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Silica supported silver nanoparticles from a silver(I) carboxylate: Highly active catalyst for regioselective hydrogenation

M. Steffan [a], A. Jakob [b], P. Claus [a,*], H. Lang [b]

[a] Institute of Chemical Technology, Department of Chemistry, Technical University Darmstadt, Petersenstr. 20, 64287 Darmstadt, Germany
[b] Technical University Chemnitz, Faculty of Natural Sciences, Department of Inorganic Chemistry, Straße der Nationen 62, 09111 Chemnitz, Germany

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ABSTRACT

The selective hydrogenation of the α,β-unsaturated aldehyde citral (3,7-dimethyl-2,6-octadienal) was investigated with nano-sized silver particles on silica (Ag/SiO_2). The catalysts were synthesized from the precursors silver nitrate and silver 2-[2-(2-methoxyethoxy)ethoxy]acetate $[AgO_2C(CH_2OCH_2)_3H]$, respectively, and a mean particle diameter in the range of 4–8 nm could be detected via TEM. The results show that these catalysts are selective for C═O hydrogenation of citral ($S_{UOL} = 71–77\%$ at $X = 50\%$) even at high conversion levels. In addition, the silver carboxylate $[AgO_2C(CH_2OCH_2)_3H]$, soluble in water as well as in polar organic solvents, offers a straightforward preparation route for nano-sized silver particles generation.

1. Introduction

The selective catalytic hydrogenation of α,β-unsaturated aldehydes to allylic alcohols and/or saturated aldehydes is of commercial relevance, for example, in the production of fine chemicals, pharmaceuticals or perfumes. This topic was recently reviewed by Gallezot and Claus [1–3]. Generally, the latter hydrogenation reaction can be carried out with most group VIII metal atoms [4] in gas and liquid phase, respectively. There are numerous different factors affecting the chemoselectivity in selective hydrogenations, including type of metal, size and morphology of metal particles, use of 2nd metal, electronic and steric influence of the support, metal-support interactions with partially reducible supports (SMSI), steric effects of substituents at the conjugated double bond, reaction conditions, and use of additives or promoters (Lewis acids or bases). In these reactions the reduction of the C═C group is thermodynamically favoured over the C═O group and hence, one has to design a catalyst which guarantees the kinetic control for the hydrogenation of the carbonyl group. The effect of different solvents on activity and selectivity in citral hydrogenation was recently described by Vannice et al. [5] with a silica supported platinum catalyst in organic solvents and by Hardacre et al. for cinnamaldehyde and citral with supported palladium catalysts in organic solvents as well as ionic liquids [6]. The group of Vannice reported that the solvents did not significantly influence the product distributions, whereas a distinct effect on the resulting activities was observed [5]. However, the variation in specific activity did not correlate with either the permittivity or the dipole moment of the solvent. In contrast, Hardacre et al. could achieve increased selectivities to citronellal (close to 100%) when using a Pd/C catalyst in ionic liquids instead of organic solvents [6].

The reaction network of citral hydrogenation is shown in Fig. 1 and it is obvious that it implies a great challenge to obtain a catalyst which matches all the terms (high selectivity towards C═O reduction, suppression of parallel and consecutive reaction, and decarbonylation) to reach high selectivities to the unsaturated alcohols geraniol and nerol (most desired products) even at high conversion levels.

Silver [7–9] and gold catalysts [10–12] are proper for hydrogenation of the C═O group of the two simplest α,β-unsaturated aldehydes acrolein und crotonaldehyde. The exceptional properties of Ag/SiO_2 in the gas phase hydrogenation of acrolein could be attributed to subsurface O which can create electropositive sites under reaction conditions [13]. These sites can now coordinate the C═O group and facilitate the hydrogenation to allyl alcohol, resulting in overall activity and selectivity increase. Furthermore, subsurface O promotes the dissociation of molecular hydrogen, which could be confirmed by recent DFT studies [14]. In the case of gold the edges of single crystalline gold clusters were identified as the active sites for the hydrogenation of the carbonyl group [12]. These results could be confirmed by van Bokhoven et al. [15] in the

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* Corresponding author. Tel.: +49 6151 165369; fax: +49 6151 164788.
E-mail address: claus@ct.chemie.tu-darmstadt.de (P. Claus).

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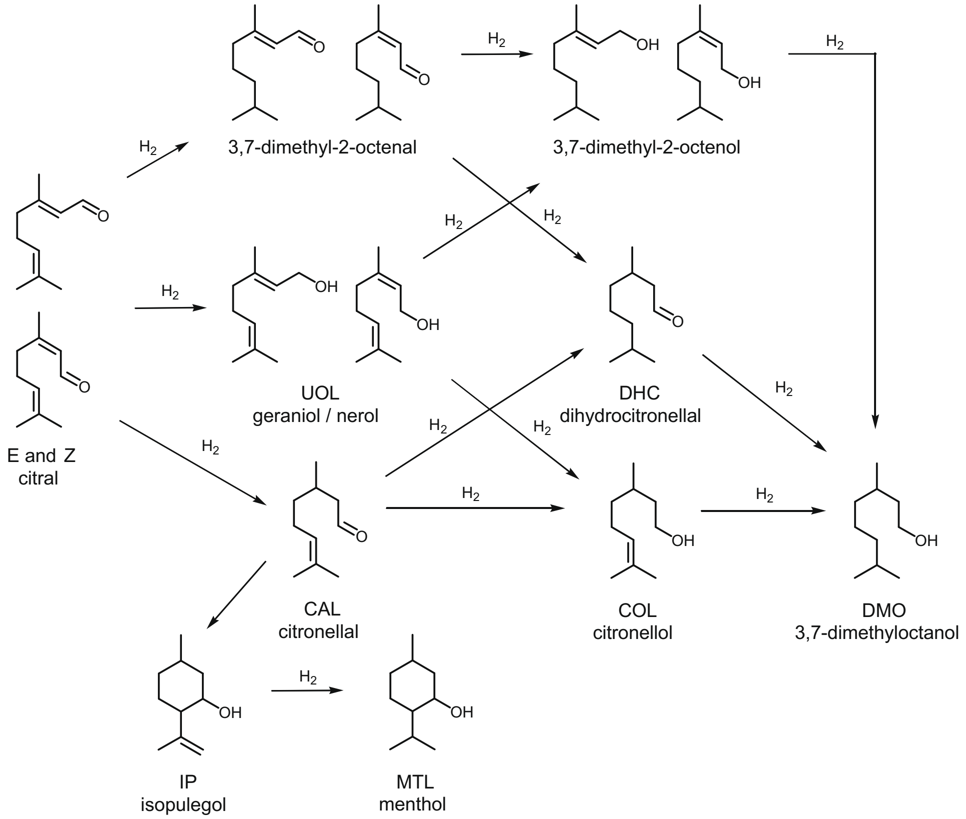

Fig. 1. Reaction network of the citral hydrogenation.

selective reduction of cinnamaldehyde over alumina supported Au catalysts. It was concluded that the higher selectivity to C=O compared to C=C arises from the higher number of d electrons of small Au clusters compared to bulk gold which promotes C=O adsorption. For both metals, Ag and Au, another effect has to be considered, namely the weaker interaction with hydrogen in comparison to conventional hydrogenation metals like Pd or Rh. It is well-known that catalysts with low hydrogen chemisorption capacities show high selectivities to unsaturated alcohol formation [2,15].

Recently, we have shown [16] that the bimetallic catalysts Rh-Sn/SiO_2 and Ag–In/SiO_2 are highly active and selective towards C=O hydrogenation of citral and comparable to technical Ru–Fe/C catalysts which need a basic additive (trimethylamine) [17].

Moreover, De Vos et al. could successfully carry out the hydrogenation of citral to geraniol/nerol with polyvinylpyrrolidone-stabilized Ag^0 nanocolloids in both alcohol and amide solvents (for example, *N*,*N*-dimethylacetamide) and thus, the high potential of silver as hydrogenation catalyst was demonstrated [18]. For the reuse of the colloids a nanofiltration techniques was used [18].

Silver(I) carboxylates of general type $[AgO_2CR]_n$, whereby n is responsible for the aggregation grade (depending on R), have been well-known for quite some time and hence, there exist a versatile number of literature regarding their synthesis, reaction chemistry, structures and ligand properties [19–21]. Recently, such compounds became of considerable interest in transition metal coordination chemistry because they can be used as representative model compounds in the fundamental study of electron-transfer and photo-induced energy-transfer processes [22–24], and offer diverse applications in the field of new materials, for example, smart system integration, including materials for micro- and nanosystems, nanostructures and devices [25–28]. In contrast, less is known about ethyleneglycol-functionalized silver(I) salts such as $[AgO_2C(CH_2OCH_2)_3H]$ [29].

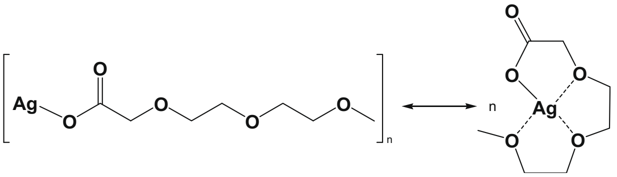

Fig. 2. Structures of $[AgO_2C(CH_2OCH_2)_3H]$ in the solid state (left) and in solution (right).

We here describe our results for the use of monometallic silver (Ag/SiO_2) catalysts in the liquid phase hydrogenation of citral. As precursors silver nitrate and, for the first time, the silver(I) carboxylate $[AgO_2C(CH_2OCH_2)_3H]$ were used.

Complex $[AgO_2C(CH_2OCH_2)_3H]$ (Fig. 2) could be synthesized by the reaction of $[AgNO_3]$ with $HO_2C(CH_2OCH_2)_3H$ in presence of triethylamine dissolved in a mixture of ethanol–acetonitrile (20:1, v/v) at room temperature. To obtain pure $[AgO_2C(CH_2OCH_2)_3H]$ it is necessary to add an excess of the carboxylic acid (Experimental).

2. Experimental

2.1. Synthesis of $[AgO_2C(CH_2OCH_2)_3H]$

To 20 g (118 mmol) of $[AgNO_3]$ dissolved in 15 mL of acetonitrile and 200 mL of ethanol was added a solution of 26.73 g (150 mmol, 23.04 mL) of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid, 13.15 mL (130 mmol) of triethylamine and 300 mL of ethanol over a period of 5 min. After 10 min of stirring the reaction solution was cooled to 0 °C, whereby the title complex $[AgO_2C(CH_2OCH_2)_3H]$ precipitated. The reaction mixture was stirred for 45 min at this temperature and was than cooled to −30 °C for 4 h. Colorless $[AgO_2C(CH_2OCH_2)_3H]$ was collected by using a