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PAPER

Palladium nanoparticle catalysts in ionic liquids: synthesis, characterisation and selective partial hydrogenation of alkynes to *Z*-alkenes†

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The simple heating (120 °C) of $Pd(OAc)_2$ in 1-butyronitrile-3-methylimidazolium-*N*-bis(trifluoromethane sulfonyl)imide ($(BCN)MI\cdot NTf_2$) under reduced pressure leads to the formation of stable and small-sized Pd(0)-NPs (diameter: 7.3 ± 2.2 nm). These metal nanoparticles were characterised by means of TEM, HRTEM and XPS analysis techniques. Moreover, the potential for partial hydrogenation of alkynes in multiphase systems was evaluated. The hydrogenation of internal alkynes at 25 °C and under 1 bar of hydrogen yields *Z*-alkenes (up to 98% selectivity). Application of higher hydrogen pressure (4 bar) in these reactions always led to the formation of alkanes without the detection of any alkenes. TOF values were attained up to 1282 h^{-1} with a good recyclability of the system which does not lose its activity for at least 4 runs.

Introduction

It is believed that nanoparticles (NPs) which are less than 10 nm in diameter have properties in between those of bulk and single particles.[1] However, NPs are solely kinetically stable and they should be stabilised against aggregation into larger particles and bulk material. The main methods used for the stabilisation of NPs in solution involve electrostatic or steric protection, for example the use of water-soluble polymers, quaternary ammonium salts, surfactants or polyoxoanions.[2–5] The development of new approaches for the synthesis and stabilisation of uniformly sized (or mono-dispersed) NPs constitutes a very important research area.[6–21]

In this context, ionic liquids (ILs) have been proven to be suitable media for the generation and stabilisation of soluble metal NPs with small sizes, narrow size distribution and different shapes.[7,22] The IL forms a protective layer, which is probably composed of imidazolium aggregates located immediately adjacent to the nanoparticle surface, providing both steric and electronic protection against aggregation and/or agglomeration.[23,24]

Palladium is among the most popular transition metal nanoparticles used in catalysis and widely used for a significant number of synthetic transformations.[25] Several synthetic methods have been reported regarding the preparation of stable Pd-NPs. Some of the methods are sonochemical,[26] γ-irradiation,[27] UV irradiation,[28] micro-emulsion technique,[29] and polyol reduction.[30] However, the use of ILs as suitable and alternative reaction media for the preparation of Pd-NPs is relatively limited.[31,32] In fact, the development of a reliable method for the generation of soluble and stable NPs is intimately bound to the nature of metal precursor and type of the IL. And the very low solubility of metal precursors in the IL, such as $PdCl_2$, usually led to a very broad size distribution and different shapes since the precursors are heterogeneously distributed in the media. On the other hand, efficient synthesis of Pd-NPs (diameter: 4.9 nm) from the reduction of $Pd(acac)_2$ (acac = acetylacetonate) by molecular hydrogen using non-functionalised ILs as unique stabilisers was demonstrated earlier.[33] However, these nanoparticles are not stable and the use of phenanthroline as additional capping agent is essential for the NPs stabilisation.[34] The use of external capping agents, or functionalised ILs such as 2,2′-dipyridylamine-functionalised imidazolium salts,[35] polymers[36] or ionic carbon nanotubes[37] have been used for the stabilisation and dispersion of Pd-NPs in ILs. Indeed, nitrile functionalised ILs seem to offer one of the best media for the generation of catalytically active Pd nanoparticles[38] since it binds to the metal surface providing the stabilisation, but allows the coordination of substrates.[22]

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We report herein our preliminary results for the synthesis of Pd(0)-NPs in ILs and their use as efficient catalysts for the partial hydrogenation of alkynes to alkenes. Real monodispersed and well-immobilised Pd(0)-NPs were prepared by simple thermal treatment of the precursor $Pd(OAc)_2$ (OAc = acetate) dissolved in $(BCN)MI\cdot NTf_2$ IL ($BCN\cdot MI\cdot NTf_2$ = 1-butyronitrile-3-methylimidazolium-*N*-bis(trifluoromethane sulfonyl)imide). Other precursors such as $Pd(acac)_2$, $Pd(dba)_2$ (dba = dibenzylidene acetone) or palladium chloride gave much less satisfying results in a variety of ILs, *i.e.* high agglomeration and precipitation of bulk palladium metal. Moreover, these Pd-NPs prove to be efficient and highly selective catalytic systems for the partial hydrogenation of alkynes to alkenes. Other examples on this topic for Pd-nanocatalysts are rare.[39–42] These are useful intermediates for the preparation of an enormous number of bioactive molecules and natural products.[14,43–49]

Experimental

General methods

All manipulations involving the palladium complexes were carried out under an argon atmosphere using Schlenk techniques. Palladium acetate, palladium acetylacetonate and palladium dibenzylidene acetone were prepared according to the known literature procedures.[50] Potassium tetrachloropalladate was purchased from Strem Chemicals, phenanthroline was purchased from Aldrich and triphenylphosphine was purchased from Acros Organics. The ILs $BMI\cdot BF_4$ (BMI: 1-*n*-butyl-3-methylimidazolium),[51] $BM_2I\cdot NTf_2$ (1-*n*-butyl-2,3-dimethylimidazolium),[51] $BMI\cdot NTf_2$,[51] and $(BCN)MI\cdot NTf_2$[52] were prepared according to known procedures. Tetrabutylammonium bromide (TBAB) and tributylamine were purchased from Acros Organics. All other chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Varian VNMRs spectrometer (300 MHz). Mass spectra were obtained using a GC-MS Shimadzu QP-5050 (EI, 70 eV). Gas chromatography analyses were performed with a Hewlett-Packard-5890 gas chromatograph with a flame ionisation detector and a 30 m capillary column with a dimethylpolysiloxane stationary phase. Transmission electron microscopy (TEM) was performed on a *JEOL JEM 1200Ex* operating at 100 kV (CME-UFRGS, Brazil) and HRTEM was performed on an FEI Tecnai20 equipment at 200 kV (CETENE, Brazil). X-Ray photoelectron spectroscopy (XPS) measurements were obtained in ultra-high vacuum (base pressure of 1×10^{-10} mbar) using an omicron station equipped with an Mg source (kα radiation of 1253.6 eV) and an EAC2000-SPHERA analyser at 53° detection angle.

The NP formation and catalytic hydrogenation reactions were carried out in a modified Fischer–Porter bottle immersed in a silicone oil bath and connected to a hydrogen reservoir. The decrease of the hydrogen pressure in the reservoir was monitored with a pressure transducer interfaced through a Novus converter to a PC, and the data were worked up *via* Microsoft Excel. The substrate/catalyst ratio was calculated from the initial quantity of palladium precursor used.

Sample preparation for TEM analysis

In order to perform the TEM analysis, a droplet of a suspension containing Pd(0)-NPs embedded in the ILs was dispersed in acetone and a slight amount of this dispersion was placed in a carbon-coated copper grid. Particle size distributions were determined from the digital images obtained with a CCD camera. The NPs diameter was estimated from ensembles of 500 particles (1000 counts) chosen in arbitrary areas of the enlarged micrographs. The diameters of the particles in the micrographs were measured using the software Sigma Scan Pro 5.

XPS analysis of Pd precursors in IL

$Pd(OAc)_2$. The precursor $Pd(OAc)_2$ (0.03 g, ~0.13 mmol) was firstly analysed by XPS.

$Pd(OAc)_2$ in IL. Further, in a Fischer–Porter bottle the same amount of the precursor was dissolved in a mixture of $(BCN)MI\cdot NTf_2$ (0.23 g, ~0.53 mmol) and acetone (1 mL). The acetone was removed under reduced pressure and the resulting solution was analysed.

Pd(0)-NPs in IL. In a typical experiment, the Fischer–Porter bottle was loaded with $Pd(OAc)_2$ (0.03 g, ~0.13 mmol), $(BCN)MI\cdot NTf_2$ (0.23 g, ~0.53 mmol) and acetone (1 mL). The acetone was removed under reduced pressure. The suspension was heated for 24 hours (or 48 hours) at 120 °C or 150 °C. The obtained black suspension was analysed by XPS.

Isolated Pd(0)-NPs. The Pd(0)-NPs could be isolated from the IL phase by the addition of acetone followed by centrifugation. The black powder was dried under reduced pressure and then analysed.

Synthesis of Pd(0)-NPs in ILs

In a typical experiment, a Fischer–Porter bottle was loaded with palladium acetate (2.3 mg, 0.01 mmol). Then $(BCN)MI\cdot NTf_2$ (0.60 g, ~1.39 mmol) in an organic solvent (acetone 1 mL) was added *via* syringe under an argon flow. The mixture was stirred at room temperature for five minutes to yield a dark yellow suspension. Afterwards, the organic solvent was removed under reduced pressure. The suspension was then heated for 1 hour at 120 °C under reduced pressure. This resulted in the formation of a black suspension. The Pd(0)-NPs embedded in the IL were analysed by TEM and used for catalytic experiments (see below).

Catalytic hydrogenation with Pd(0)-NPs in ILs

In a typical experiment, a Fischer–Porter bottle loaded with freshly prepared Pd(0)-NPs in IL (see above) was mixed with an alkyne as the substrate (substrate/catalyst ratio see Table 3). The mixture was stirred under a constant pressure of hydrogen gas (1 or 4 bar) at room temperature for the indicated times and analysed by GC, GC-MS and NMR (Table 3).

Table 1 Reaction conditions for the Pd(0)-NP synthesis[a]

Entry	Precursor	IL	$T/°C$	t/min	Immobilisation
1	$Pd(acac)_2$	$BMI \cdot BF_4$	75	15	Metal precipitation
2	$Pd(cod)_2$	$BM_2I \cdot NTf_2$	40	15	Metal precipitation
3	$Pd_2(dba)_3$	$BM_2I \cdot NTf_2$	75	15	Metal precipitation
4	$PdCl_2$	$(BCN)MI \cdot NTf_2$	75	15	Metal precipitation
5	$Pd(OAc)_2$	$(BCN)MI \cdot NTf_2$	75	15	Metal precipitation
6	K_2PdCl_4	$(BCN)MI \cdot NTf_2$	75	15	Metal precipitation
7	$Pd(acac)_2$	$(BCN)MI \cdot NTf_2$	75	15	Metal precipitation
8[b]	$PdCl_2 + Ph_3P$	$BMI \cdot NTf_2$	80	20	Metal precipitation
9	$Pd(OAc)_2$ + Phen	$(BCN)MI \cdot NTf_2$	75	15	Dispersed NPs
10[c]	$Pd(OAc)_2$	TBAB + Bu_3N	120	360	Dispersed NPs
11[c]	$Pd(OAc)_2$	$(BCN)MI \cdot NTf_2$	120	60	Dispersed NPs

[a] Reactions carried out under 4 bar of H_2 (constant pressure). [b] System without H_2 (under argon). [c] System under vacuum. Phen = Phenanthroline.

Results and discussion

Synthesis of mono-dispersed Pd(0)-NPs in ILs and characterisation by TEM and XPS analysis

The NP catalysts were prepared with metal precursors dispersed in ILs by using different reduction methods (I) using hydrogen as a reducing agent (II), thermal reduction of $Pd(OAc)_2$ in IL without any additional reducing agent, where the acetate acts as a reductant and (III) hydrogen as the reducing agent with the addition of a ligand (Table 1). The reactions employed show that the simple thermal treatment of palladium acetate provides the best results towards the formation of well-dispersed and immobilised NPs. Instead, other reducing agents provoke that NP formation is followed by metal precipitation (Table 1). In most cases it can be assumed that the reduction with hydrogen as the reductant is too fast, therefore the local concentration of Pd(0) is too high which provokes fast agglomeration and metal precipitation. In contrast, the heating (120 °C) of $Pd(OAc)_2$ in $(BCN)MI \cdot NTf_2$ under reduced pressure leads to the formation of stable and small-sized metal Pd(0)-NPs (7.3 ± 2.2 nm, Fig. 1 and 2, Table 1: entry 11). Pointing out that the NP dispersion remains stable for several months without any metal precipitation. Noteworthy, Dyson and co-workers reported in a previous work the synthesis of metal Pd-NPs in the same nitrile-functionalised IL using an ionic polymer as additional stabiliser.[25,53] In that case, the metal NPs are around 5 nm in diameter and the NP solution was stable for a long time without precipitation. Additionally, these metal NPs were successfully employed for typical catalytic C–C coupling reactions.[53] In the present case, the TEM micrographs of the "soluble" NPs in the IL $(BCN)MI \cdot NTf_2$ showed mono-dispersed Pd(0)-NPs with a mono-modal distribution with a mean diameter of 7.3 ± 2.2 nm (Fig. 1a). Here, the obtained size distribution histogram was reasonably fitted to a Gaussian curve (Fig. 1b). Furthermore, high magnification and high-resolution TEM images of these Pd(0)-NPs showed the planar defects and interplanar distances. These NPs could be isolated from the IL by the addition of acetone and centrifugation.

Although the use of additional *N*-donor ligands such as phenanthroline (entry 9) or tributylamine (entry 10) as stabiliser provides the formation of immobilised NPs, the ligands are not necessary in the presence of an anchored nitrile group like in IL $(BCN)MI \cdot NTf_2$. The conditions are summarised in Table 1.

In order to further investigate the elemental chemical state of the precursors, the IL and the NPs isolated and dispersed in $(BCN)MI \cdot NTf_2$, samples corresponding to different steps of the processing were subjected to XPS analyses (Fig. 3). XPS results show the presence of palladium, fluorine, carbon, nitrogen, oxygen and a small contribution of silicon (from the glassware). No significant changes are observed on the fluorine 1s, nitrogen 1s and sulfur 2p regions (Fig. 3b,c and f). In addition, the nitrogen 1s signal represents two components with roughly the same intensity. The component centered near 399.7 eV corresponds to nitrogen in the nitrile group and the NTf_2 anion, while the one near 402 eV corresponds to nitrogen located in the imidazolium ring.

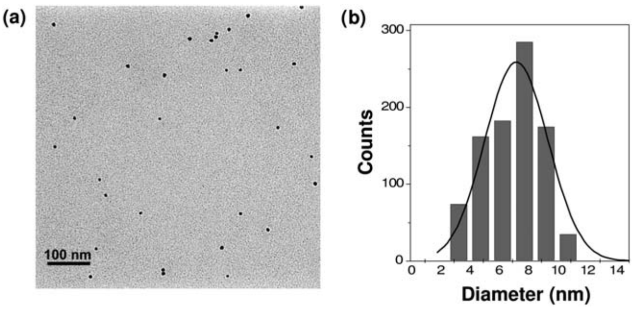


Fig. 1 (a) Selected TEM image of Pd(0)-NPs dispersed in $(BCN)MI \cdot NTf_2$ and (b) the histogram showing the particle size distribution of Pd(0)-NPs dispersed in $(BCN)MI \cdot NTf_2$. The particles display an irregular shape with a monomodal particle size distribution of 7.3 ± 2.2 nm.

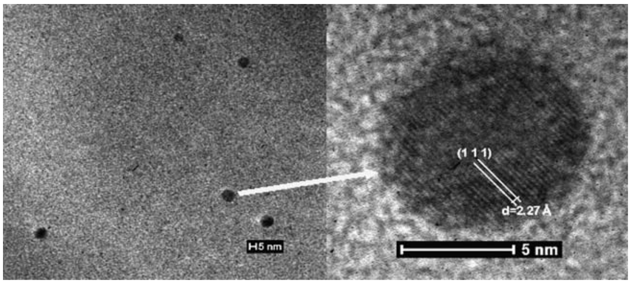


Fig. 2 Experimental HRTEM images of Pd(0)-NPs in $(BCN)MI \cdot NTf_2$, showing the planar defects and interplanar distance indicated by arrows.

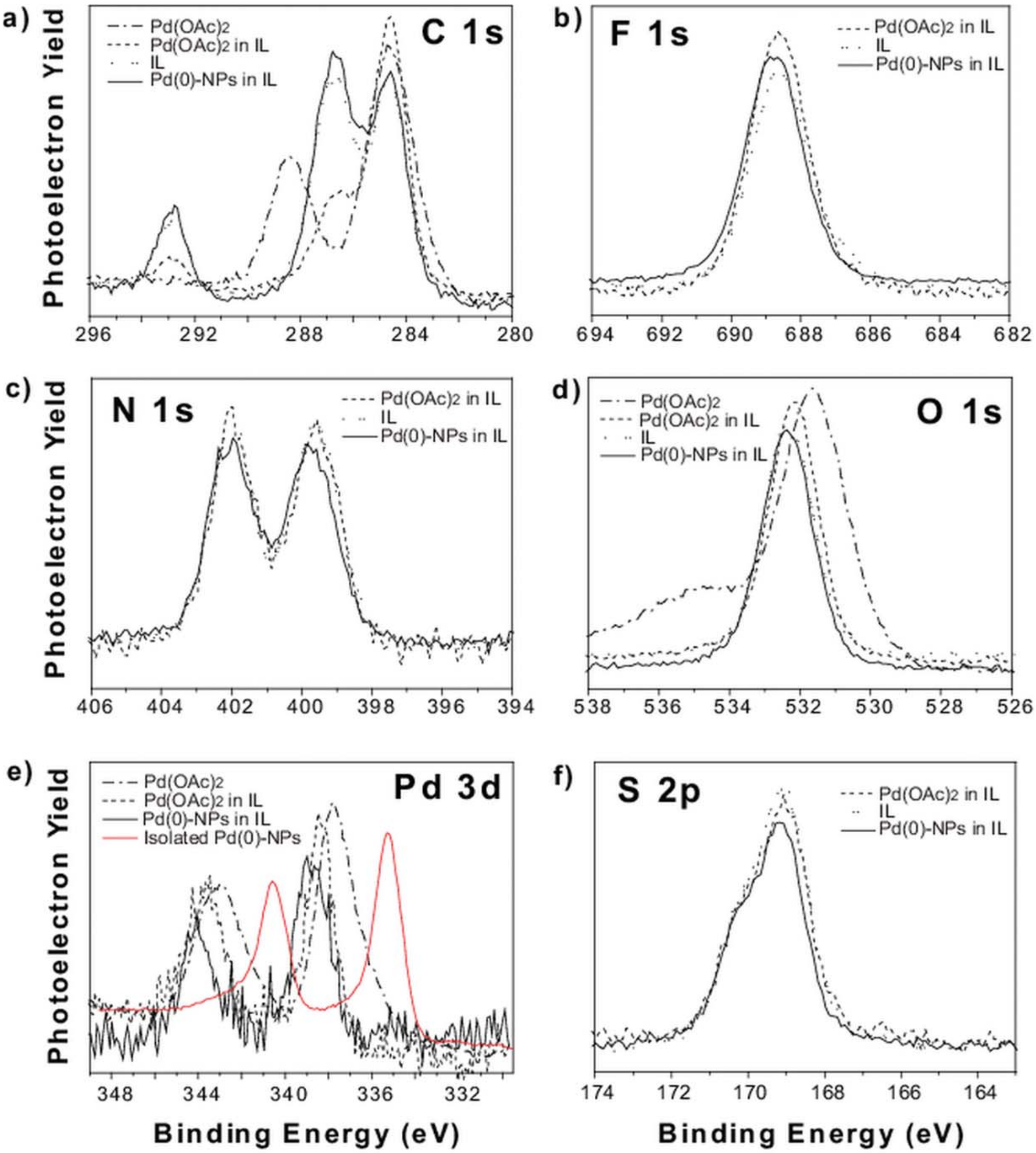


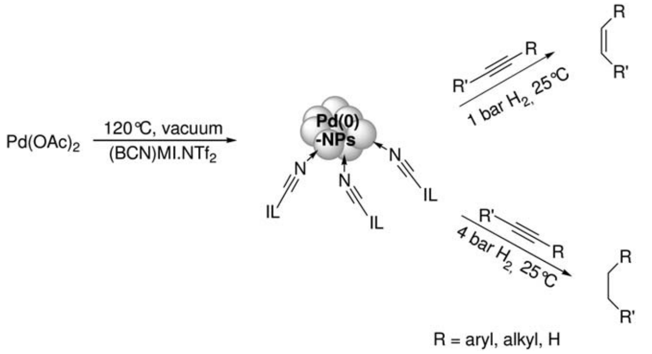
Fig. 3 XPS analyses of palladium in IL. (A larger image of Fig. 3 is provided in the ESI†).

Fig. 3e shows the XPS signal corresponding to the palladium 3d transition from the $Pd(OAc)_2$ salt (dashed dotted line), $Pd(OAc)_2$ in IL (dashed line), metal Pd-NPs in IL after thermal treatment of the palladium salt (black line) and isolated Pd(0)-NPs (red line). It was observed that two peaks for each palladium 3d signal were 5.25 eV apart, corresponding to the spin orbit splitting. Thus these peaks do not represent different chemical states. The binding energies for the palladium $3d_{5/2}$ transition corresponding to the analysed samples are shown in Table 2.

The Pd $3d_{5/2}$ transition in the palladium acetate was observed to occur with a binding energy of 337.7 eV. Moreover, dissolving this salt in IL, a small shift of 0.7 eV to a higher binding energy in the transition was observed. One would expect to observe palladium shifting towards a metallic state after $Pd(OAc)_2$ is heated for 24 hours at 120 °C as this would explain the catalytic activity. Surprisingly, the sample containing Pd(0)-NPs in IL showed a similar binding energy (338.7 eV) as the palladium precursor $Pd(OAc)_2$ dispersed in the IL (338.4 eV). Presumably, the surface of the IL layer only contains small quantities of Pd(0)-NPs and the majority is located in the inner regions of the IL aliquot, and the low concentration is not accessible by XPS.

Table 2 Palladium $3d_{5/2}$ binding energies as determined by XPS using Mg kα radiation of 1253.6 eV

Sample	Palladium $3d_{5/2}$ binding energy/eV
$Pd(OAc)_2$	337.7
$Pd(OAc)_2$ in (BCN)MI·NTf_2	338.4
Pd(0)-NPs in IL (24 h @ 120 °C)	338.7
Pd(0)-NPs in IL (48 h @ 120 °C)	338.7
Pd(0)-NPs in IL (24 h @ 150 °C)	—
Pd(0)-NPs in IL (48 h @ 150 °C)	—
Isolated Pd(0)-NPs	335.1



Scheme 1 Hydrogenation of alkynes with Pd(0)-NPs in IL.

In order to investigate the possibility of incomplete reduction of the palladium salt when dissolved in IL and explain the peaks at 338.7 eV, the thermal treatment of $Pd(OAc)_2$ in IL was conducted for 48 hours at 120 °C and 24 or 48 hours at 150 °C prior to XPS analysis. No changes were observed in the energy of the Pd $3d_{5/2}$ transition after 48 hours at 120 °C and at 150 °C no signal corresponding to the Pd 3d signal was observed by XPS (not shown). This indicates that (I) the reduction of $Pd(OAc)_2$ in (BCN)MI·NTf_2 was not completed at 120 °C, even after 48 hours. And (II) the resulting Pd(0)-NPs are repelled from the first few nanometres near the IL surface, preventing photoelectrons generated on the Pd(0)-NPs from reaching the electrostatic energy analyser. This effect may be attributed to the same mechanism that prevents the formation of metal Pd aggregates, resulting in the observed stable NP dispersion. However, metallic palladium could only be located by XPS after isolating the NPs from the IL phase. The signal centred at 335.1 eV corresponds to the metallic Pd indicating that isolated Pd(0)-NPs are indeed in the metallic state. Although no sensible modifications on C 1s binding energies (Fig. 3a) were observed, it cannot be discarded that classical and abnormal *N*-heterocyclic carbenes (NHCs) are formed *in situ* and these species might act as ligand.[54,55] Therefore, Pd(II)carbene complexes may be formed, most likely by reaction of the imidazolium cation with Pd(0) species.[25,56–59]

Fig. 3a shows the carbon 1s transition corresponding to the pure (BCN)MI·NTf_2 (dotted line) $Pd(OAc)_2$ in (BCN)MI·NTf_2 (dashed line) and Pd(0)-NPs in the same IL (solid line). The intensity of this peak was found to vary between samples, as adventitious carbon contaminations are known to represent this binding energy.

Partial hydrogenation of alkynes in liquid–liquid biphasic systems with Pd(0)-NPs in ILs

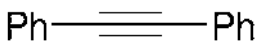
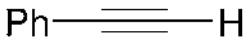
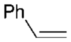
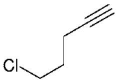
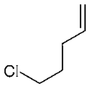
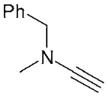
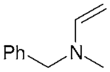
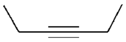
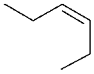
The catalyst system Pd(0)-NPs in (BCN)MI·NTf_2 was applied for partial hydrogenation of a substrate scope of internal and terminal alkynes with a high selectivity and under very mild reaction conditions (Scheme 1).

Concerning the semi-hydrogenation of internal alkynes (Table 3), symmetrical diaryl-substituted alkynes (diphenyl acetylene, entry 1) as well as dialkyl-substituted alkynes (3-hexyne, entry 5) were reduced to the corresponding alkenes with good conversions (75–100%) and with exclusive *Z*-stereochemistry. Also, the benzylated terminal alkyne was hydrogenated to the terminal olefin without debenzylation (entry 4, Table 3) which is usually observed using Pd/C as a catalyst.[60] It is noteworthy that even the more labile and isomerisation prone 3-hexyne was partially hydrogenated to the corresponding olefin without any trace of isomerised by-products such as 1-hexene and 2-hexene (entry 5). This result is in agreement with those reported for the hydrogenation of 1,3-butadiene catalysed by metal Pd-NPs in IL.[33] In that case, the difference in solubility between the substrate (1,3-butadiene) and the major product 1-butene plays the role for the observed selectivity (up to 72% in 1-butene). Moreover, no isomerisation process was detected at the different stages of the diene consumption, indicating that the NPs dispersed in IL act as heterogeneous catalysts. In the present case, the same conclusion can be adopted, *i.e.* the absence of isomerisation during the 3-hexyne hydrogenation process suggests that the Pd(0)-NPs in (BCN)MI·NTf_2 possess a typical behaviour of surface-like (multi-site) catalytic properties. Noteworthy, no hydrogenation of the nitrile group of the IL was observed under the applied mild conditions, this shows the suitability of the functional IL–solvent for such hydrogenation reactions.

Notably, the pressure of hydrogen has a great influence on these reactions. The application of higher pressure (4 bar) in these reactions always led to the formation of alkanes without the detection of any alkenes. Interestingly, when the reactions are carried out under mild conditions of 1 bar of hydrogen it was possible to stop the reaction at the alkene stage with a good *Z*-selectivity. In the case of diphenylacetylene, exclusively *Z*-stilbene was formed without further hydrogenation to the corresponding alkane, even when higher pressure (4 bar) was applied. In most cases, the catalyst remained highly immobilised in the IL phase even after hydrogenation. The high selectivity observed is most likely related to the surface electronic modification induced by the coordination of functionalised nitrile ionic liquid. Although we have not observed sensible modifications on C 1s binding energy by XPS, it cannot be discarded that a modification of the near-surface region of palladium, in which carbon (from fragmented feed molecules) occupies interstitial lattice sites could be also responsible for the high partial alkyne hydrogenation as observed in more classical Pd heterogeneous catalysts.[61]

Moreover, the partial hydrogenation of the selected alkynes provides TOFs up to 1282 h^{-1}. The TOF values were calculated considering (I) all the metal amounts employed in the reaction and (II) only the metallic atoms exposed on the NP surface. Although it is not possible to exclude that in heterogeneous systems some partial aggregation and topology changes can occur on the metallic surface,[62] the second case is more accurate

Table 3 Pd(0)-NP-catalysed partial hydrogenation (1 bar) of alkynes at 25 °C with $Pd(OAc)_2$ as a catalyst precursor in (BCN)MI·NTf_2

Entry	Alkyne[a] (substrate)	Alkene (product)	*t*/h	Conv. (%)	Selectivity (%)	TOF (h^{-1})[e]
1			6.5	87	98 : 2[b]	13 (74)
2			2.8	97	95 : 5[c]	35 (193)
3			2.8	75	97 : 3[c]	80 (446)
4			3.5	96	100	55 (305)
5			1.3	100	92 : 4 : 4[d]	231 (1282)

[a] Substrate/catalyst ratio (mol/mol) based on $Pd(OAc)_2$: entries 1 and 2 ($S/C = 100$), entry 3 ($S/C = 300$), entry 4 ($S/C = 200$), entry 5 ($S/C = 300$). [b] Selectivity determined by analytical GC, *cis*-alkene : *trans*-alkene. [c] Selectivity determined by analytical GC, alkene : alkane. [d] Selectivity determined by analytical GC, *cis*-alkene : *trans*-alkene : alkane. [e] TOF = [product (mmol)]/[catalyst (mmol) × time (h)]; the TOFs in parenthesis were calculated considering only the exposed metal atoms on the NP surface. The TOF values are considered to be under-estimated, because the initial conversions were already high (>20%). In the case of entry 2, pentane (1 mL) was added as co-solvent; in the case of entries 1, 3 and 4, cyclohexane (1 mL) was added as co-solvent.

in catalysis, once merely the surface atoms are able to catalyse the reaction. In order to determine the percentage of surface atoms on the Pd(0)-NPs, firstly we calculated the volume of one particle considering spherical NPs with a mean diameter of 7.3 nm. The volume obtained was around 203.7 nm^3 for each metal NP leading to around 14 048 atoms per particle. Using the method based on "*magic numbers*"[63] which is an established tool for the evaluation of cluster formation, the estimation of the number of layers and the percentage of surface atoms per particle. The number of layers per particle was estimated as 16, which means that ~18% of Pd atoms are on the NP's surface. These results were used to determine the corrected TOFs for the hydrogenation reactions promoted by the metal Pd-NPs in ILs. Note that in all cases the TOF values had to be estimated once the reduction of $Pd(OAc)_2$ was not completed as observed by XPS analysis. These conditions are summarised in Table 3.

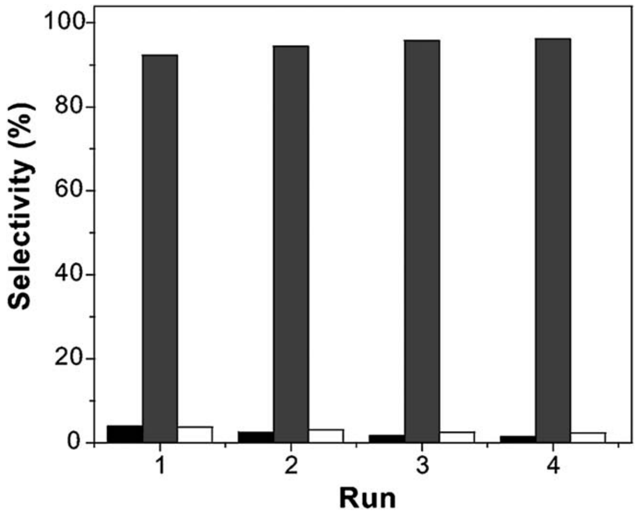


Fig. 4 Catalyst recycles for the hydrogenation of 3-hexyne (~0.25 g; 3.0 mmol) promoted by Pd(0)-NPs ($S/C = 300$) in (BCN)MI·NTf_2 (0.60 g; ~1.39 mmol) at 25 °C and 1 bar of hydrogen gas (constant pressure). In all catalytic runs the conversion was 100% and the *cis*-hexene (grey) was detected as the major product, but the presence of *trans*-hexene (white) and *n*-hexane (black) was also observed in small amounts.

In order to test the recyclability of the system, 3-hexyne was chosen as the standard substrate for the hydrogenation reactions.

The Pd(0)-NPs in IL showed efficient catalytic activity during recycles providing a selective formation of the *Z*-alkene (selectivity up to 96%) with total 3-hexyne conversions (Fig. 4). These results evidenced the robustness of the catalyst which did not lose its activity for at least 4 runs.

Conclusions

In summary, a new mild and simple methodology for the efficient selective partial hydrogenation of alkynes has been developed based on the generation of metal Pd-NPs in ILs. The thermal treatment of $Pd(OAc)_2$ in (BCN)MI·NTf_2 results in the formation of stable and highly mono-dispersed Pd(0)-NPs which are catalytically active for hydrogenation of alkynes. Remarkably, depending on the hydrogen pressure it is possible to influence the selectivity towards alkenes or alkanes as final products. The catalytic system showed TOFs up to 1282 h^{-1} and there is no significant loss in its activity for at least 4 runs. Further research on the application of these Pd(0)-NPs for the selective reduction of other multiple bonds in ILs is currently underway.

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