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Ionic liquid layer on Pd/C catalyst: Membrane-like effect on the selectivity for multistep hydrogenation reactions

Evelisy C.O. Nassor^a, Juliana C. Tristão^b, Eduardo N. dos Santos^a, Flávia C.C. Moura^a, Rochel M. Lago^a, Maria Helena Araujo^{a,*}

^a Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte – MG 31270-901, Brazil ^b Universidade Federal de Viçosa, Campus Florestal, Florestal – MG 35690-000, Brazil

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ABSTRACT

In this work, it has been investigated a membrane-like effect of ionic liquid (IL) in the multistep catalytic hydrogenation of *trans*-cinnamaldehyde (CALD) and 1,5-ciclooctadiene (1,5-COD). A commercial Pd/C catalyst was impregnated with 1-hexyl-3-methyl-imidazolium at 0.5–10 wt%. SEM, EDS, XRD, TG and BET data suggested that the IL penetrates the carbon pore structure coating the catalyst, especially at 5 and 10% concentration. The presence of the IL layer strongly affected the selectivities of the hydrogenations of CALD and 1,5-COD. In the case of CALD, the IL favored the formation of the fully hydrogenated product (hydrocinnamyl alcohol). This result is discussed in terms of a membrane-like effect, in which the small H_2 molecule diffuses more easily from toluene through the IL layer as compared to the larger cinnamaldehyde. This effect results in the product OOE (cyclooctene). In this case, a membrane-like effect was also used to discuss the result, where the IL layer has the effect to expel the intermediate COE hindering its contact with the Pd surface.

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1. Introduction

The use of ionic liquids (ILs) in catalysis has been extensively investigated in the last years [1-13]. Although commercially available, ILs are still relatively expensive compared to traditional solvents [14-17]. Besides, some of them show evidence of low biodegradability and (eco)toxicological properties [11]. Hence, the immobilization of ILs onto a support is an attractive strategy to minimize the amount of ILs used, maintaining their catalytic properties. Additionally, supported ILs have the advantage of easy separation and recyclability, as well as the potential to facilitate the development of continuous processes [14,15,18]. Therefore, the concept of immobilized ionic liquids entrapped, for instance, on the surface and pores of various solid materials offers an attractive cost-effective alternative. Furthermore, due to the high relative viscosity of many RTILs (Room Temperature Ionic Liquids), mass transfer limitations are usually an issue and the established thin ionic liquid layer minimizes this problem [17].

Improvement of the selectivity of heterogeneous catalysts has been achieved recently by Jess and coworkers, by covering solid catalysts with an ionic liquid layer [19]. This method known as SCILL has been patented in cooperation with Süd-Chemie [20]. Since then, several reports involving the SCILL concept have appeared in the literature, for example, Ni/SiO₂ catalyst coated with [BMIM][n- $C_8H_{17}OSO_3$ was used for the hydrogenation of 1,5-COD [19] with an increase in the selectivity for cyclooctene; Ru/Al₂O₃ coated with [C₁₀mim]NTf₂ was investigated for the hydrogenation of limonene and the results have shown an increase in the selectivity for the intermediate *p*-menthene [21]. Furthermore, Pd and Pt supported on SiO₂ and Al₂O₃ catalysts coated with $[BMIM][N(CN)_2]$ have been the subject of several investigations related to H₂ adsorption and interaction of IL with the metals [22-25]. In a recent study, SiO₂ and Al₂O₃ supported Pd catalysts coated with [BMIM][N(CN)₂] have also been investigated for the hydrogenation of citral resulting in increased selectivity for citronelal [26]. SCILL concept has been also successfully tested in the consecutive hydrogenation of butadiene to butene and butane, in a gas phase reaction, it was observed that the IL strongly favors formation of butane over a Pd-catalyst [27,28].

Although hydrogenations with Pd/C catalysts are well known and have been the subject of a number of recent reports [29–32], the strategy of impregnating these catalysts with IL to modulate selectivity has been little explored.

In this work, we have investigated a potential membrane-like effect of a thin IL layer to create a special surface environment, which modifies the selectivity of hydrogenations on a Pd/C

^{*} Corresponding author. Tel.: +55 3134097557; fax: +55 3134095700.

E-mail addresses: maria.araujo@pq.cnpq.br, mharaujo1993@yahoo.com.br (M.H. Araujo).

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Scheme 1. General simplified reaction scheme showing possible pathways for the multistep hydrogenation of A to produce B and C on a Pd/C catalyst coated with IL.

catalyst. The systems studied were composed of two liquid phases. i.e. toluene and the IL 1-hexyl-3-methyl-imidazolium bromide (HMIm.Br), and the probe substrates were *trans*-cinammaldehvde and 1.5-cyclooctadiene. For multistep reactions involving the formation of intermediates (e.g. a consecutive hydrogenation $A \rightarrow B \rightarrow C$) the kinetics and selectivity might be strongly influenced by the equilibrium and mass transfer of the species between the two phases, i.e. toluene and IL (Scheme 1). The diffusion of the substrate and H₂ through the IL layer to reach the Pd surface can have a significant effect on the reaction selectivity by controlling the relative concentration of the surface species H-Pd, A_{Pd} and B_{Pd} (Scheme 1). Also, in a multistep reaction, in which C is a secondary product formed from B, the interaction of B with the IL layer might also influence the selectivity. If the IL interacts well with the intermediate B, this species probably stays longer near the Pd surface, favoring formation of the final product C. On the other hand, if the IL interacts poorly with B, the IL layer tends to expel the intermediate, increasing its selectivity.

Two important model substrates were used for the hydrogenations, *i.e. trans*-cinnamaldehyde and 1,5-cyclooctadiene. These molecules have been selected due to their different polarities and interactions with the phases toluene/IL. Cinnamaldehyde (CALD) and all the hydrogenation products, hydrocinnamaldehyde (HALD) and hydrocinnamyl alcohol (HALC) are fairly polar molecules and should interact better with the polar IL compared to toluene. On the other hand, the hydrogenation products of 1,5-COD, *i.e.* ciclooctene (COE) and ciclooctane (COA) are much more hydrophobic and should interact better with the solvent toluene.

2. Experimental

2.1. Synthesis of ionic liquid

1-hexyl-3-methyl-imidazolium bromide, HMIm.Br, was synthesized by direct alkylation of N-methylimidazol with an excess of 1-bromohexane, using acetonitrile as solvent, on a round bottom flask at 80 °C for 48 h under nitrogen atmosphere. The product was crystallized by adding toluene dropwise in an ice bath until a solid starts to precipitate. The mixture was let still for 2 h and the solid was separated by filtration and dried under vacuum (5 × 10⁻² mbar) at 60 °C, resulting in an almost pure ionic liquid [33] (see Supplementary material).

2.2. Catalysts preparation

The catalyst 5% Pd/C (E-101) was obtained from Evonik. The ionic liquids used were HMIm.Br (synthesized) and BMIm.BF₄ (Aldrich 98.5%, for catalysis). The SCILL catalysts were prepared by simple impregnation of the commercial Pd/C catalyst with different

amounts of the ILs, *i.e.* 0.5, 1, 2.5, 5 and 10 wt% for HMIm.Br, 1 and 5 wt% for BMIm.BF₄. Typically 0.150 g of Pd/C catalyst was added to solution of the ionic liquid in 30 mL of methanol and the solvent was slowly evaporated (*ca.* 2 h) under magnetic stirring at room temperature.

2.3. Hydrogenation reactions

The *trans*-cinnamaldehyde (Aldrich, 99%) and 1,5-cyclooctadiene (Aldrich, 99%) hydrogenations were carried out in a 100 mL stainless steel bomb (Parr 4560) at 80, 100 or 120 °C, H₂ pressure of 20 bar and mechanic stirring at 300 rpm. In a typical run, the bomb was loaded with Pd/C-IL (0.017 g), *trans*-cinnamaldehyde (0.53 g) or 1,5-cyclooctadiene (0.433 g) and toluene (60 mL). The reaction was followed by collecting liquid samples through a dip tube. The samples were analyzed by gas chromatography using dodecane as internal standard in a Shimadzu GC-2010 apparatus equipped with split/splitless injector, flame ionization detector and a capillary column RTX[®] – 5MS (5% phenylmethylsilicone) 30 m × 0.25 mm × 0.25 µm.

2.4. Materials characterization

HMIm.Br was analyzed by ¹H and ¹³C {¹H} Nuclear Magnetic Resonance (Bruker CXP 200 MHz, CDCl₃, 25 °C), Infrared Spectroscopy (Perkin Elmer Spectrum GX FT-IR System) in transmittance mode using KBr windows, and Thermogravimetric Analysis (TGA-60 Shimadzu Instruments) under the following operational conditions: 5 mg powder sample heated to 800 °C in dynamic N₂ atmosphere (100 mLmin⁻¹) with heating rate of 10 °C min⁻¹.

SCILL catalysts based on Pd/C covered with different amounts of the ILs HMIm.Br and BMIm.BF₄ were analyzed by X-ray diffraction XRD (Rigaku, Geigerflex) with Co-K α radiation from 4° min⁻¹ from 10 up to 80°. Thermogravimetric analysis (TGA-60 Shimadzu Instruments) was carried out under dynamic N₂ atmosphere (100 mL min⁻¹) with heating rate 10°C min⁻¹ up to 800°C. The morphology of the catalysts was analyzed by scanning electron microscopy SEM (Jeol JSM 840A). Surface area and porosity measurements (Autosorb 1 Quantachrome) were determined by B.E.T. method, using 22 cycles of N₂ adsorption/desorption using HK and BJH method for pore volume calculations. Infrared Spectroscopy (Perkin Elmer Spectrum GX FT-IR System) was performed in transmittance mode using KBr pellets.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

The coated Pd catalysts were prepared by impregnation with different amounts of HMIm.Br (1-hexyl-3-methyl-imidazolium bromide), *i.e.* 0.5, 1, 2.5, 5 and 10 wt%, on a commercial Pd (5%)/C.

Powder XRD analyses of the prepared IL-coated catalysts showed Pd metal (Pd⁰, PDF 1-1201) and a broad peak at *ca*. 27° related to the carbon support (see Supplementary material). As IL concentration increased, the intensity of the Pd⁰ diffraction peaks gradually decreased due to the formation of a coating on the catalyst surface.

Under the employed conditions IR (Supplementary material) of the pure Pd/C catalyst did not show any significant absorption. As the IL was impregnated on the catalyst surface, some of the HMIm.Br absorptions were observed, *e.g.* at 3400–3600 cm⁻¹ hydroxyl groups or water adsorbed, 2880–3160 cm⁻¹ for imidazolium ring and γ (CH) aromatic stretches, C=C at 1465 cm⁻¹ (low intensity), C=C and C=N stretching at 1573 and 1627 cm⁻¹, C–H



Fig. 1. SEM images of Pd/C and Pd/C-IL catalysts.

and N–H deformations at 1300–1400 $\rm cm^{-1},$ C–C and C–N stretches in 800–1200 $\rm cm^{-1}.$

The Pd/C-IL catalysts were also characterized by TG analyses (Supplementary material). The Pd/C catalyst did not show any significant weight loss up to 800 °C under N₂ atmosphere. On the other hand, all Pd/C-IL materials showed a weight loss between 220 and 350 °C related to the thermal decomposition of HMIm.Br. Based on these weight losses, IL contents of *ca.* 1, 5 and 10 wt% were estimated for the different materials.

SEM images were obtained for the commercial Pd/C catalyst and for the Pd/C-IL (Fig. 1). The commercial Pd/C catalyst showed an irregular surface with visible pore structure. Upon impregnation of only 1% of IL the surface becomes slightly smoother and some of the very small pores seemed to disappear. The addition of IL at 5 and 10% completely coats the porous surface in some areas.

BET measurements for the catalyst Pd/C showed a surface area of 717 m² g⁻¹ with pore volume of *ca*. 0.36 cm³ g⁻¹. As expected, the impregnation of IL at 1 and 10% reduced the BET surface area to 583 and 425 m² g⁻¹, respectively. However, pore volume measurements from the N₂ adsorption for the catalysts Pd/C-IL did not show consistent results. For example, the impregnation of 1% IL decreased the pore volume from 0.36 to 0.30 cm³ g⁻¹. Unexpectedly, when the Pd/C was impregnated with 10% IL the pore volume was greater than 0.30, *i.e.* 0.34 cm³ g⁻¹. During the BET measurements of the samples Pd/C-IL, especially 10% IL, it was necessary very long times to reach N₂ adsorption equilibrium. This anomalous effect could be related to the dissolution of N₂ into IL layer and diffusion into the pores. Therefore, the amounts of N₂ during adsorption and desorption cannot be used consistently to obtain representative surface area and pore structure of the catalysts Pd/C-IL. The pore filling degree was estimated considering the total pore volume $(0.36 \text{ cm}^3 \text{ g}^{-1})$ of the catalyst Pd/C and the IL volume impregnated. Considering that the IL with density $1.23 \text{ g} \text{ cm}^{-3}$ completely fills the pore structure of the catalyst, the impregnation of Pd/C with 1, 5 and 10% should produce a pore filling degree of *ca*. 3, 13 and 25%, respectively.

3.2. Hydrogenation reactions

The selective hydrogenation of cinnamaldehyde (CALD) has a great scientific and technological interest [34–37]. The addition of one molecule of hydrogen may lead to cinnamyl alcohol (CALC) or hydrocinnamaldehyde (HALD) (Scheme 2). Both products of the primary hydrogenation can be further hydrogenated to yield 3-phenyl-1-propanol (hydrocinnamyl alcohol, HALC). Nevertheless, under the examined reaction conditions, CALC was not observed and the only two products were HALD and HALC, as observed in previous work for palladium catalysts [29–32]. The obtained reaction profiles for the different catalysts can be seen in Fig. 2.

It can be observed that neat Pd/C converts near 100% of the cinnamaldehyde in only 15 min producing mainly hydrocinnamaldehyde (HALD) with *ca*. 60% yield. After 30 min the reaction apparently approaches the end as no significant change on product distribution takes place. This result is related to the difficulty of Pd catalyst to hydrogenate C=O bond of the intermediate HALD molecule as reported in theoretical and experimental previous work [29–32,38,39]. Our data, as well as previous ones [39,40], suggest that the product HALC is formed directly by a consecutive double addition of hydrogen to the CALD adsorbed over the Pd surface.



Scheme 2. trans-Cinnamaldehyde (CALD) hydrogenation routes.

(7)

These results can be rationalized in terms of a reaction scheme depicted in Eqs. (1)–(7). Cinnamaldehyde (CALD) and H₂ are absorbed on the Pd surface (Eqs. (1) and (2)). The activated hydrogen is transferred to the C=C bond and HALD is desorbed (Eq. (3)). The results shown in Fig. 2 suggest that this desorbed HALD from the Pd catalyst is not significantly converted into HALC_(soln). Therefore, under the reaction conditions employed over pure Pd/C Eqs. (4) and (5) do not occur significantly and Eqs. (6) and (7) are the main path for the production of HALC.

$$CALD_{(soln)} \rightarrow CALD_{(IL)} \rightarrow CALD_{(Pd)}$$
 (1)

 $H_{2(soln)} \rightarrow H_{2(IL)} \rightarrow H_{2*(Pd)} \rightarrow H_{*(Pd)}$ (2)

$$CALD_{*(Pd)} + H_{2}_{*(Pd)} \rightarrow HALD_{(soln)}$$
 (3)

$$\text{HALD}_{(\text{soln})} \rightarrow \text{HALD}_{(\text{Pd})}$$
 (4)

 $HALD*_{(Pd)} + H*_{(Pd)} \rightarrow HALC_{(soln)}$ (5)

 $CALD_{*(Pd)} + H_{*(Pd)} \rightarrow HALD_{*(Pd)}$ (6)

$$HALD_{*(Pd)} + H_{*(Pd)} \rightarrow HALC_{(soln)}$$

The catalyst coated with small amounts of IL, i.e. 0.5 Pd/C-IL, showed similar results to the uncoated one. The catalysts containing 5 or 10% of IL (i.e. Pd/C-5IL or Pd/C-10IL) led to lower conversion rates as it can be observed by the smoother decrease in CALD curves (see also Table 1 in Supplementary material). These lower reaction rates are likely related to the lower solubility of H₂ and trans-cinnamaldehyde in the IL layer, which reduces the effective concentration of the reactants at the surface of the catalyst. However, it is remarkable the complete change in product distribution caused by the presence of IL layer, *i.e.* the selectivity/yield for HALC is much higher in the presence of IL. These results clearly show that the presence of the IL favors the total hydrogenation product HALC and this effect is more pronounced for higher amounts of IL. Although, the origin of the effect of IL on the reaction selectivity observed in this work is not clear and more detailed investigations are necessary, one can speculate some of the possible effects of the IL on the reaction. The diffusion limitations caused by the IL layer is possibly more important for the larger molecule of cinnamaldehyde (Eq. (1)) compared to the small H₂ molecules (Eq. (2)) [21]. As result, the relative concentration of H_2 on the Pd surface is higher, also increasing the Pd-H concentration. The presence of higher concentrations of Pd-H would favor the HALC according to Eq. (7).

Also, the presence of acidic species which interact with the carbonyl group of the aldehydes is known to favor its hydrogenation. For example, several works suggested that the presence of Lewis acid, such as FeCl₂ [41], SnCl₂, FeCl₃, MnCl₂, or CoCl₂ [42,43] and

ZnCl₂ [44,45] favors the hydrogenation of carbonyl groups of α , β unsaturated aldehydes, e.g. citral and CALD, on Pd catalysts. This promoting effect is explained in terms of an interaction of the carbonyl group with the Lewis acid center (A⁺-O=C), which facilitates the hydride transference from the Pd surface to the carbon of the carbonyl group. Based on these results one can suggest that the IL can interact with the C=O of the HALD surface intermediate species and promote its hydrogenation into HALC by Pd. In fact, the acid Lewis properties of IL have been reported in some works [46,47]. For example, the ILs derivate from dialkylimidazolium bromides and trifluoroacetates showed good activity as catalyst for the Diels-Alder reactions indicating that this kind of dialkylimidazolium salts can act as Lewis acids [48]. Also, the ionic liquid is a medium with a high dielectric constant, which enhances the polarization on the carbon-oxygen bond and helps to promote the hydride attack to the carbon of the CO double bond by an effect analogous to the Lewis acid.

Therefore, a possible role of the IL layer is to function as an active membrane where the more facile diffusion of H_2 and a potential effect of the IL as Lewis acid or dielectric medium will favor the total hydrogenation of cinnamaldehyde.

The Pd/C catalyst with and without IL was also employed in the multistep hydrogenation of 1,5-cyclooctadiene (1,5-COD). Selective hydrogenation of 1,5-COD to monoolefin COE is of great interest especially in the industrial synthesis of polymers and olefins [49]. As depicted in Scheme 3, this reaction may result in the formation of four main products: 1,4-cyclooctadiene (1,4-COD) and 1,3-cyclooctadiene (1,3-COD) due to isomerization, cyclooctene (COE) due to the selective hydrogenation and cyclooctane (COA) due to the exhaustive hydrogenation.

As it can be observed in Fig. 3 for the uncoated catalyst (Pd/C), near 100% of the 1,5-COD is converted in only 15 min producing approximately 90% of the intermediate product COE. It can also be observed the 1,5-COD isomerization to produce very small amounts of 1,4-COD and 1,3-COD, which are consumed by hydrogenation to COE. Further hydrogenation of COE rapidly takes place, mainly after the dienes (1,5-, 1,4- or 1,3-COD) concentrations are reduced. Similar results are described in the literature for the hydrogenation of 1,5-COD in the presence of different Pd catalysts [50,51]. The reason for this great selectivity for COE is that dienes (*e.g.* COD) bind much more strongly to metals than the corresponding monoenes. Thus, the catalytic sites on the metal surface at the beginning of the reaction are saturated by dienes. As hydrogen is added to the first C—C double-bond, the resulting monoene (COE) is immediately displaced by a diene [52].

Only when the diene concentration is comparatively low, the monoene in higher concentration competes for the catalyst sites. A



Fig. 2. Molar distribution (%) of reagent and products as a function of time in CALD hydrogenation (100 $^\circ$ C, H_2: 20 bar, HMIm.Br).



Scheme 3. Reaction products during catalytic 1,5-COD hydrogenation.



Fig. 3. Conversion of 1,5-cyclooctadiene and selectivities (80 $^\circ\text{C},~\text{H}_2\text{:}$ 20 bar, HMIm.Br).



Scheme 4. Schematic representation of the possible processes taking place on the IL coated Pd catalyst surface (bold lines are supposed to be the more important pathways).

similar behavior is observed for Pd/C and Pd/C-0.5IL. On the other hand, the behavior completely changes for IL contents higher than 2.5%, *i.e.* Pd/C-2.5IL – 5IL and 10IL. One clear effect observed when IL was added to the Pd/C is a gradual decrease on the reaction rate, which is expected due to a diffusion barrier on the catalyst surface. This effect is very pronounced for the catalyst Pd/C-10IL.

It is also interesting to observe for the catalysts Pd/C-2.5IL and 5IL a good 1,5-COD conversion but fail to convert COE to COA. As a consequence, the COE concentration remains high, which is desirable from the point of view of the selective hydrogenation of COD to COE. The results displayed in Fig. 3 suggest that the Pd/C catalyst is very efficient to convert COE in COA. On the other hand, in the presence of 2.5IL the hydrogenation of COE is very low even at low diene concentration. This behavior seems to be repeated for Pd/C-5IL and Pd/C-10IL, but as these catalysts are slower, the 1,5-COD conversion did not reached the maximum value during the observed time span. These results suggest a strong effect of the IL layer on the hydrogenation selectivity.

Besides the chemical steps, the hydrogenation of 1,5-COD should involve a complex equilibrium with several phase transfer steps. 1,5-COD should diffuse from toluene to the IL phase and adsorb on Pd surface (Eq. (8)). This step is probably critical, since the apolar 1,5-COD molecule is very soluble in toluene but has limited solubility in the more polar IL HMIm.Br. In fact, as the IL content increases, the 1,5-COD conversion rate gradually decreases, likely due to this diffusion/solubility limitations into the IL. Once in the IL, 1,5-COD adsorbs on Pd and is hydrogenated to form the intermediate COE on the Pd surface (Eq. (9)). The adsorbed intermediate (COE) can desorb from Pd to the IL phase (Eq. (10)) and then follow two different paths: (i) diffusion to toluene (Eq. (11)) or (ii) adsorption back onto Pd for hydrogenation to produce COA (Eq. (12)).

$$COD_{tol} \rightarrow COD_{IL} \rightarrow (COD_{IL})_{ads} - Pd$$
 (8)

$$(COD_{II})_{ads}-Pd + H_2 \rightarrow (COE_{II})_{ads}-Pd$$
(9)

$$(COE_{IL})_{ads}$$
-Pd $\rightarrow COE_{IL}$ (10)

$$COE_{IL} \rightarrow COE_{tol}$$
 (11)

$$COE_{IL} \rightarrow (COE_{IL})_{ads} - Pd + H_2 \rightarrow (COA_{IL})_{ads} - Pd \rightarrow COA_{IL} \rightarrow COA_{tol}$$
(12)

Different from the reaction of cinnamaldehyde, where the IL favors the final hydrogenation product, for the 1,5-COD hydrogenation the IL favors the formation of the intermediate hydrogenation product, *i.e.* COE. This result can be explained in terms of the partition coefficients among the toluene and IL phases. These partition

coefficients should be proportional to the tabled octane/water partition coefficient (K_{ow}). The K_{ow} for 1,5-COD and COE are 3.2 and. 3.9, respectively. These values suggest that both substrates, but specially COE, should have low solubility in polar media such as the IL. Indeed, the water solubility for 1,5-COD (64.1 mg L⁻¹) is greater than COE's one (13.5 mg L⁻¹). Therefore, once formed and desorbed to the IL, the COE should be expelled to toluene. The diffusion back into the IL layer for further hydrogenation is an unfavorable process. These steps are depicted in Scheme 4.

Therefore, in the case of the hydrogenation of 1,5-COD the IL layer has a membrane like effect to expel the intermediate COE and avoid its return to the catalyst surface after the first hydrogenation.

4. Conclusions

The IL HMIm.Br (1-hexyl-3-methylimidazolium bromide) coating on a commercial Pd/C catalyst seems to show a membrane-like effect during the hydrogenation of *trans*-cinnamaldehyde (CALD) and 1,5-cyclooctadiene (1,5-COD).

The small H_2 molecule diffuses more easily from toluene through the IL layer than the larger cinnamaldehyde molecule producing higher concentrations of the Pd-H species, which leads to the total hydrogenated product hydrocinnamyl alcohol. The role of the IL as a weak Lewis acid or medium with high dielectric constant is also considered as a possible explanation for the activation of the carbonyl group. In contrast with the cinnamaldehyde hydrogenation, the effect of the IL layer for the hydrogenation of 1,5-COD was to favor the selective hydrogenation to form the intermediate product COE (cyclooctene). In this case, the IL layer has the effect of expel the intermediate COE avoiding its contact with the Pd surface.

This membrane-like effect observed for the IL having an apolar solvent as a counterpart can potentially be exploited to change the selectivity of many multi-step hydrogenation processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. molcata.2012.05.019.

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