The promoting effect of a dicyanamide based ionic liquid in the selective hydrogenation of citral†

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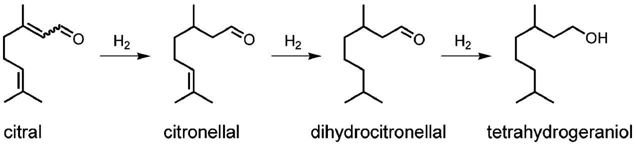
Conventional supported heterogeneous palladium catalysts in combination with a dicyanamide based ionic liquid are highly active with excellent selectivity in enabling the one-pot synthesis of citronellal through citral hydrogenation.

Heterogeneously catalysed selective hydrogenations play an evident role in the production of fine chemicals on a multi-ton scale.[1] The determination of factors influencing activity and selectivity of solid catalysts is still challenging, whereby α,β-unsaturated aldehydes, *e.g.* acrolein, crotonaldehyde or citral, are widely used as model substrates.[2]

Citral—nowadays a valuable intermediate for the production of vitamins and perfumes—consists of three unsaturated bonds (a carbonyl group, and a conjugated as well as an isolated double bond) and its hydrogenation on supported palladium catalysts results often in a consecutive reaction network (Scheme 1). On the industrial scale, citronellal is produced through the hydrogenation of citral over palladium/carbon catalysts in a continuous slurry-phase, with methanol as the solvent and trimethylamine as an additive.[3]

Over the past decade, the application of ionic liquids (ILs) in catalysis has been of growing interest due to their unique properties.[4] Principally, in catalysed reactions, ILs were widely used as solvents or as stabilising agents for transition metal complexes.[4] Due to their non-volatility, supported ionic liquid phase catalysis (SILPC) was established for olefin hydroformylation,[5] methanol carbonylation,[6] and olefin hydrogenation.[7]

In the selective hydrogenation of citral on supported metal catalysts, ILs were applied at first as bulk organic solvents with good selectivities towards citronellal.[8] Compared to organic solvents such as toluene, the reaction rate was lower in [EMIM][NTf$_2$]‡ and quantitative yields of citronellal were obtained. The heterogeneous Pd/C catalyst could be reused several times, but product extraction is still necessary and restricts the utilisation of ILs on a larger scale.



Scheme 1 Reaction network of palladium catalysed citral hydrogenation.

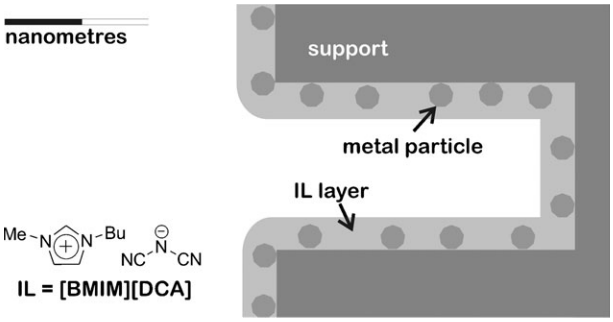
On applying monometallic Pd/Al$_2$O$_3$ or bimetallic Ni–Sn/Al$_2$O$_3$ catalysts in either *n*-hexane and [BMIM][NTf$_2$], a modification of the selectivity pattern could not be observed.[9]

Detailed studies concerning solid ionic liquid coated catalysts were published recently,[10] where fluorous based ILs served to stabilise palladium nanoparticles on an activated carbon cloth (ACC). The structure of the applied Pd/ACC catalyst is comparable to the SCILL (solid catalyst with ionic liquid layer) system, which was used in the nickel catalysed hydrogenation of cyclooctadiene. The IL-coated catalysts revealed higher selectivities towards the intermediate cyclooctene than under IL-free conditions.[11]

The aim of this study was to investigate systematically the role of ionic liquids in the selective hydrogenation of citral, whereby conventional heterogeneous palladium catalysts were applied. Among commonly used ILs, we introduce—for the first time in selective hydrogenations—a hydrophilic, low-viscosity ionic liquid based on the dicyanamide anion ([DCA]$^-$ = [N(CN)$_2$]$^-$),[12] which allows the selective production of citronellal in quantitative yields. Furthermore, we wish to present that ionic liquids, even in small amounts, could affect the selectivity pattern for this kind of reaction.

Hydrogenation experiments were performed using different catalyst types: IL-free catalyst, IL coated catalyst or IL as additive. The catalysts were characterised by ICP-OES, TEM and nitrogen physisorption.‡

Physisorption characteristics for Pd/SiO$_2$ revealed a decrease in pore volume and BET surface area after treating with ionic liquid (Table S1†). Post-reaction BET surface analysis showed that the pore texture remained unaltered; the catalysts can be assumed as mechanically stable.



Scheme 2 Supposed structure of an IL coated solid catalyst.

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† Electronic supplementary information (ESI) available: TEM images, physisorption data and selectivity *vs.* conversion plots (recycling, DHC and other products, respectively). See DOI: 10.1039/b810291k

Table 1 Citral hydrogenation using different reaction conditions with Pd/C as catalyst and [BMIM][DCA] as IL[a]

Reaction type	Conversion (%)	Selectivity (%)		
		CAL	DHC	Others[e]
IL free	100	41	49	10
IL coated[b]	100	>99	<1	<1
Additive[c]	42	>99	<1	<1
Bulk solvent[d]	100	97	1	2

[a] Conditions: 323 K, 200 mg catalyst, $c_{\mathrm{Citral,0}} = 1.1$ mol L^{-1}, 1.0 MPa H_2, 360 min. [b] Catalyst with 50 wt% IL loading. [c] 200 mg [BMIM][DCA] added to the citral–*n*-hexane mixture. [d] *n*-Hexane was replaced by [BMIM][DCA]. [e] 3,7-Dimethylocta-2,7-dienal, isopulegol and non-identified products.

An exemplified structure for this kind of catalyst is given in Scheme 2, whereby the ionic liquid covers the catalytically active metallic nanoparticles.

In a first approach, the influence of ILs was investigated under different reaction modes with a conventional Pd/C (10 wt%, Aldrich) catalyst (Table 1). Under IL-free conditions, a product mixture was obtained containing principally citronellal (CAL) and dihydrocitronellal (DHC). Generally, in the presence of [BMIM][DCA], citronellal was the exclusive product ($S > 99\%$), even at high conversion levels with IL coated catalyst. A high citral conversion with excellent selectivity was revealed in a reference experiment with [BMIM][DCA] as bulk solvent.

Validating the selectivity enhancement towards the primary product, citronellal was used as starting material and the hydrogenation was performed under similar conditions. Hereby, the course of hydrogenation was strongly inhibited if the [BMIM][DCA] coated catalyst was applied and a very low conversion ($\sim$1%) was detected. In contrast, the IL-free Pd/C catalyst showed high conversion (X) and an excellent yield (Y) towards dihydrocitronellal ($X = 89\%$, $Y = 85\%$).

In order to exclude influences of the support material, palladium was also deposited on silica. The results with [BMIM][DCA] coated Pd/SiO_2 catalysts are given in Table 2 and support the findings with Pd/C. The catalyst activity was lowered if the IL content of the catalyst was about 50 wt%, without affecting the high citronellal selectivity. Leaching of [BMIM][DCA] into the substrate solution can be excluded, because a recycling experiment of the IL coated catalyst gave congruent selectivity–conversion profiles (Fig. S2†).

Table 2 Citral hydrogenation with [BMIM][DCA] coated Pd/SiO_2 catalysts[a]

[BMIM][DCA] content (wt%)	Conversion (%)	Selectivity (%)		
		CAL	DHC	Others[b]
Without [BMIM][DCA]	95	37	43	20
33	89	>99	<1	<1
50	49	>99	<1	<1

[a] Conditions: $m_{\mathrm{citral}}/m_{\mathrm{Pd}}$ = const., 323 K, $c_{\mathrm{Citral,0}} = 1.1$ mol L^{-1}, 2.0 MPa H_2, 360 min. [b] 3,7-Dimethylocta-2,7-dienal, isopulegol and non-identified products.

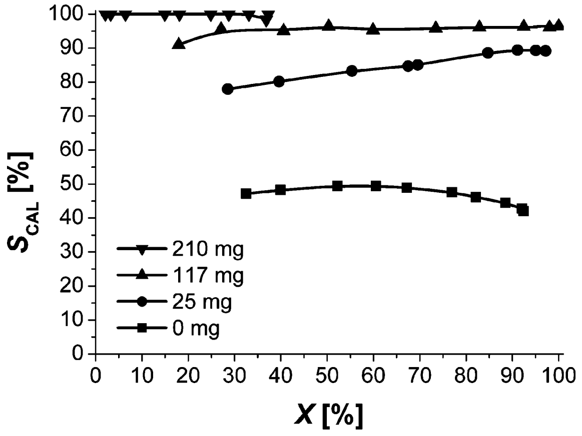

Fig. 1 Selectivity *vs.* conversion plot for different [BMIM][DCA] quantities during citral hydrogenation (conditions: 323 K, 250 mg Pd/SiO_2, $c_{\mathrm{Citral,0}} = 1.1$ mol L^{-1}, 2.0 MPa H_2).

A variety of reactions with different quantities between 0 and 210 mg of [BMIM][DCA] as additive were carried out to study the influence on product selectivity. Fig. 1 shows that the selectivity towards citronellal is dependent on the quantity of the added [BMIM][DCA].

Except for the highest amount of [BMIM][DCA] (210 mg), the conversion levels of the performed reactions were nearly quantitative. Moreover, coating of catalysts prior to reaction gave slightly higher conversion levels.

Post reaction physisorption of an "IL-as-additive-catalyst" indicated that the ionic liquid was deposited on Pd/SiO_2, because the BET surface area and pore volume were in the same range as for an IL coated catalyst prepared prior to reaction (Table S1†).

It is important to note that similar selectivity enhancement could also be achieved with other ionic liquids, but to a much lower extent ($S_{\mathrm{CAL,max}} = 62\%$ with [BMPL][NTf_2]). Palladium catalysed citral hydrogenations with basic promoters such as sodium hydroxide lead to higher selectivities towards citronellal.[13] We propose that the dicyanamide based ionic liquid takes also the role of a basic promoter, which was assumed previously in the acetylation of sugars and alcohols.[14]

In conclusion, ionic liquids—even in small amounts as coated catalyst or additive—can manipulate tremendously the selectivity pattern of conventional solid catalysts in the regioselective hydrogenation of citral. By minimising diffusion limitations through the thin film of ionic liquid, the conversion levels were similar to IL-free catalysts. In addition, product extraction could be circumvented compared to the use of ionic liquids as bulk solvents. As it seems, the role of the anion is more crucial than that of the cation. Although some other ILs such as [BMPL][NTf_2] could increase the selectivity and hence the yield to citronellal, one could not allude to a more "greener" process or even of an intensification of the latter. Up to now, only the DCA-based ionic liquid could improve the hydrogenation of citral to citronellal in a way which has not been observed with other ones yet, because consecutive hydrogenation to dihydrocitronellal is strongly inhibited leading to a selectivity of $>99\%$ at full conversion, *i.e.* the desired product is exclusively formed. Therefore, we propose that this function is not only suitable for palladium catalysed citral hydrogenation, but also for other regioselective hydrogenations.

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Notes and references

‡ *Abbreviations*: [EMIM][NTf_2] = 1-ethyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)amide, [BMIM][NTf_2] = 1-butyl-3-methylimidazolium-bis(trifluoromethanesulfonyl)amide, [BMIM][DCA] = 1-butyl-3-methylimidazolium-dicyanamide, [BMPL][NTf_2] = *N*-butyl-*N*-methylpyrrolidinium-bis(trifluoromethanesulfonyl)amide.
Catalyst preparation: silica was treated with palladium acetate as metal precursor and acetone as solvent, applying an incipient-wetness technique. After drying at room temperature overnight, the orange powder was reduced at 373 K in a flow of hydrogen to obtain palladium in metallic state.
Preparation of IL coated catalysts: a calculated amount of ionic liquid was dissolved in acetone and impregnated over the solid catalyst (Pd/C and Pd/SiO_2) *via* incipient-wetness. The catalyst was then dried at 343 K (3 h) to remove traces of the organic solvent.
Catalyst characterisation: the palladium content of the IL-free Pd/SiO_2 was 4.6 wt% as revealed by ICP-OES. TEM examinations (JEOL JEM, 300 kV) showed palladium particles in diameters between 5 and 10 nm (Fig. S1†). Textural properties were determined by nitrogen physisorption (Quantachrome Autosorb) at 77 K; the samples were dried *in situ* at 423 K prior to investigation.
Hydrogenation experiments: in a batch reaction vessel (Parr Co.), citral (c = 1.1 mol L^{-1} in *n*-hexane) was hydrogenated with Pd catalysts at 323 K and a hydrogen pressure of 2.0 MPa. Samples were taken periodically and analysed by gas chromatography (HP 6890, DB-Wax) using *n*-tetradecane as internal standard. With [BMIM][DCA] as bulk solvent, the samples were extracted with *n*-hexane prior to analysis (sample–*n*-hexane 1 : 5 v/v, 2 times).

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