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# Structural, electronic and catalytic properties of palladium nanoparticles supported on poly(ionic liquid)

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Graphical abstract



#### Highlights

- Poly(ionic liquid) (PIL) supports were decorated with Pd nanoparticles (NPs)
- Naked NPs composed mainly of Pd(0) were produced by sputtering deposition
- Best catalytic performance was achieved with naked NPs over PIL/IL mixture support
- Cyclohexenone hydrogenation by PIL/IL-Pd follows Langmuir-Hinshelwood mechanism
- Rate determining step is the independent adsorption of reagents

ABSTRACT: The structural, electronic and support effect on palladium nanoparticles (Pd NPs) prepared by sputtering deposition and chemical reduction of a Pd(II) precursor in/on a poly(ionic liquid) (PIL) was investigated in the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds and dienes. Sputtering deposition generates naked NPs with a narrow size distribution (3.2–3.8 nm) that are predominantly composed of Pd(0) (85–100%). Conversely, chemical reduction produces PIL-covered NPs with almost twice the average size (6.6 nm) and only 15% Pd(0). Regard the catalytic performance, support composition (by ionic liquid (IL) addition or not) and NP location are decisive. The best activity and selectivity was obtained with imprinted Pd NPs on a PIL/IL mixture (D-MPIL.NTf2/IL-Pd catalyst). A kinetic investigation was conducted using 2-cyclohexen-1-one (CHN) and D-MPIL.NTf<sub>2</sub>/IL-Pd catalyst revealing that this reaction follows the Langmuir-Hinshelwood mechanism. Enthalpies obtaining from a Van't Hoff plot show that the adsorption of the CHN substrate on the surface of the PIL-Pd catalyst is an exothermic process (-9 kJ mol<sup>-1</sup>), whereas  $H_2$  adsorption occurs by an endothermic process (12 kJ mol<sup>-1</sup>). This distinct behavior is consistent with the rate determining step proposed, in which the independent adsorption of reagents is followed by the hydrogenation of a  $\pi$ -allyl intermediate on the catalyst surface.

KEYWORDS: palladium nanoparticles, poly(ionic liquid), PIL, hydrogenation, sputtering

#### 1. Introduction

Supported ionic liquid phase (SILP) catalysis is emerging as an important alternative for the generation of more active and selective catalysts for several transformations.<sup>1–3</sup> Transition metal compounds, nanoparticles (NPs) and enzymes supported in inorganic,<sup>4,5</sup> polymeric,<sup>6</sup> bio-based<sup>7,8</sup> and hybrids materials<sup>9,10</sup> display, in most cases, distinct and more efficient catalytic performances compared to those of neat ionic liquids (ILs) (Table S1). A simple thin film of IL is necessary to induce the desired properties for the catalytic device (stability, selectivity and so on)<sup>11</sup> and significantly reduce at mass transfer problems.<sup>12</sup> These processes can involve the modification of conventionally enzymatic, homogeneous, heterogeneous and nano-based catalysts by non-covalent thin IL films. However, covalently grafting ILs onto the surface of solid materials, as well as the use of poly(ionic liquid)s (PILs), offers significant opportunities to investigate the support effect on homogeneous metal complexes or metal NPs. Indeed, the SILP effect on the catalyst can be either geometrical and/or electronic, and also can act as a physical barrier controlling the access or removal of reagents, intermediates and products from the catalytically active site.<sup>13</sup> It has been recently proposed that this process may be regarded as flowing liquid(s) (reagents and products) through a chemically active membrane-like composed of SILP NPs in a confined space.<sup>14-16</sup> Hence, SILP catalysts under the multiphase regime ("dynamic asymmetric mixture")<sup>17</sup> operate akin to catalytically active membranes<sup>18</sup>, i.e., away from the thermodynamic equilibrium.<sup>19</sup> On this basis, catalysts based on PILs offer a distinct opportunity to investigate the SILP effect on metal NPs.

An ideal hydrophobic PIL<sup>20</sup> polyDADMA.NTf<sub>2</sub> derived from a commercial poly(diallyldimethylamonium) chloride source was prepared. The obtained material is a white powder, chemical, thermal and mechanical stable, which be easily process by a solvent film casting method.<sup>21</sup> This interesting characteristic has already made its application as a CO<sub>2</sub> separation membrane<sup>22,23</sup> and polymer electrolyte for batteries and supercapacitors<sup>24,25</sup> possible. Moreover, in general, PILs have been used in chemical methods of metal NP preparation, acting as stabilizing supports.<sup>6,26–29</sup>

The goal of this paper is to investigate the support effect on the catalytic proprieties of poly(ionic liquid)/ionic liquid/Pd nanoparticle combinations. For this study, we prepared Pd NPs by sputtering deposition over polyDADMA.NTf<sub>2</sub> in both membrane and powder forms. This physical method was chosen because it provides well-dispersed NPs with a clean surface and uniform sizes.<sup>10,30</sup> For comparison, we also synthesized NPs over this PIL by the chemical reduction of Pd(II). Finally, the catalytic properties of the prepared composites were probed in hydrogenation reactions of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds and dienes. Also, a kinetic investigation showed details regarding the mechanism of hydrogenation conducted by a PIL-Pd catalyst,

which differs from that observed in the hydrogenation by naked Pd NPs imprinted in inorganic and hybrid supports.

#### 2. Experimental Section

#### 2.1 General methods

The reagents and solvents were purchased from commercial sources (Acros, Sigma Aldrich, Tedia) and used without further purification. The infrared Fourier transform spectroscopy (FT-IR) was performed on a Bruker alpha P. Solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance analysis (CP/MAS-NMR) were obtained on a Varian 500 MHz spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were performed on a Varian 400 MHz spectrometer. Textural characterization was performed using  $N_2$  adsorption-desorption isotherms at liquid  $N_2$  boiling point temperature, using a Tristar Kr 3020 Micromeritics equipment. The samples were previously degassed at 90 °C under vacuum, for 30 h. The specific surface area was determined by BET (Brunauer, Emmett and Teller) multipoint technique, and the pore size distribution was obtained by using the BJH (Barret, Joyner and Halenda).<sup>31</sup> Thermogravimetric analysis (TGA) were performed with a Q50 TA under N<sub>2</sub> atmosphere. Palladium deposition of nanoparticles was performed at Med 020 (Bal-Tech) in sputtering mode, using a high purity target (99.99%). Transmission electronic microscopy (TEM) analysis were carried out on a JEOL JEM-1200 EXII. For scanning electron microscopy (SEM) studies, the sample (5 mg) was fixed in a carbon ribbon and analyzed in a JEOL JSM 5800 microscope operating at 15 kV, coupled with energy-dispersive X-ray spectroscopy (EDS) detector. XPS measurements were obtained with an energy of 1840 eV, into the SXS station of the National Laboratory of Synchrotron Light (LNLS), considering C 1s peak value of 284.6 eV as reference. For metal quantification, the samples were decomposed and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Analyst 200 Perkin Elmer. GC analyses were run with an Agilent Technologies GC System 6820 with DB-17 and HP-5 columns. GC-MS analyses were run with a Shimadzu QP50 with a Rtx-5MS column employing ionising voltage of 17 eV. X-ray diffraction (XRD) experiments were performed by using a Philips X'Pert MPD diffractometer with Bragg-Brentano geometry using a graphite curved-crystal with the Cu Kα X-ray radiation (1.5406 Å).

#### 2.2 Preparation of supports

The supports are based on neat polyDADMA.NTf<sub>2</sub> or a mix of polyDADMA.NTf<sub>2</sub> and BMI.NTf<sub>2</sub> (1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) (1:1 wt.). Both PIL and IL were prepared according to procedures described in the literature.<sup>24,32</sup> To obtain the PIL.NTf<sub>2</sub> support, the white powder polyDADMA.NTf<sub>2</sub> were macerated. To obtain MPIL.NTf<sub>2</sub>, 0.3 g of polyDADMA.NTf<sub>2</sub> was dissolved in 5 mL of acetone. The final solution was poured into a petri plate (diameter 3.5 cm). After evaporating the solvent at room temperature, the formation of a white solid membrane was observed. To obtain MPIL.NTf<sub>2</sub>/IL, 0.15 g of polyDADMA.NTf<sub>2</sub> and 0.15 g of BMI.NTf<sub>2</sub> were dissolved in 5 mL of acetone in the solution obtained was stirred for 30 min and then poured into a petri plate (diameter 3.5 cm). After evaporature, the formation of a solvent at room temperature, the solution obtained was stirred for 30 min and then poured into a petri plate (diameter 3.5 cm). After evaporature, the formation of a solvent at room temperature, the solvent at room temperature, the solvent was stirred for 30 min and then poured into a petri plate (diameter 3.5 cm). After evaporating the solvent at room temperature, the

#### 2.3 Preparation of catalysts

Sputtering deposition was used to prepare the catalysts A-PIL.NTf<sub>2</sub>-Pd, C-MPIL.NTf<sub>2</sub>-Pd, D-MPIL.NTf<sub>2</sub>/IL-Pd and E-MPIL.NTf<sub>2</sub>/IL-Pd. As a general procedure, a certain amount of each support was placed in a petri plate and inserted into a MED 020 chamber, operating in sputtering mode. After 30 min. under reduced pressure of 0.2 mbar, argon was admitted into the chamber until the pressure reached 3 mbar. Then deposition was initiated on the support, at 40 mA (465V) and during different times. When the deposition was finished, the chamber pressure slowly returned to ambient conditions and the catalyst was stored for later used.<sup>33</sup> Further details of conditions can be viewed in Table S2. To prepare the catalyst B-PIL.NTf<sub>2</sub>-Pd, a Fisher-Porter reactor was charged with 0.5 g of PIL.NTf<sub>2</sub> support, 0.01 g of Pd(OAc)<sub>2</sub> and 10 mL of methanol. The reactor was pressurized with 4 bar of H<sub>2</sub>, and the reaction was carried out for 1 h at 75 °C under stirring. Finally, the system was cooled and depressurized. The grey solid formed was removed from the solution by centrifugation, washed with methanol, dried under reduced pressure and stored under argon.

#### 2.4 Hydrogenation reactions

In a typical procedure, 10 mL of ethanol solution with 0.5 mmol of  $\alpha$ , $\beta$ -unsaturated carbonyl compound was added in a Fisher-Porter reactor containing an appropriated amount of catalyst (0.26  $\mu$ mol Pd). The reactor was pressurized with 4 bar H<sub>2</sub> and

maintained at 40 °C in an oil bath. Samples were collected during the reactions, and their conversion and selectivity were determined by GC-analysis. Further characterization of the products obtained were performed by GC-MS.

#### 2.5 Recycling reactions

The stability of the catalyst D-MPIL.NTf<sub>2</sub>/IL-Pd was evaluated through recycling reactions. After a typical reaction (40 °C, 4 bar H<sub>2</sub>, 8 h), the liquid phase was removed from the Fisher-Porter reactor under reduced pressure. The catalyst was washed with three portions of ethanol and dried under reduced pressure. After, a fresh solution of the substrate was introduced into the reactor, which was pressurized and immersed in an oil bath to restart the reaction.

#### 3. Results and Discussion

#### 3.1 Design of supports and catalysts

The composites were designed to evaluate the influence of support shape and composition, the method of obtaining the NPs and the location/accessibility of NPs in the catalyst on their structures and catalytic performances. The different pathways to prepare each support and catalyst are shown in Scheme 1 (for more details see Experimental Section). The PIL polyDADMA.NTf<sub>2</sub> was prepared by anion exchange of poly(diallyldimethylamonium) chloride,<sup>24</sup> from which three types of supports were prepared (Scheme 1). The neat polyDADMA.NTf<sub>2</sub> was used as support in its original powder shape (PIL.NTf<sub>2</sub>). PolyDADMA.NTf<sub>2</sub> forms membranes when dissolved in the appropriate organic solvent (acetone, for instance) and molded,<sup>21,23</sup> and two other supports were produced based on this property. One of the membranes was composed of neat polyDADMA.NTf<sub>2</sub> (MPIL.NTf<sub>2</sub>), and the other was a blend with BMI.NTf<sub>2</sub> 1:1 wt. (MPIL.NTf<sub>2</sub>/IL). The naked Pd NPs were imprinted through the sputtering deposition method<sup>33–36</sup> on each support to form the A-PIL.NTf<sub>2</sub>-Pd, C-MPIL.NTf<sub>2</sub>-Pd and D-MPIL.NTf<sub>2</sub>/IL-Pd catalytic materials. D-MPIL.NTf<sub>2</sub>/IL-Pd was re-dissolved and molded to form E-MPIL.NTf<sub>2</sub>/IL-Pd. Also, over the PIL.NTf<sub>2</sub> support was synthesized Pd NPs by the classical reduction method using Pd(OAc)<sub>2</sub> under 4 bar of hydrogen at 75 °C, thereby producing the catalytic material B-PIL.NTf<sub>2</sub>-Pd.

#### 3.2 Structural characterization of supports

FT-IR analyses (Fig. S1) of the PIL.NTf<sub>2</sub> and MPIL.NTf<sub>2</sub> supports show characteristics peaks of the polyDADMA.NTf<sub>2</sub> cation at 2900 and 1470 cm<sup>-1</sup>.<sup>24</sup> The similarity of these spectra suggests that the contact of polyDADMA.NTf<sub>2</sub> with acetone to produce the membrane MPIL.NTf<sub>2</sub> did not promote any change in its structure. The MPIL.NTf<sub>2</sub>/IL support also shows typical signals for an imidazolium ring between 3160–2880 and 1620–1580 cm<sup>-1</sup>. Peaks associated with the NTf<sub>2</sub><sup>-</sup> anion were found at 1350, 1170, 1130 and 1050 cm<sup>-1</sup>, confirming anion exchange.<sup>37</sup>

Solid-state CP/MAS <sup>13</sup>C-NMR (Fig. S2) corroborates the FT-IR results. Signals corresponding to the pyrrolidine cation appear at around 12, 26, 36, 52 and 70 ppm in all samples.<sup>38</sup> Furthermore, the MPIL.NTf<sub>2</sub>/IL support exhibits characteristics peaks of BMI.NTf<sub>2</sub>. Although most are superimposed by the PIL signals, the peak corresponding to the carbon between nitrogens in the imidazolium ring stands out at 133 ppm. The signal at 120 ppm can be assigned to the NTf<sub>2</sub><sup>-</sup> anion.

The isotherms obtained by  $N_2$  adsorption-desorption experiments are characteristic of non-porous solids<sup>31</sup> (Fig. S3). It is noted that both the surface area and pore volume are slightly improved by the presence of BMI.NTf<sub>2</sub>, when the supports with membrane shape MPIL.NTf<sub>2</sub> and MPIL.NTf<sub>2</sub>/IL are compared. IL addition also promoted a slight increase in the porosity (Fig. S4).

The stability of the PIL polyDADMA.NTf<sub>2</sub> and the support MPIL.NTf<sub>2</sub>/IL was tested by means of TGA (Fig. S5). Both PIL and PIL/IL are stable up to 350 °C, which makes these materials suitable for a wide range of applications in catalysis.

The SEM images (Fig. S6) show a clear difference in the morphologies of the PIL.NTf<sub>2</sub> support (powder) and the MPIL.NTf<sub>2</sub> and MPIL.NTf<sub>2</sub>/IL supports (membranes). In the first case, the sample is composed of aggregate spherical particles. Meanwhile, in the second and third cases, a denser superficial structure was observed, which is in agreement with characteristics described for other polymeric membranes.<sup>39</sup> In all cases, it is possible to identify some macroporosity at the micrometric level.

#### 3.3 Structural characterization of imprinted Pd NPs

The formation of small Pd NPs was confirmed by transmission electron microscopy (TEM) and the images obtained are shown in Fig. S7. It was observed that sputtering generated NPs with a very similar average size and regular distribution  $(3.2 \pm 1.3 \text{ nm for A-PIL.NTf}_2$ -Pd,  $3.2 \pm 1.7 \text{ nm for C-MPIL.NTf}_2$ -Pd,  $3.2 \pm 1.0 \text{ nm for D-MPIL.NTf}_2$ /IL-Pd and  $3.8 \pm 1.8 \text{ nm}$  for E-MPIL.NTf}\_2/IL-Pd, Table 1). This trend is valid since the same sputtering deposition conditions were used.<sup>30</sup> Metal NPs in B-PIL.NTf}\_2-Pd (prepared by the classical reduction method) have twice the average size of others ( $6.6 \pm 3.2 \text{ nm}$ ), which indicates that the size of the NPs is related to the synthetic route employed. In fact, it is expected that each method has its own specific and different ways of controlling the size of the NPs.<sup>35</sup> Moreover, a high local concentration of metal precursor (Pd(OAc)\_2) may generate larger NPs and/or more aggregate particles, which is consistent with the present data, once B-PIL.NTf\_2-Pd has almost ten times more metal than other catalysts (Table 1).

The concentration of Pd in the catalysts was determined by ICP-OES and the percentages found were 0.33%, 0.17%, 0.18% and 0.30% for A-PIL.NTf<sub>2</sub>-Pd, C-MPIL.NTf<sub>2</sub>-Pd, D-MPIL.NTf<sub>2</sub>/IL-Pd and E-MPIL.NTf<sub>2</sub>/IL-Pd, respectively (Table 1). The values measured were expected in each case, considering the relationship between the mass support and the deposition time, since the same current was used for samples (Table S2).<sup>40</sup>

The X-ray powder diffraction (XRD) pattern of the D-MPIL.NTf<sub>2</sub>/IL-Pd catalyst is shown in Fig. S8. The peak indexed to the (111) plane of face-centered cubic Pd diffractions (JCPDS, Card N°. 05-0681) could be found at 20 values of ~40°. The presence of the crystallographic planes (200), (220) and (311) at 47°, 68° and 82°, respectively, were almost indiscernible, which may be due to the low concentration of metal in the sample.<sup>41</sup> The wide-scan X-ray photoelectron spectroscopy (XPS) spectra (Fig. S9) show the presence of F, O, N, C and S in all samples, as expected. Their binding energies are in agreement with the values reported in the literature.<sup>41,42</sup>Furthermore; the Pd 3d region is not well evidenced for B-PIL.NTf<sub>2</sub>-Pd and is not detected under the analysis conditions employed for E-MPIL.NTf<sub>2</sub>/IL-Pd. This result indicates that the Pd NPs are covered by the support and located at the innermost PIL layers, since the photoelectrons generated from Pd 3d at 1840 eV have an inelastic mean free path of  $\lambda \approx 4$  nm.<sup>10</sup> This is also indicative that "naked" Pd NPs are present on the surface of the A-PIL.NTf<sub>2</sub>-Pd, C-MPIL.NTf<sub>2</sub>-Pd and D-MPIL.NTf<sub>2</sub>/IL-Pd catalysts. The main peak of Pd 3d<sub>5/2</sub> for B-PIL.NTf<sub>2</sub>-Pd (Fig. 1 and Table S3) has a positive shifted at 0.7 eV compared to the specimens of clusters of Pd(0) (335.0 eV).<sup>43</sup> This behaviour is probably related to the Pd NPs size of this catalyst, which is largest than others.44

An important aspect to be considered is the predominant metallic Pd component (87– 100% of Pd(0)) for the samples prepared by sputtering against the material synthesized by a classical chemical reduction process (15% of Pd(0)) (Fig. 1 and Table 1). These results evidenced the role of the synthetic technique employed and the nature of the supported Pd. Indeed, imprinted Pd NPs on hybrid and inorganic supports usually display much higher proportions of the Pd(II) surface component.<sup>10</sup> Hence, this indicates that the PIL provides better protection for the Pd(0) surface atoms than the other supports.

The F 1s region shows positive shifts above 0.3 eV for D-MPIL.NTf<sub>2</sub>/IL-Pd and E-MPIL.NTf<sub>2</sub>/IL-Pd (Fig. S10; 0.88 eV and 1.04 eV, respectively) compared to the neat supports. This result is attributed to the interaction between IL contact pairs<sup>45</sup> and the metal surface. Moreover, an additional component over the F 1s region (670.65 eV) appears in D-MPIL.NTf<sub>2</sub>/IL-Pd (Fig. S11), confirming the interaction of the coordinated contact pairs of the BMI.NTf<sub>2</sub> with the Pd atoms.<sup>46,47</sup> In this case, an XPS analysis was also used to estimate the surface composition of the PIL over the Pd NPs. A ratio of 1:5 surface IL/Pd was estimated from the ratio between the coordinated signals that appears in the F 1s region (10% NTf<sub>2</sub><sup>-</sup>) and the Pd-X component.

#### 3.4 Hydrogenation reactions using 2-cyclohexen-1-one and PIL-Pd catalysts

Initially, PILs containing Pd NPs were tested in the hydrogenation of 2-cyclohexen-1-one (CHN), and the results are shown in Table 2. In all reactions, the only product observed was cyclohexanone. A blank experiment, where no catalyst was used, did not show any conversion. Also, no conversion was observed for the reactions employing only the support, indicating that the hydrogenation activity comes from Pd NPs and not from the PIL components. Regarding the activities observed in Table 2, the catalysts could be divided into (i) those that have exposed NPs without IL on the support; (ii) those that have NPs covered by PIL or PIL/IL and (iii) one that has exposed Pd atoms with IL in the support.

In the first group, there are the A-PIL.NTf<sub>2</sub>-Pd and C-MPIL.NTf<sub>2</sub>-Pd catalysts (entries 1 and 3, Table 2), which obtained the lowest TOF values. In both cases, the composition of supports are neat PILs and the method of obtaining NPs was by sputtering. This combination may generate catalysts with more exposed surface Pd atom NPs, i.e.,

located at outermost PIL layer. The metal location at the outermost layer and hence less "protected" may facilitate the forming aggregates during the reaction, decreasing the catalytic activity. By TEM measurements it was possible to confirm the metal aggregation after 8 h, since the NP size doubles (from 3.2 to 7.5 nm after the hydrogenation reaction, see Fig. S12 (a)). In the second group, there are the B-PIL.NTf<sub>2</sub>-Pd and E-MPIL.NTf<sub>2</sub>/IL-Pd catalysts (entries 2 and 5, Table 2), which have intermediate TOF values. Although they have different supports and methods of metallization, they have in common their preparation with the aid of a solvent. Thus, both had NPs dispersed in a solution of PIL, and it is suggested that after removal of the solvent, the NPs were almost completely covered by the support. These observations are reinforced by the XPS survey spectrum, as mentioned earlier (Fig. S9). Regarding B-PIL.NTf2-Pd, the concentration of metal detected by ICP-OES was higher than expected, considering the initial proportion between the metal precursor and the support (see Experimental Section). This indicates that part of the PIL.NTf<sub>2</sub> support was dissolved under the conditions used for the reduction of the metal precursor and removed in the washings with methanol, thereby increasing the amount of NPs in the remaining solid. With this configuration, fewer NPs should be agglomerated, which explains the superior activity compared to the catalysts of entries 1 and 3 (Table 2). Simultaneously, NPs were located at the innermost PIL layers and were less accessible to the substrate, leading to values lower than those obtained with D-MPIL.NTf<sub>2</sub>/IL-Pd, as discussed below. The catalyst that showed a better response to hydrogenation of CHN was D-MPIL.NTf<sub>2</sub>/IL-Pd (entry 4, Table 2). Compared to C-MPIL.NTf<sub>2</sub>-Pd (entry 3, Table 2), the studied reaction was strongly influenced by the presence of BMI.NTf<sub>2</sub>. In this case, the MPIL.NTf<sub>2</sub>/IL support displays more liquid-like properties than the PIL due to the presence of the IL. Indeed, the use of IL has proved effective for increasing the activity and stability of Pd NPs for the hydrogenation of CHN.<sup>48</sup> To further investigate the effect of these two components, a reaction with C-MPIL.NTf<sub>2</sub>-Pd and adding BMI.NTf<sub>2</sub> in the reaction medium was performed. The TOF obtained was 3 min<sup>-1</sup>, which was the same obtained using C-MPIL.NTf<sub>2</sub>-Pd without the additive (entry 3, Table 2). This suggests that the catalytic activity achieved by D-MPIL.NTf<sub>2</sub>/IL-Pd should be the result of a synergistic effect between PIL and IL. In addition, metal aggregation after 8 h of reaction with D-MPIL.NTf<sub>2</sub>/IL-Pd was observed in smaller proportions than that obtained with A-PIL.NTf<sub>2</sub>-Pd, since NPs size increase from 3.2 nm to 4.0 nm (Fig. S12(b)). Recycling experiments for CHN hydrogenation using D-MPIL.NTf<sub>2</sub>/IL-Pd for five cycles showed no loss in selectivity, although the conversion decreased significantly (97% conversion for the first cycle down to 34% conversion in the fifth cycle).

#### 3.5 Catalytic tests using other substrates

The scope of the catalytic reaction was investigated for other unsaturated compounds using the best performance catalyst, D-MPIL.NTf<sub>2</sub>/IL-Pd. The results are presented in Table 3. It is notable that  $\alpha,\beta$ -unsaturated carbonyls with less sterically hindered C=C bonds provided excellent conversions and selectivities through quick reactions (entries 1 and 2, Table 3). Simultaneously, the presence of substituent groups (entries 3 and 4, Table 3) required vigorous reaction conditions to achieve similar conversion than others. Otherwise, hydrogenation is not favored. Among conjugated dienes (entries 5, 6 and 7, Table 3), moderate to excellent conversions and activities were reached. It is noteworthy that the case of 1,3-cyclohexadiene (entry 5, Table 3) formed a significant amount of benzene, which is a disproportionation product.<sup>30</sup> This may be indicative of agglomerated NPs in the reaction medium.<sup>49</sup> NPs with larger diameters can favor the coordination of two 1,3-cyclohexadiene molecules and the hydrogen transfer between them, thus generating the disproportionation reaction.<sup>50</sup> It is interesting to mention that when this hydrogenation was tested in DMSO (not reported here), dissolving the MPIL.NTf<sub>2</sub>/IL support completely, the selectivity for benzene doubles. This result reinforces the idea described above since a total absence of support must generate an environment of even more agglomerated NPs. Disproportionation of  $\alpha$ -terpinene did not occur (entry 7, Table 3), probably because methyl and isopropyl groups hinder the hydrogen transfer. It is worth highlighting, regarding conjugated dienes, the important selectivities achieved for monoenes.

This result from the action of the SILP/Pd NP system, which can control the access or removal of reagents, intermediates and products from the catalytically active site.<sup>13</sup> In addition, it is known that dienes are more soluble in IL than monoenes.<sup>11,51</sup> These indicate that the IL layer in D-MPIL.NTf<sub>2</sub>/IL-Pd favors the hydrogenation of diene to monoene. The nonconjugated diene  $\gamma$ -terpinene (entry 8, Table 3), as well as the monoenes, are not reactive in the presence of D-MPIL.NTf<sub>2</sub>/IL-Pd.

#### 3.6 Kinetics of CHN hydrogenation using PIL-Pd catalysts

A kinetic study was conducted to gain information concerning the catalytic hydrogenation mechanism of CHN. The most active catalyst, D-MPIL.NTf<sub>2</sub>/IL-Pd, was chosen to lead these

experiments. The influences of hydrogen pressure (Fig. S13) and substrate concentration at different temperatures (Fig. S14) were evaluated and the initial rates of these reactions are dependent on both factors. Given these initial catalytic evidences, the kinetics of the CHN hydrogenation was investigated using the Langmuir–Hinshelwood kinetic model.<sup>52–56</sup> This model proposes some elementary steps for hydrogenation reactions that include: (I) substrate adsorption, (II) H<sub>2</sub> dissociation, (III) surface reaction and (IV) desorption of product. From this information, the following simplified mechanism is suggested for the hydrogenation of CHN (Scheme 2):

The kinetic model of Langmuir-Hinshelwood also provides a means to investigate the rate determining step (RDS) of the studied reaction, by associating a particular equation with each elementary step of the hydrogenation. In order for the model to be applied in the kinetic investigation of CHN hydrogenation, some minor adaptations were made. Among them are the subdivision of step III, so that it can cover two situations: (a) competitive adsorption<sup>10,54,57,58</sup> and (b) non-competitive adsorption 53,55,56,59,60 between the substrate and H<sub>2</sub> for the active sites of the catalyst surface. In addition, the possibility of desorption of the cyclohexanone product being the slow reaction step was discarded due to the small percentage of it in the reaction medium during the determination of reaction rates (conversions below 20%). By the application of linear forms of these model equations (Table S4) to our data, followed by the evaluation of the best correlation coefficient (R<sup>2</sup>), the RDS suggested for CHN hydrogenation was the surface reaction between the independently adsorbed substrate and hydrogen. Similar behavior was observed when a Pt-Au/SiO<sub>2</sub> catalyst was used in cinnamaldehyde hydrogenation.<sup>53</sup> Indeed, H<sub>2</sub> dissociation could not be the RDS, since only a secondary isotopic effect (TOF ratio  $H_2/D_2 = 1.1$ ) was found when the reaction was carried out under  $D_2$  pressure (Fig. S15).<sup>10</sup> Moreover, if the dissociation of  $H_2$  was the RDS, the reaction rate should decrease with CHN concentration augmentation (entry 2, Table S4). Instead, the increase in the CHN concentration leads to an increase in the rate with saturation behavior (Fig. S14), which also excludes CHN adsorption as the RDS (entry 1, Table S4). Thus, the equation suggested by the Langmuir-Hinshelwood kinetic model when the RDS is a surface reaction with independent adsorption (entry 4, Table S4) was used for a nonlinear fitting of the concentration profiles at different temperatures (Fig. S14) and determine the rate constant for the surface reaction  $(k_3)$ , the equilibrium constant for substrate adsorption ( $K_1$ ) and the equilibrium constant for H<sub>2</sub> adsorption ( $K_2$ ) (Table 4).

From the  $k_3$  values at different temperatures, it was possible to build an Arrhenius plot and estimate the apparent activation energy (E<sub>a</sub>) for the CHN hydrogenation. Fig. 2 shows that there are two trends for E<sub>a</sub> under the studied conditions: one related to the reactions at higher temperatures (37 kJ mol<sup>-1</sup>), in agreement with the literature reports (36–57 kJ mol<sup>-1</sup>) for hydrogenation of  $\alpha$ , $\beta$ -unsaturated compounds using Pd catalysts;<sup>61,62</sup> and another associated with lower temperatures (9 kJ mol<sup>-1</sup>), resulted in an E<sub>a</sub> smaller than expected, related to the enthalpy of the reaction.

The determined  $K_1$  and  $K_2$  values at different temperatures allowed for estimation of the enthalpies of adsorption for CHN and H<sub>2</sub> ( $\Delta$ H<sub>1</sub> and  $\Delta$ H<sub>2</sub>, respectively) through the use of Van't Hoff plots (Fig. 3 and 4). The calculated value for ΔH<sub>1</sub> was -9 kJ mol<sup>-1</sup>, showing that the adsorption of the substrate on the surface of the D-MPIL.NTf<sub>2</sub>/IL-Pd catalyst is an exothermic process. The low enthalpic value is typical of physisorption and was also observed by other authors in similar systems, such as chalcone adsorption in Ni NPs ( $\Delta H = -6 \text{ kJ mol}^{-1}$ ).<sup>58</sup> However, the calculated value for  $\Delta H_2$  was 12 kJ mol<sup>-1</sup>, indicating the occurrence of an endothermic process. This distinct behavior between CHN and  $H_2$  adsorption is consistent with the independent mechanism proposed for the reaction. In addition, it can justify the two trends observed in the Arrhenius plot (Fig. 2): at lower temperatures, the exothermic CHN adsorption step should be favored, generating a lower value for  $E_a$ ; however, at higher temperatures, the endothermic  $H_2$ adsorption step is promoted and the effect is a higher  $E_a$ . Although the  $H_2$  adsorption is endothermic, the process is spontaneous due to a high entropy energy ( $\Delta S = 55 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ), which suggests that the interaction between the support MPIL.NTf<sub>2</sub>/IL and H<sub>2</sub> is accompanied with a possible catalyst restructuration. The same trend was observed for hydrogenation of the acetylene with Pd-Al<sub>2</sub>O<sub>3</sub> catalyst and in the presence of a carbonaceous species<sup>57</sup> and also observed for Pd nanocrystals.<sup>63</sup> Note that in the case of imprinted Pd NPs on hybrid IL containing inorganic supports<sup>9</sup> the catalyst restructuration is not significant as that observed for the Pd NPs on PILs.

#### 4. Conclusions

In this work, we prepared five catalysts based on polyDADMA.NTf<sub>2</sub>, which differ from each other considering the following aspects: (i) presence (or not) of IL in the support, (ii) the shape (powder or membrane) of the support and (iii) the method used to produce Pd NPs (chemical or physical). Naked NPs with a narrow size composed mainly of Pd(0) were produced by the physical method. In contrast, covered NPs with broad distribution and high percentage of Pd(II) were obtained by the chemical method.

This imprinted Pd NPs on PILs are active catalysts for the selective hydrogenation of several substrates, like dienes and  $\alpha$ , $\beta$ -unsaturated carbonyl compounds, especially towards the C=C bond and under mild conditions (40 °C, 4 bar of H<sub>2</sub>). The relative order of activity observed for the catalysts during the hydrogenation of CHN was found as catalysts with exposed NPs and supported in pure PIL< covered NPs < exposed NPs and supported in a mixture of PIL and IL. The presence of IL on the support promotes an increase in the activity and stability of Pd NPs for the hydrogenation of CHN. The PIL imposes a physical barrier (membrane-like effect) for the substrates to access the Pd catalytic active sites.

Indeed, a kinetic investigation based on the Langmuir-Hinshelwood mechanism shows that the independent adsorption of substrates, followed by the hydrogenation of the  $\pi$ -allyl intermediate on the PIL-Pd catalyst surface, is the RDS of this reaction. Moreover, and corroborating with the independent adsorption of the substrates proposed, the Van't Hoff plot suggests that the adsorption of the CHN substrate on the surface of the PIL-Pd catalyst is an exothermic process (-9 kJ mol<sup>-1</sup>), whereas H<sub>2</sub> adsorption occurs by an endothermic process (12 kJ mol<sup>-1</sup>). It also can justify the two trends observed in the Arrhenius plot: at lower temperatures, the exothermic CHN adsorption step should be favored, generating a lower value for E<sub>a</sub> (9 kJ mol<sup>-1</sup>); however, at higher temperatures, the endothermic H<sub>2</sub> adsorption step is promoted and the effect is a higher E<sub>a</sub> (37 kJ mol<sup>-1</sup>).

Finally, the catalytic behavior of Pd NPs on PILs, hybrid and inorganic supports in ILs, can be regarded as catalytic membrane-like devices. The membrane-like approach paves the way for the design and synthesis of more efficient metal catalysts in/on IL-based materials.

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#### Notes

Supplementary Material available: additional characterization data (FT-IR, CP/MAS <sup>13</sup>C-NMR, BET, TGA, SEM, XPS, TEM) and other kinetic details.

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**Scheme 1.** Pathways to prepare supports and Pd NPs catalyst (i = maceration; ii = acetone,  $BMI.NTf_2$ , moulding in petri plate; iii = acetone, moulding in petri plate; iv = sputtering deposition; v =  $Pd(OAc)_2$ , methanol, 75 °C, 4 bar  $H_2$ ).





Scheme 2 Mechanism proposed for hydrogenation of CHN using PIL-Pd catalysts.

**Fig. 1** XPS analysis performed on the Pd 3d region for (a) A-PIL.NTf<sub>2</sub>-Pd, (b) B-PIL.NTf<sub>2</sub>-Pd, (c) C-MPIL.NTf<sub>2</sub>-Pd and (d) D-MPIL.NTf<sub>2</sub>/IL-Pd. Black line = Shirley background; blue line = fitting; red line = Pd(0); green line = Pd(II); 0 = experimental data.



Fig. 2 Arrhenius plot of CHN hydrogenation over D-MPIL.NTf<sub>2</sub>/IL-Pd.



**Fig. 3** Van't Hoff plot from the equilibrium constant for substrate adsorption ( $K_1$ ) of CHN hydrogenation by D-MPIL.NTf<sub>2</sub>/IL-Pd.



**Fig. 4** Van't Hoff plot from the equilibrium constant for  $H_2$  adsorption ( $K_2$ ) of CHN hydrogenation by D-MPIL.NTf<sub>2</sub>/IL-Pd.

TABLES

| Entry | Catalyst                       | Ø <sub>PdNPs</sub> (nm) <sup>a</sup> | Pd (wt%) <sup>b</sup> | Pd(II)/Pd(0)c |
|-------|--------------------------------|--------------------------------------|-----------------------|---------------|
| 1     | A-PIL.NTf <sub>2</sub> -Pd     | 3.2                                  | 0.33                  | 0/100         |
| 2     | B-PIL.NTf <sub>2</sub> -Pd     | 6.6                                  | 1.50                  | 85/15         |
| 3     | C-MPIL.NTf <sub>2</sub> -Pd    | 3.2                                  | 0.17                  | 09/91         |
| 4     | D-MPIL.NTf <sub>2</sub> /IL-Pd | 3.2                                  | 0.18                  | 13/87         |
| 5     | E-MPIL.NTf <sub>2</sub> /IL-Pd | 3.8                                  | 0.30                  | -             |

| Table 1 Summar | v of the nh | vsical and | chemical   | characteristics | of PIL-Pd catal | vsts  |
|----------------|-------------|------------|------------|-----------------|-----------------|-------|
| Table I Summar | y or the ph | ysical and | ciferinear | characteristics |                 | ysts. |

<sup>a</sup>Determined by TEM analysis. <sup>b</sup>Determined by ICP-OES analysis. <sup>c</sup>Determined by XPS analysis.

| Table 2 H | ydrogenation | of CHN using | PIL-Pd catal | ytic materials. <sup>a</sup> |
|-----------|--------------|--------------|--------------|------------------------------|
|-----------|--------------|--------------|--------------|------------------------------|

| Entry | Catalyst                       | Conversion (%) | TOF (min <sup>-1</sup> ) |
|-------|--------------------------------|----------------|--------------------------|
| 1     | A-PIL.NTf <sub>2</sub> -Pd     | 54             | 4.5                      |
| 2     | B-PIL.NTf <sub>2</sub> -Pd     | 63             | 9.5                      |
| 3     | C-MPIL.NTf <sub>2</sub> -Pd    | 32             | 3.5                      |
| 4     | D-MPIL.NTf <sub>2</sub> /IL-Pd | 97             | 21.1                     |
| 5     | E-MPIL.NTf <sub>2</sub> /IL-Pd | 44             | 8.6                      |

<sup>a</sup>Conditions: 0.5 mmol of substrate, 0.26  $\mu$ mol Pd, 10 mL of ethanol, 4 bar H<sub>2</sub>, 8 h of reaction. <sup>b</sup>TOF = mol CHN converted/(mol of surface Pd x time); calculated from the slope of plots of TON vs. time at 20% of conversion.

Table 3 Hydrogenation of various substrates promoted by D-MPIL.NTf<sub>2</sub>/IL-Pd.<sup>a</sup>



<sup>a</sup>Conditions: 0.5 mmol of substrate, 0.26 μmol Pd, 10 mL of ethanol, 40 °C, 4 bar H<sub>2</sub>, 8 h of reaction. <sup>b</sup>TOF = mol substrate converted/(mol Pd at surface x minute); calculated from the slope of plots of TON vs. time at low conversion. <sup>c</sup> 2 h. <sup>d</sup> 5 h. <sup>e</sup> Substrate/metal molar ratio = 1000, 80 °C.

| Entry | Temperature<br>(°C) | <i>k</i> ₃ x10 <sup>-3</sup><br>(mol L⁻¹ min⁻¹) | <i>К</i> 1<br>(L mol <sup>-1</sup> ) | <i>К</i> 2<br>(L mol <sup>-1</sup> ) |
|-------|---------------------|---|--------------------------------------|--------------------------------------|
| 1     | 20                  | 0.889   | _c                                   | 4.5                                  |
| 2     | 40                  | 1.318   | 12.6                                 | 6.0                                  |
| 3     | 60                  | 1.684   | 11.2                                 | 8.3                                  |
| 4     | 70                  | 2.407   | 9.9                                  | 9.7                                  |
| 5     | 80                  | 4.503   | 8.3                                  | 10.7                                 |

Table 4 Kinetic parameters for hydrogenation of CHN by D-MPIL.NTf\_2/IL-Pd catalyst.<sup>a,b</sup>

<sup>a</sup>Reaction conditions: 0.26 µmol Pd, 10 mL of ethanol, 4 bar H<sub>2</sub>. <sup>b</sup>Kinetic parameters determined by nonlinear fitting using the equation described in entry 4, Table S3. <sup>c</sup>The error from the adjustment did not allow an accurate determination of this parameter.