

Modification of catalytic properties over carbon supported Ru–Cu and Ni–Cu bimetallics

I. Functional selectivities in citral and cinnamaldehyde hydrogenation

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Abstract

Two series of bimetallic catalysts, Ru–Cu and Ni–Cu, supported on a high surface area graphite were prepared. These catalysts were characterized by TPR, H₂ chemisorption and X-ray photoelectron spectroscopy. The results obtained with these techniques indicate that for the Ru–Cu series, Ru and Cu atoms are in more intimate contact for the catalyst with lowest Cu content than for the other bimetallic catalysts belonging to this series. This conclusion was also reached when these catalysts were employed in the hydrogenation reactions of citral and cinnamaldehyde. For both substrates similar selectivity patterns were obtained over each of the Ru–Cu catalysts. As for the Ni–Cu series, characterization results proved the existence of alloy formation between Ni and Cu. When these catalysts were employed in the hydrogenations of citral and cinnamaldehyde the saturated aldehydes were the main products obtained owing to the high selectivity of Ni towards the formation of these hydrogenation products. Therefore when Cu, which is not very active in these reactions, is added significant changes in the selectivity are not observed.

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1. Introduction

The use of heterogeneous catalysts in the fine chemistry industry is expanding daily due to their unique advantages, such as its easier separation and reuse after reaction, over the homogeneous catalysts. The hydrogenation of unsaturated aldehydes to the corresponding alcohols is an important step in the preparation of various fine chemicals. However, this is still a challenge as the reduction of the C=C bond is thermodynamically favoured in comparison with that of the C=O bond.

Citral and cinnamaldehyde hydrogenations are two important reactions in the field of fine chemistry industry. Figs. 1 and 2 illustrate the main products obtained in these

reactions. A lot of studies have been carried out with both substrates (both with homogeneous and heterogeneous catalysts) in order to obtain results of industrial interest [1–5]. It is known that the choice of the adequate catalyst plays an important role in the activity and selectivity of these reactions. The nature of the active metal [6], its particle size, support [7,8] and the addition of promoters [9,10] are some examples of factors that exert influence on the performance of the catalyst. Other parameters like the solvent used have also been taken into consideration [11–13].

In the case of citral several studies have been carried out employing different active metals and we can conclude that selectivity towards the production of citronellal can be obtained with palladium [14] and nickel [15,16]. Osmium [17] and rhodium [18] give rise to the unsaturated alcohols while with the use of platinum and ruthenium the selectivity could be modified by the addition of a second metal [19–22].

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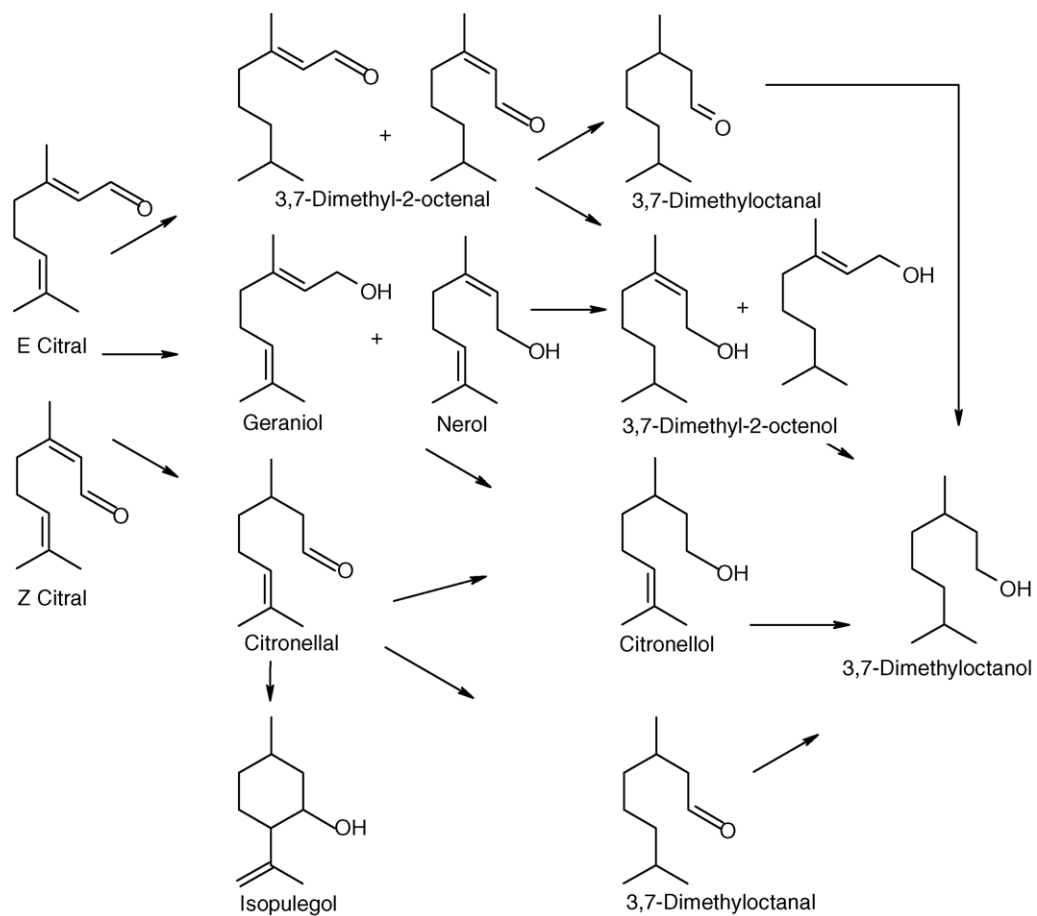


Fig. 1. Scheme of citral hydrogenation reaction.

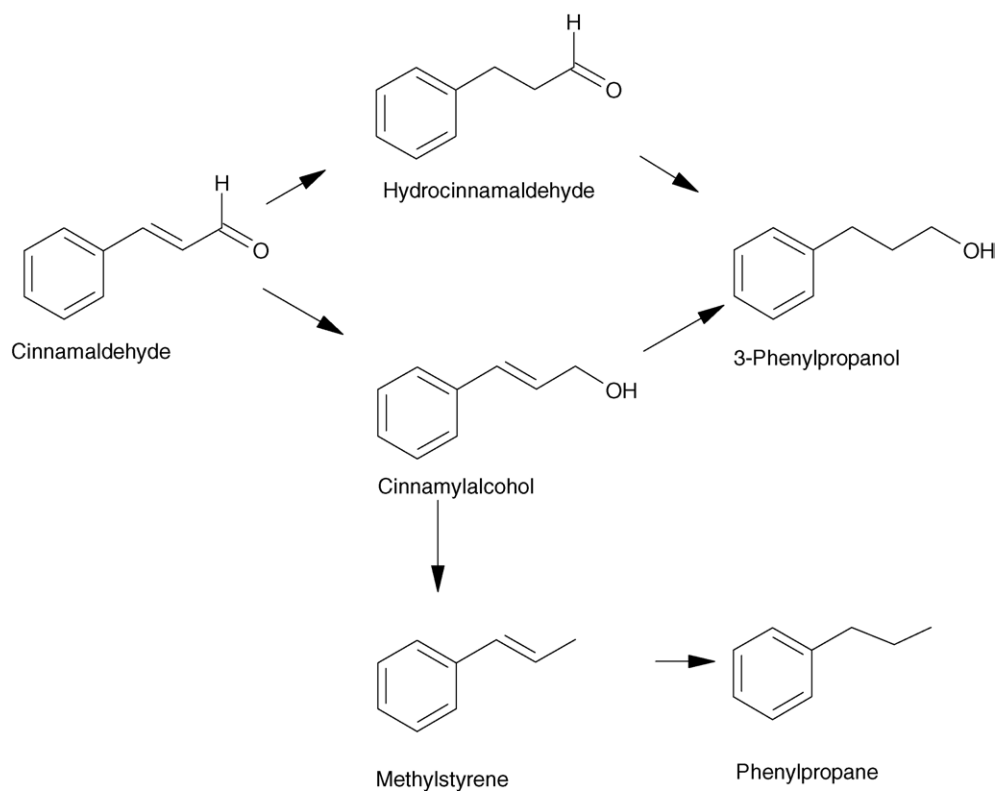


Fig. 2. Scheme of cinnamaldehyde hydrogenation reaction.

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