

Supported copper catalysts for hydrogen transfer reactions involving allylic alcohols

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Introduction

Oxidation of alcohols to carbonyl compounds is undoubtedly a fundamental organic transformation. To substitute the stoichiometric oxidants usually used, some catalytic approaches have been developed using molecular oxygen. However, safety problems with oxygen in organic solvents may hinder the practical application.

Catalytic transfer dehydrogenation of alcohols in anaerobic conditions appears as an attractive alternative method, potentially safe, efficient and selective, in which the alcohol is directly dehydrogenated to the corresponding aldehyde or ketone in the presence of a readily available unsaturated organic molecule (alkene) which acts as hydrogen acceptor [1].

Homogeneous complexes (Ru, Ir) have been reported, which suffer from air sensitivity or requirement of a base additive. Only few heterogeneous catalysts have been shown to be effective, and they are usually substrate sensitive [2, 3]. More specifically, the catalytic dehydrogenation of allylic alcohols such as geraniol is little reported.

In this work, Cu-catalysts on different supports were studied in geraniol dehydrogenation using styrene as H-acceptor.

Materials and Methods

The Cu supported catalysts were commercially available solids (Cu/C) or were prepared on Al₂O₃, MgO, La₂O₃CO₃, La₂O₃, hydrotalcite of Mg and Al, hydrotalcite of Mg and La, using various methods. The catalysts were characterized by XRD, and TEM. All catalysts were reduced under H₂ at 180-300 °C before catalytic tests. The catalytic performances for geraniol dehydrogenation were evaluated in 50 mL glass vessels with a reflux condenser in an oil bath at 150°C under N₂. The typical conditions were: geraniol (0.39 g, 0.1 mol/L), styrene (0.26 g, 0.1 mol/L), catalyst (0.1 g), in mesitylene (25 mL). After purging, the mixture was heated to the reaction temperature while stirring. The reaction products were analyzed by GC chromatography.

Results and Discussion

Together with the desired geranial, some by-products may be formed like nerol (by isomerization), neral (by isomerization/dehydrogenation), citronellal (CAL) (by isomerization) or citronellol (COL) (by hydrogenation), (Figure1).

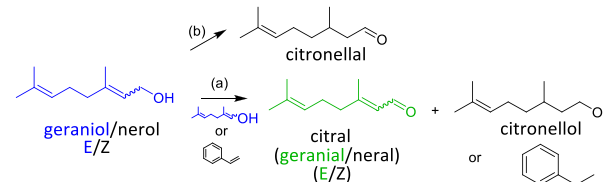


Figure 1. Possible reactions from geraniol: (a) H transfer between two geraniol molecules or between geraniol and H-acceptor, (b) isomerization.

Supported-Cu catalysts have great potential for achieving transfer dehydrogenation of geraniol to citral in the presence of styrene (Figure 2). Cu/C, Cu/Al₂O₃ and Cu/MgO were the most active catalysts but they lead to an incomplete molar balance (due to the production of deoxygenated compounds for Cu/C, cyclized products for Cu/Al₂O₃ and some non-detected compounds for Cu/MgO). The activity of the catalysts consisting in copper supported on La-containing solids was dependent on the preparation method. Cu/ HT(Mg,La) seem to be a good compromise for geraniol conversion and selectivity to citral (yield = 50 % at 97 % conversion).

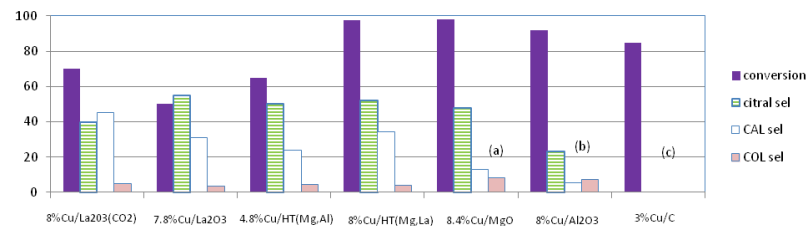


Figure 2. Catalytic performances of some Cu-catalysts. Reaction conditions: 25 mL geraniol 0.1 mol L⁻¹ in mesitylene; 1 eq. styrene, 0.1 g catalyst, 150°C, N₂, 6 h (1 h for MgO, Al₂O₃ and C).

(a) 20% molar balance loss,

(b) 20% isopulegol + 40% unknown by-products,

(c) unknown products.

Significance

Cu-catalysts supported on basic oxides showed promising results for geraniol dehydrogenation to citral when styrene was used as the hydrogen-acceptor. Selectivity towards citral > 50% at total conversion was observed over Cu/HT(Mg,La).

References

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