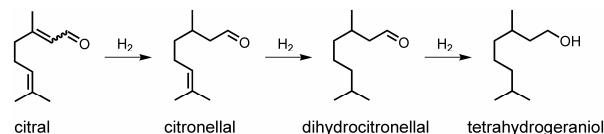


# Promoting effect of ionic liquids in citral hydrogenation: one-pot production of citronellal on modified metal/support catalysts

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## Introduction

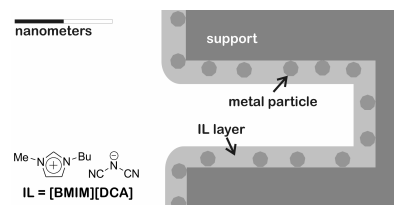
The  $\alpha,\beta$ -unsaturated aldehyde citral – as a valuable intermediate in the production of fine chemicals – consists of three unsaturated bonds (C=C conjugated to C=O and isolated C=C bond) and is often applied as model molecule to study different factors of catalysts influencing their selectivity properties (nature of metal, support, modifiers). Citral can be hydrogenated on supported palladium in consecutive reactions to citronellal, dihydrocitronellal or tetrahydrogeraniol (Figure 1).



**Figure 1.** Reaction scheme for palladium catalyzed citral hydrogenation.

In the last decade, ionic liquids (ILs) gained much interest in various fields due to their unique properties, e. g. non-volatility. For citral hydrogenation, they were used first as bulk solvents on monometallic palladium<sup>1,2</sup> or bimetallic nickel-tin<sup>2</sup> supported catalysts. The concept of immobilizing ionic liquids on metal/support catalysts (“solid catalyst ionic liquid layer” = SCILL) was introduced for the selective hydrogenation of cyclooctadiene and a selectivity enhancement towards the intermediate cyclooctene was observed.<sup>3</sup>

Aim of this study was to determine the influence of ionic liquids on the selectivity pattern of conventional supported palladium catalysts in citral hydrogenation. Focussed on low-viscous, water-soluble dicyanamide based ionic liquids, different catalyst types were employed: IL as bulk solvent, as additive and as SCILL (Figure 2).



**Figure 2.** SCILL concept.<sup>4</sup>

## Materials and Methods

Palladium supported catalysts were prepared by incipient-wetness on SiO<sub>2</sub> with Pd(OAc)<sub>2</sub> in acetone or purchased by Aldrich (Pd on charcoal). Several ionic liquids (e. g. [BMIM][PF<sub>6</sub>], [BMIM][NTf<sub>2</sub>], [BMIM][DCA]) dissolved in acetone were deposited on the supported palladium catalyst by incipient-wetness and after drying, SCILL catalysts were obtained. IL-free and SCILL catalysts were characterized by nitrogen physisorption, CO pulse chemisorption, transmission electron microscopy and IR spectroscopy. Citral hydrogenation was carried out in a batch-reactor (Parr Inst.), whereby the respective catalyst (0.2–0.5 g) was suspended in citral solution (1.1 mol L<sup>-1</sup> in *n*-hexane). Samples were analysed by gas chromatography (HP6890) and *n*-tetradecane was used as internal standard.

## Results and Discussion

In general, ionic liquids as catalyst coating or as additive are able to modify the selectivity pattern of conventional catalysts for citral hydrogenation. With [BMIM][PF<sub>6</sub>] and [BMIM][NTf<sub>2</sub>] as coating, the citronellal selectivity (~ 60%) was moderately enhanced at equal conversion in comparison to the IL-free catalyst (~ 45%). Surprisingly, [BMIM][DCA] gave nearly full selectivity towards the preferred citronellal independent if they were introduced as coating or as additive (Table 1).

**Table 1.** Pd/C-catalysed citral hydrogenation under various applied conditions of [BMIM][DCA] ( $C_{0,citral} = 1.1 \text{ mol L}^{-1}$  in *n*-hexane, 323 K, 0.2 MPa H<sub>2</sub>, 1200 rpm, 6 h).

Catalyst	<i>X</i> [%]	<i>S</i> <sub>citronellal</sub> [%]	<i>S</i> <sub>dihydrocitronellal</sub> [%]	<i>S</i> <sub>others</sub> [%]
IL-free	100	41	49	10
IL coated (SCILL)	100	>99	<1	<1
IL as additive	42	>99	<1	<1
Bulk solvent	100	97	1	2

Recycling experiments of SCILL catalysts proved the stability of the ionic liquid layer. Furthermore, the consecutive hydrogenation of citronellal is inhibited if dicyanamide based SCILL catalysts were used, whereas in presence of IL-free Pd/C dihydrocitronellal was obtained in high yields. IR spectroscopy indicated a special interaction between palladium and the dicyanamide anion.

## Significance

Modifying palladium supported catalysts with dicyanamide based ionic liquids either as additive or coating enables the one-pot production of industrial relevant citronellal by citral hydrogenation with nearly quantitative yield.

## References

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