

Table 2
Hydrogenation of alkenes and alkynes catalyzed by **PdB** in glycerol.^a

Entry	Substrate	Product	$p\text{H}_2$ (bar)	Conv. (yield) ^b (%)
	 <p style="text-align: center;">2-10 $\xrightarrow[\text{glycerol, 80 } ^\circ\text{C, 2 h}]{\text{PdB (1 mol\%)}, \text{H}_2}$ 2H-10H</p>			
1	 2	 2H	3 20	100 ^c 100 ^d
2	 3	 3H  3G	20 (3)	88 ^e [65 ^f]
3	 4	-	20	n.r.
4	 5	 5H	3	100 (99) ^g
5	 6	 6H	3	100 (98) ^g
6	 7	 7H	3 (20)	86 (n.d) [100 (n.d)]

7			1	100 (97)
8			3	100 (99)
9			1	50 (49)
10			3	100 (90/10) ^{h,i}
11			3	100 (96) ^h

^a Results from duplicated experiments. Reaction conditions: 1 mmol of substrate (**2-10**) and 1 mL of the catalytic glycerol solution of **PdB** (10^{-2} mol L⁻¹, 0.01 mmol of total Pd); n.r. means no reaction; n.d. means not determined. ^b Determined by GC and GC/MS using decane as internal standard. ^c Dodecane/internal alkenes = 54/46. ^d Dodecane/internal alkenes = 55/45. ^e Ratio **3/3G/3H** = 12/70/18. ^f Ratio **3/3G/3H** = 35/43/22. ^g Isolated yield. ^h Cyclooctane as internal standard. ⁱ *cis*-5-decene/n-decane = 90/10.

We were also interested in the hydrogenation of other organic functional groups, such as nitro and carbonyl derivatives (Table 3). As expected, nitrobenzene gave aniline in quantitative yield (entry 1, Table 3). **PdB** was also an efficient catalyst for the reduction of carbonyl groups, coming from both aldehydes (**12-14**) and ketones (**15-17**). Concerning the formyl groups, benzaldehyde derivatives exhibiting substituents inducing different electronic effects, were fully converted into the corresponding benzyl alcohols under smooth conditions (3 bar H₂; entries 2-4, Table 3). Aromatic ketones **15** and **16** were hydrogenated to give the corresponding secondary alcohols, but under higher hydrogen pressure (entries 5-6, Table 3). The non-conjugated ketone (**1H**) gave a moderate conversion to the corresponding secondary alcohol (**1I**) at 40 bar H₂ pressure (entry 7, Table 3). The 1-phenylprop-2-yn-1-one (**17**) mainly gave the saturated ketone (**17H**) with only 15% of the corresponding secondary alcohol (**17I**) (entry 8, Table 3). This reactivity behavior concerning the reduction of carbonyl groups follows the same trend than that reported recently by J. Dupont and co-workers using supported palladium nanoparticles on poly (ionic liquid) materials based on pyrrolidinium salts [32(a)].

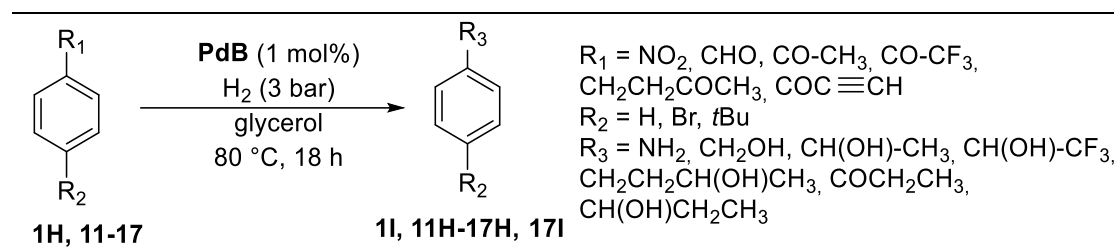
Alkyl ketones (such as 3-pentanone and 2,2,4,4-tetramethyl pent-3-one) and alkyl aldehydes (like hexanal) were not reduced (up to 20 bar H₂). Similarly, benzonitrile was not hydrogenated under harsh conditions.

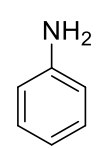
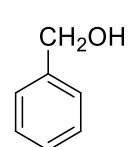
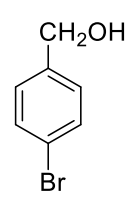
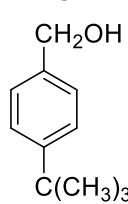
After catalysis, no leaching of Pd was detected by ICP-AES analyses. But, some aggregation was observed by TEM preserving the zero-valent PdNPs (see Figs. S5 and S6 in the Supplementary

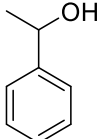
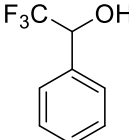
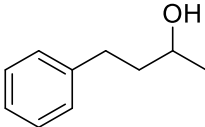
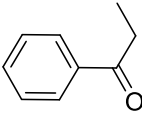
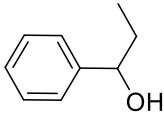
Material); the formation of aggregates may be the reason for the observed decrease of the catalytic activity and hence it was difficult to use the PdNPs for an efficient recycling (see Fig. S7 in the Supplementary Material).

Table 3

Hydrogenation of nitro and carbonyl groups catalyzed by **PdB** in glycerol.^a



Entry	R ₁	R ₂	Product	Conv. (yield) ^b (%)
1 ^{c, d}	NO ₂ (11)	H	 11H	100 (99)
2	CHO (12)	H	 12H	98 (95)
3	CHO (13)	Br	 13H	99 (97)
4	CHO (14)	C(CH ₃) ₃	 14H	90 (89)

5 ^e	COCH ₃ (15)	H		100(98) ^f
			15H	
6 ^e	COCF ₃ (16)	H		100 (97)
			16H	
7 ^g	CH ₂ CH ₂ COCH ₃ (1H)	H		40 (37)
			1H	
				
			17H	
8 ^e	COC≡CH(17)	H		100 (85/15) ^h
				
			17I	

^a Results from duplicated experiments. Reaction conditions: 1 mmol of substrate (**1H**, **12-18**) and 1 mL of the catalytic glycerol solution of **PdB** (10⁻² mol L⁻¹, 0.01 mmol of total Pd). ^b Determined by GC and GC/MS using decane as internal standard. ^c H₂ pressure 10 bar. ^d Reaction for 2 h. ^e H₂ pressure 20 bar. ^f Isolated yield. ^g H₂ pressure 40 bar. ^h **17H/17I** ratio.

4. Conclusions

To sum up, we efficiently prepared and fully characterized new palladium nanocatalysts, stabilized by environmentally friendly choline-based ionic liquids in glycerol. The counter anion of the choline derivative showed a non-innocent effect on the catalytic activity, probably due to the higher adsorption of chloride than tosyl-alaninate at the metallic surface [34], and consequently hindering the interaction of reagents with palladium.

PdB was active for the hydrogenation of C-C multiple bonds and also for C=O bond of aldehydes and ketones, being more active for conjugated substrates. For non-conjugated substrates, such as internal alkyl alkynes, **PdB** was highly selective to the formation of the corresponding alkene. The organic products extracted from the catalytic glycerol phase did not contain palladium according to ICP-AES analyses, proving the efficient immobilization of PdNPs in the glycerol phase.

Based on these results, the immobilization of the catalytic glycerol phase on solid supports in order to improve the recyclability is under study.

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