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Continuous selective hydrogenation of citral in a trickle-bed reactor using ionic liquid modified catalysts

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1. Introduction

The selective hydrogenation of α , β -unsaturated aldehydes is still a challenging task in heterogeneous catalysis [1–4]. Citral (CIT; 3,7-dimethyl-2,6-octadienal) belongs to this class of compounds and may be used as model substance. Its hydrogenation leads to a highly complex reaction network depending on the catalyst. Applying palladium as active metal, hydrogenation of the carbonyl group may be hindered and the conjugated C=C bond is hydrogenated prior to the terminal isolated one [5–8]. This results in a simplified reaction network with citronellal (CAL) and dihydrocitronellal (DHC) as main products. The unsaturated alcohols geraniol and nerol as well as citronellol are usually not produced via supported palladium catalysts. Furthermore, dimethyloctanol, isocitral and the two isomers of 3,7-dimethyl-2-octenal are usually produced in minor amounts (Fig. 1).

The application of ionic liquids (IL) in catalysis [9,10] is of growing interest enabling novel concepts of catalysts immobilization, e.g. the supported ionic liquid phase (SILP) catalysis [11,12]. Furthermore, ionic liquids were introduced in the selective hydrogenation of citral, whereby they were used as solvents [13] or reaction modifiers [14–16]. With the aid of dicyanamide based ionic liquids, we managed to completely inhibit the consecutive hydrogenation of citronellal realizing its one-pot production [14,15]. The

ABSTRACT

The influence of the ionic liquid [BMIM][$N(CN)_2$] on the palladium catalyzed hydrogenation of citral in a trickle-bed reactor has been investigated. Applying the SCILL concept (solid catalyst with ionic liquid layer), it was possible to attain citronellal selectivities close to 100% at the cost of catalyst activity. However, the yield of this intermediate was approximately four times higher compared to the neat palladium catalyst. The latter and its SCILL counterpart both seem to have long-term stability, which is relevant for any future industrial application. This is the first time that SCILL systems have been compared directly to their IL-free equivalents in continuous mode.

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utilized conventional Pd/C or Pd/SiO₂ catalysts were impregnated via incipient wetness with the ionic liquid, e.g. [BMIM][N(CN)₂] (1-butyl-3-methylimidazolium dicyanamide). The so-called SCILL concept was applied (solid catalyst with ionic liquid layer), which was first introduced by Kernchen et al. in the nickel catalyzed hydrogenation of cyclooctadiene [17]. The ionic liquid is assumed to cover the catalytically active metallic nanoparticles on its porous support causing solvent- as well as co-catalytic effects.

Trickle-bed reactors (TBR) are part of packed-bed reactors characterized by a two-phase flow of gas and liquid reactants. The liquid is in downflow mode and the gaseous components can either be cocurrent or countercurrent. TBR are utilized in numerous industrial hydrogenations [18] and criteria to ensure their ideal behavior have recently been reviewed by Mederos et al. [19]. Recchia and co-workers have studied the hydrogenation of citral on Pt-Sn/MgO in a micropilot trickle-bed reactor [20]. The authors reported 97% selectivity to the unsaturated alcohols (geraniol and nerol) at full conversion as well as long-term stability of the applied catalyst. Recently, Virtanen et al. [21] examined the hydrogenation of citral in a tubular reactor applying palladium as active metal and N-butyl-4-methylpyridiniumtetrafluoroborate [NB₄MPy][BF₄] as IL layer on active carbon cloths. The catalyst cloths were packed in layer by layer on a stainless steel net in order to immobilize the catalyst. The authors mentioned a maximum dihydrocitronellal selectivity of ~58%. Unfortunately, a comparison of the results to the equivalent catalyst without IL layer was not provided. To the best of our knowledge this is the only work dealing with the hydrogenation of citral in continuous mode making use of modifiers based on ionic liauids.

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Fig. 1. Simplified reaction network of the palladium catalyzed citral hydrogenation.

The aim of this study was to transfer the SCILL concept from batch-mode to the continuous hydrogenation of citral in a tricklebed reactor and to investigate its future industrial application, especially for the production of citronellal. To date, the latter may be produced in a bubble column with feedback and the aid of an organic base, e.g. triethylamine, over palladium or ruthenium catalysts [22]. We wish to demonstrate that ionic liquids as modifiers, prepared onto the catalyst surface, may be an alternative to classical additives such as organic bases.

2. Experimental

2.1. Catalyst preparation and characterization

 $1Pd/SiO_2~(1\,wt\%~Pd)$ and $5Pd/Al_2O_3~(5\,wt\%~Pd)$ have been provided from KataLeuna GmbH Catalysts/CRI or supplied by Sigma-Aldrich, respectively. The catalysts have been pretreated with hydrogen (20 mL min^{-1} $g_{Cat}{}^{-1})$ for 1 h at 100 $^\circ C.$ For the SCILL preparation, the ionic liquid [BMIM][N(CN)₂] (1-butyl-3methylimidazolium dicyanamide, Merck) was dissolved in acetone (Merck) and impregnated over the corresponding catalyst. To obtain a SCILL system containing 32 wt% IL, typically 12 g of the IL was dissolved in 25 mL of acetone and impregnated over 25 g of the pure palladium catalyst. In this example addition of the IL reduced the mass fraction of palladium based on the total mass of the SCILL system (37 g) from 1 wt% to 0.7 wt%. The IL content will be displayed as index, whereas the content of active metal will be stated as prefix in the following (e.g. 0.7Pd/SiO₂@[BMIM][N(CN)₂]₃₂). To accomplish uniform distribution of the IL layer, it was important that the amount of liquid solution was sufficient to cover the solid catalyst completely. The impregnated catalyst was then dried over night at room temperature in the laboratory hood to remove excess organic solvent. It is to mention that all IL contents refer to their theoretical amounts after preparation but applying ICP-OES it has

been proven that they equal their corresponding experimental amounts.

Pulse H₂ chemisorption was performed on a TPDRO1100 (Thermo-Porotec) to obtain hydrogen uptakes of the studied catalysts. Prior to the investigation, the catalysts were reduced under hydrogen flow (Linde 5.0, 3 K min^{-1} , $100 \,^{\circ}\text{C}$, $20 \,\text{mL}\,\text{min}^{-1}$, 1 h) and desorbed under helium flow (Linde 5.0, $100 \,^{\circ}\text{C}$, $20 \,\text{mL}\,\text{min}^{-1}$, 1 h) and desorbed under helium flow (Linde 5.0, $100 \,^{\circ}\text{C}$, $20 \,\text{mL}\,\text{min}^{-1}$, 2 h). Then, pulses of hydrogen ($V_{\text{loop}} = 450 \,\mu\text{L}$, $\Delta t_{\text{Pulse}} = 12 \,\text{min}$, $N_{\text{Pulse}} = 10 \,\text{times}$) under argon flow (Linde 5.0, $20 \,\text{mL}\,\text{min}^{-1}$) at $21 \,^{\circ}\text{C}$ were exposed on the investigated catalysts. The SCILL catalysts were investigated the same way as their IL-free counterparts except that they have been coated with IL prior to the experiment (Table 1).

For a detailed catalyst characterization (N_2 physisorption, pulse CO chemisorption, infrared spectroscopy, transmission electron microscopy, ICP-OES), especially of the SCILL system, we refer to our previous publications [14–16]. Recently, we studied the adsorption of hydrogen on palladium based SCILL catalysts, whereby XANES/EXAFS, XPS, hydrogen chemisorption and adsorption microcalorimetry were applied [23]. On the basis of these experiments we could conclude that the catalytically active palladium interacts with the ionic liquid enabling a complexation of Pd by [N(CN)₂]. The adsorption indicated a ligand effect known from bimetallic catalysis.

2.2. Hydrogenation experiments

All reactions were conducted in a thermostated trickle-bed reactor (Vinci Technologies). Two thermocouples were located inside the reactor and two were placed at its outer wall. The reactor was equipped with a two zone heating jacket, which could either use the inside or outside temperature as reference (inside temperature in this work). Supply of liquid and gaseous reactants was

Table 1

Hydrogen uptakes of	various supported palladium	SCILL catalysts at 21 °C af	ter reductive pre-treatment.

Entry	Catalyst	IL	Pd content (wt%)	IL content (wt%)	$n_{\mathrm{H}_2,\mathrm{ads}}(\mu\mathrm{mol}\mathrm{g}^{-1})$
1	Pd/SiO ₂	-	1	-	13.5
2	Pd/SiO ₂	[BMIM][N(CN) ₂]	0.8	20	3.1
3	Pd/SiO ₂	[BMIM][N(CN) ₂]	0.7	32	1.6
4	Pd/Al ₂ O ₃	[BMIM][N(CN) ₂]	3.4	32	6.3



Fig. 2. Conversion and selectivities vs. time on stream of the 1Pd/SiO₂ catalyzed citral hydrogenation ($V_{Cat} = 40 \text{ mL}$, $m_{Cat} = 15.9 \text{ g}$, $d_{Particle} = 3-3.5 \text{ mm}$ (spherical), $c_{CTT,0} = 1.2 \text{ mol } L^{-1}$, $V_{H_2} = 27 \text{ L} \text{ h}^{-1}$). I: T = 50 °C, p = 20 bar, $L = 2 \text{ mL} \text{ min}^{-1}$. II: T = 70 °C, p = 20 bar, $L = 1 \text{ mL} \text{ min}^{-1}$. IV: T = 70 °C, p = 10 bar, $L = 1 \text{ mL} \text{ min}^{-1}$. IV: T = 70 °C, p = 10 bar, $L = 1 \text{ mL} \text{ min}^{-1}$.

accomplished in cocurrent downflow using HPLC pumps and mass flow controllers, respectively. Data recording and system control were managed online. The cylindrical reactor with an inner diameter of 16 mm had a total volume of 67 mL, but usually only 40 mL was used for catalyst loading. The top and bottom part of the tube were filled with quartz wool. Typically, 1L citral (Merck), 0.2 L n-tetradecane (Merck) and 3.8 L n-hexane (Roth, ROTIPU-RAN > 99%) were premixed to obtain the starting liquid solution, hence, containing 1.2 mol L⁻¹ citral. Quantitative analyses of the reaction mixtures were performed off-line by gas chromatography (Hewlett-Packard 6890 with flame ionization detector operating at 250 °C) with helium as mobile phase. The capillary column in the system was an Agilent DB-Wax column with a length of 30 m, an inner diameter of $0.25\,\text{mm}$ and a film thickness of $0.25\,\mu\text{m}$. The samples were analyzed with the following temperature program: temperature was at first set to 85 °C, and then increased with 5 °C/min to 175 °C.

Selectivities and citral conversion were calculated assuming negligible changes in the liquid volume and concentrations were determined using *n*-tetradecane as internal standard. It is to mention that most compounds exhibit stereochemistry, but their discrimination is beyond the scope of this article. Therefore, given concentrations and selectivities are summations over all stereoisomers. For further simplification, dimethyloctanol, isocitral, both isomers of 3,7-dimethyl-2-octenal as well as unknown compounds are combined as "others".

3. Results and discussion

3.1. Citral hydrogenation with pure 1Pd/SiO₂

To elucidate the influence of the ionic liquid on the catalyst properties, it was necessary to investigate the neat catalyst as reference first. So, the trickle-bed reactor was charged with 40 mL (15.9 g) of the spherical catalyst with particle diameters of 3–3.5 mm. The corresponding citral conversion and product selectivities vs. time on stream (*TOS*) are shown in Fig. 2. Marked fields indicate changes in reaction conditions, whereas the parameters hydrogen flow $(27 L h^{-1})$ and citral concentration $(1.2 mol L^{-1})$ remained constant in all cases. Linear approximations with prefixed slopes of zero were conducted to obtain mean values (*y*-intercept) of each conversion and the corresponding selectivities, which are summarized in Table 2.

Obviously, dihydrocitronellal was the main product followed by citronellal. As already mentioned, dimethyloctanol, isocitral, both isomers of 3,7-dimethyl-2-octenal as well as unknown compounds (<5%) were combined as "others" for simplification purposes. As expected, geraniol and nerol could not be found within the product spectrum. This product distribution is quite typical for palladium catalysts and is similar to previously conducted batch experiments [15]. With rising conversion, the selectivity to dihydrocitronellal increased while the selectivity to citronellal decreased, which is a common feature of consecutive reactions. Elevated temperature as

Table 2

Influence of the ionic liquid [BMIM][N(CN)₂] on the Pd/SiO₂ catalyzed continuous hydrogenation of citral in a trickle-bed reactor. V_{Cat} = 40 mL, d_{Cat} = 3–3.5 mm (spherical), $c_{CIT,0}$ = 1.2 mol L^{-1} , V_{H_2} = 27 L h^{-1} .

Entry	Pd content (wt%)	IL content (wt%)	<i>T</i> (°C)	<i>p</i> (bar)	$L(\mathrm{mLmin^{-1}})$	X _{CIT} (%)	S _{CAL} (%)	S _{DHC} (%)	S_{Others} (%)	Y _{CAL} (%)
1	1	-	50	20	2	77	36	51	13	28
2	1	-	70	20	2	88	26	61	13	23
3	1	-	70	20	1	96	15	76	9	14
4	1	-	70	10	1	89	25	61	14	22
5	0.7	32	70	20	1	52	>99	-	<1	52
6	0.7	32	70	40	1	52	>99	-	<1	52
7	0.7	32	100	40	1	67	97	2	1	65
8	0.7	32	100	40	0.75	83	94	4	2	78
9	0.8	20	70	20	2	45	99	-	1	45
10	0.8	20	70	20	1	57	95	1	4	54
11	0.8	20	70	20	0.5	70	89	2	9	62



Fig. 3. Conversion and selectivities vs. time on stream of the citral hydrogenation applying the SCILL system $0.7Pd/SiO_2@[BMIM][N(CN)_2]_{32}$ ($V_{Cat} = 40$ mL, $m_{Cat} = 23.4$ g, $d_{Particle} = 3-3.5$ mm (spherical), $c_{CIT,0} = 1.2$ mol L⁻¹, $V_{H_2} = 27$ L h⁻¹). I: T = 70 °C, p = 20 bar, L = 1 mL min⁻¹. II: T = 70 °C, p = 40 bar, L = 1 mL min⁻¹. III: T = 100 °C, p = 40 bar, L = 1 mL min⁻¹. IV: T = 100 °C, p = 40 bar, L = 0.75 mL min⁻¹.

well as reduced liquid flow rates (*L*) resulted in higher conversions of citral. At 70 °C and L = 1 mL min⁻¹ almost complete citral conversion was achieved. Lowering the total pressure from 20 bar to 10 bar caused a decrease in conversion of about 7%. This was associated with diminished dihydrocitronellal selectivity and increased selectivity to the less hydrogenated product citronellal. After 97 h *TOS*, the initial conditions have been reset to examine catalyst deactivation. Approximately identical conversion and selectivities could be observed in comparison to the initial state. Apparently, the utilized catalyst exhibits long-term stability.

3.2. Influence of [BMIM][N(CN)₂]

To obtain comparable results, it was necessary not to change the amount of active metal and the hydrodynamic behavior of the trickle-bed reactor. Hence, again 40 mL of the catalyst 1Pd/SiO₂ was used and coated with [BMIM][N(CN)₂], which resulted in a higher catalyst mass, but led to a matching absolute amount of palladium. Assuming that the IL layer did not affect the bulk porosity, 40 mL of the SCILL system should equal its neat counterpart and hydrodynamics stayed the same. Fig. 3 refers to a SCILL system with 32 wt% IL. Results of other modifications are summarized in Table 2.

As shown in Fig. 3, the product spectrum has completely changed compared to the catalyst without [BMIM][N(CN)2]. In all cases, almost no production of dihydrocitronellal could be observed and citronellal was the main product with nearly guantitative selectivity. It is to mention that besides the consecutive hydrogenation of citronellal to dihydrocitronellal, all other reaction pathways seem to be inhibited as well. Only at conversions higher than 80%, selectivities to dihydrocitronellal became significant. An increase in temperature from 70 °C to 100 °C was associated with 15% gain of conversion. Further reduction of the liquid flow rate $(L=0.75 \text{ mL min}^{-1})$ led to the highest measured citronellal yield of 78% at 83% citral conversion (S_{CAL} = 94%). In contrast to the neat catalyst, total pressure did not affect the performance at all. Because the partial pressure of hydrogen definitely influences its solubility within the IL [24], this characteristic may be attributed to the fact that in presence of the IL layer, hydrogen does not appear in the rate-determining step.

To test for catalyst deactivation in the presence of the IL, the same procedure has been chosen as already described. Apparently, the selectivity remained constant, whereas a slight increase of conversion could be observed after resetting the initial conditions. In view of analytical errors, the utilized catalyst was stable within the total duration of the experiment (TOS = 78 h). However, at temperatures higher than 100 °C desorption of the ionic liquid could be observed. This was indicated by the emergence of a second phase at the reactor outlet. Below this threshold value desorption did not occur and steady-state conditions regarding conversion and selectivities remained unchanged. Virtanen et al. observed strong deactivation in case of a palladium based SCILL system containing [NB4MPy][BF4] as IL [21]. Unfortunately, the authors neither compared their results to the IL-free catalyst nor did they run the experiments sufficiently long (TOS = 100 min) to disentangle the startup phase from deactivation.

Experiments with lower IL content (20 wt%) showed the same behavior in respect of the operating conditions (Table 2). However, the citral conversion has slightly increased, whereas the selectivity to citronellal has decreased compared to the experiments with 32 wt% IL. Fig. 4 demonstrates the influence of the IL content on the catalyst performance under same conditions in other respects. Obviously, presence of the ionic liquid was associated with higher



Fig. 4. Influence of [BMIM][N(CN)₂] on the palladium catalyzed citral hydrogenation. Variation of the IL content under same conditions in other respects: $V_{Cat} = 40$ mL, T = 70 °C, p = 20 bar, L = 1 mL min⁻¹, $d_{Particle} = 3-3.5$ mm (spherical), $c_{CIT,0} = 1.2$ mol L⁻¹, $V_{H_2} = 27$ L h⁻¹.

Table 3

Hydrogenation of citral in a trickle-bed reactor using $3.4Pd/Al_2O_3@[BMIM][N(CN)_2]_{32}$ (3.4 wt% Pd and 32 wt% IL content) as catalyst. $V_{Cat} = 35$ mL, $d_{Cat} = 2-6$ mm (grit), $c_{CIT,0} = 1.2$ mol L^{-1} , $V_{H_2} = 27$ L h⁻¹ in all cases.

Entry	T (°C)	<i>p</i> (bar)	$L(\mathrm{mLmin^{-1}})$	X _{CIT} (%)	S _{CAL} (%)	S _{DHC} (%)	S _{Others} (%)	Y _{CAL} (%)
1	70	20	2	99	36	55	9	36
2	70	20	3	92	45	43	12	41
3	50	20	3	80	61	23	16	49
4	50	10	4	72	63	20	17	45

citronellal selectivity but lower conversion in both cases. Nevertheless, the citronellal yield could be considerably enhanced due to the IL from 14% (no IL) to 52% (32 wt% IL) and 54% (20 wt% IL), respectively.

There are plenty of ways to heighten the conversion of citral, but several of them exhibit some drawbacks. Elevated temperatures should be avoided because the IL could possibly desorb or even decompose. Further reduction of the liquid flow rate would decrease the output of citronellal and may lead to dry zones in the trickle-bed reactor, which consequently comes along with diminished catalyst efficiency. Therefore, another approach to enhance conversion was attempted. A commercial powder of 5Pd/Al₂O₃ was applied to synthesize a SCILL system containing 32 wt% [BMIM][N(CN)₂] and 3.4 wt% palladium. The preparation method was similar to the description in Section 2. In order to avoid a severe pressure drop, it was necessary to press the powder of the SCILL system into pellets (pressing procedure: 7-10t for 2 min), which were crushed into 2-6 mm grit subsequently. 35 mL of the catalyst was packed into the reactor. Again quartz wool was placed on top and bottom to fill the reactor and to distribute the flows evenly over the catalyst.

As shown in Table 3, it was possible to enhance the catalyst activity and to achieve 99% conversion at $T = 70 \,^{\circ}\text{C}$ and $L = 2 \,\text{mLmin}^{-1}$, with a selectivity towards citronellal of 36%. Increasing the liquid flow rate and reducing the temperature, both resulted in higher citronellal selectivities and lower dihydrocitronellal selectivities. It is important to compare the selectivity of citronellal at similar conversions between the SCILL system and the neat catalyst (1Pd/SiO₂ as reference). At 96% citral conversion, the latter exhibited a citronellal selectivity of 15% (Table 2). Hence, in case of 3.4Pd/Al₂O₃@[BMIM][N(CN)₂]₃₂ the citronellal selectivity could be more than doubled at almost full conversion. Nevertheless, it is still necessary to optimize this system regarding its IL content. The ratio of palladium to IL seems to be a crucial variable in respect of the citronellal yield. Apparently, higher IL amounts increase the selectivity of the desired intermediate at the cost of activity, but it is to mention that in all cases its yield could be enhanced.

3.3. Interpretation of the selectivity enhancement

Within this section we try to elucidate the observed beneficial effect of [BMIM][N(CN)₂]. Besides some new results also findings of our earlier studies will be considered and discussed in respect to this work.

First of all, the texture of a SCILL system should be illustrated. It has been assumed that the ionic liquid forms a thin layer onto the porous support covering the active metal sites. This has been deduced from N₂ physisorption experiments which indicate reduced pore volumes and BET-surfaces of SCILL catalysts compared to their neat counterparts [15,16]. The thickness of the IL layer is supposed to depend on the loading of IL [17] and consequently there may be a threshold for a complete coverage. Whether the latter is uniform or maldistributed still needs to be clarified. To explain the effect of the modification ex situ characterizations have been applied. The results may then be related to the observed changes in the catalyst performance.

H₂ chemisorption experiments conducted in this work confirm the already stated trend [15,23] that presence of an ionic liquid strongly reduces the hydrogen uptake and that this is even more pronounced with higher IL contents. The determined hydrogen uptakes of the investigated catalysts are shown in Table 1. Considering a coverage of the palladium nanoparticles with an ionic liquid layer, the lower hydrogen uptakes in the case of [BMIM][N(CN)₂] coated Pd/SiO₂ can be interpreted by the low hydrogen solubility in ionic liquids. In particular, Dyson et al. have applied ¹H NMR to measure the Henry-coefficient of hydrogen in ionic liquids. The authors figured out that the concentration of dissolved hydrogen in ionic liquids is much lower than in typical organic solvents and in the same range as for water [25]. A small local concentration of hydrogen in vicinity to the active sites may cause the reduced activity observed in case of SCILL catalysts. It is a common feature of consecutive reactions that the selectivity to intermediates will be increased with decreasing activity. Consequently, this might be one reason for the selectivity enhancement. On the other hand this may not explain the fact that SCILL systems exhibit much higher selectivities to citronellal even at similar conversions compared to their IL-free equivalents.

It has been shown that an ionic liquid tremendously influences the adsorption of hydrogen. Potentially, the adsorption of citral and citronellal is also affected. A rapid desorption associated with an inhibited re-adsorption of the intermediate citronellal could explain the enhanced selectivity even at high citral conversion. First experiments indicate that citral dissolves better within [BMIM][N(CN)₂] than citronellal but further studies still need to be performed [26]. Kernchen et al. have already proposed this way of explanation in case of the hydrogenation of cyclooctadiene applying SCILL catalysts [17].

Besides the reduced hydrogen uptake, a modification with IL results in some changes in respect of the catalyst itself [23]. In particular, XPS analysis revealed that Pd is transformed into Pd²⁺ due to its coating with [BMIM][N(CN)₂]. Even a complexation of Pd may be possible. This was also indicated by a blue shift in the nitrile vibrations when comparing IR spectrometric results of neat Pd/SiO₂ with its corresponding SCILL system [15]. The results have recently been published and should not be repeated here. Nevertheless, they have not been interpreted in view of the hydrogenation reaction and the selectivity enhancement. Although there is no incontrovertible proof it is quite obvious that this drastic electronic change may alter adsorption coefficients as well as rate constants. Hence, this will modify selectivities within the reaction network.

To summarize the effects investigated so far, the observed benefit of dicyanamide based ionic liquids has two main causes. First, there is a transport limitation reducing the local concentration of hydrogen in vicinity to the active sites which leads to a reduced activity of the catalytic system which inherently comes along with an increased selectivity to citronellal. Second, we were able to detect a strong electronic interaction between palladium and the dicyanamide anion. This may affect adsorption coefficients as well as rate constants in a way that the citronellal consumption tends to almost zero maximizing its yield.

4. Conclusion

In this work, the so-called SCILL concept (solid catalyst with ionic liquid layer) could successfully be applied in the continuous hydrogenation of citral in a trickle-bed reactor. In good accordance with previous findings on palladium based SCILL systems in discontinuous batch reactors [14,15], the advantages of the SCILL concept could be demonstrated once again. This means that despite lower citral conversions, highly improved citronellal vields due to selectivities close upon 100% could be achieved in continuous mode as well. To our knowledge, this is the first time that SCILL systems have been investigated in continuous experiments and compared to their neat counterparts. Besides, this is even the only study dealing with the hydrogenation of citral in a trickle-bed reactor applying neat palladium based catalysts at all. The selectivity enhancement may not be ascribed to the reduced activity of the catalyst exclusively because the SCILL system exhibited higher citronellal yields even at comparable conversions.

In case of $1Pd/SiO_2$, the performance of the catalyst could be significantly enhanced using [BMIM][N(CN)₂] as ionic liquid layer. The citronellal selectivity was found to be close to 100% in almost all conducted experiments (Table 2), which may be ascribed to the inhibited consecutive reaction of citronellal to dihydrocitronellal. The yield of citronellal was approximately four times higher compared to the neat palladium catalyst under same conditions in other respects. However, this was associated with a reduced conversion of citral (Fig. 4). To circumvent this feature, a SCILL system with higher palladium content has been investigated. It was possible to achieve full conversion, but at lower citronellal selectivities. All

investigated catalysts exhibited long-term stability, which is quite important for any industrial application.

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