

Selective liquid-phase hydrogenation of citral over supported bimetallic Pt–Co catalysts

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ABSTRACT

The liquid-phase hydrogenation of citral was studied at 393 K and 10 bar on Pt–Co/C catalysts, having different Pt/(Pt + Co) ratios and containing a total metal load of about 2%. The monometallic and bimetallic Pt–Co/C catalysts were prepared by impregnation and co-impregnation, respectively, with cobalt tris(acetylacetonate) and platinum bis(acetylacetonate). Monometallic Pt/C and Co/C catalysts showed very low activity and selectivity to the desired products. Undesirable reactions, such as citral decarbonylation and hydrogenolysis, were observed with these monometallic catalysts. Instead, bimetallic Pt–Co/C proved very active and selective to geraniol/nerol and the main products detected were geraniol/nerol, citronellal and citronellol. Hydrogenation kinetic constants were determined by modeling catalytic data and using a pseudo-homogeneous kinetics. From the analysis of the kinetic parameters, an optimum Pt/(Pt + Co) ratio was found for both the catalytic activity and selectivity towards geraniol/nerol. Furthermore, it was determined that this optimum ratio depends on the activation conditions. Temperature-programmed reduction (TPR) experiments and X-ray absorption spectroscopy (XAS) demonstrated the existence of Pt–Co bimetallic compounds on the carbon support. On the basis of these results, it was proposed that cobalt improves the catalytic performance of platinum by electron transfer. This electron transfer is favored by the high interaction of both metals existing in these types of bimetallic compounds.

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1. Introduction

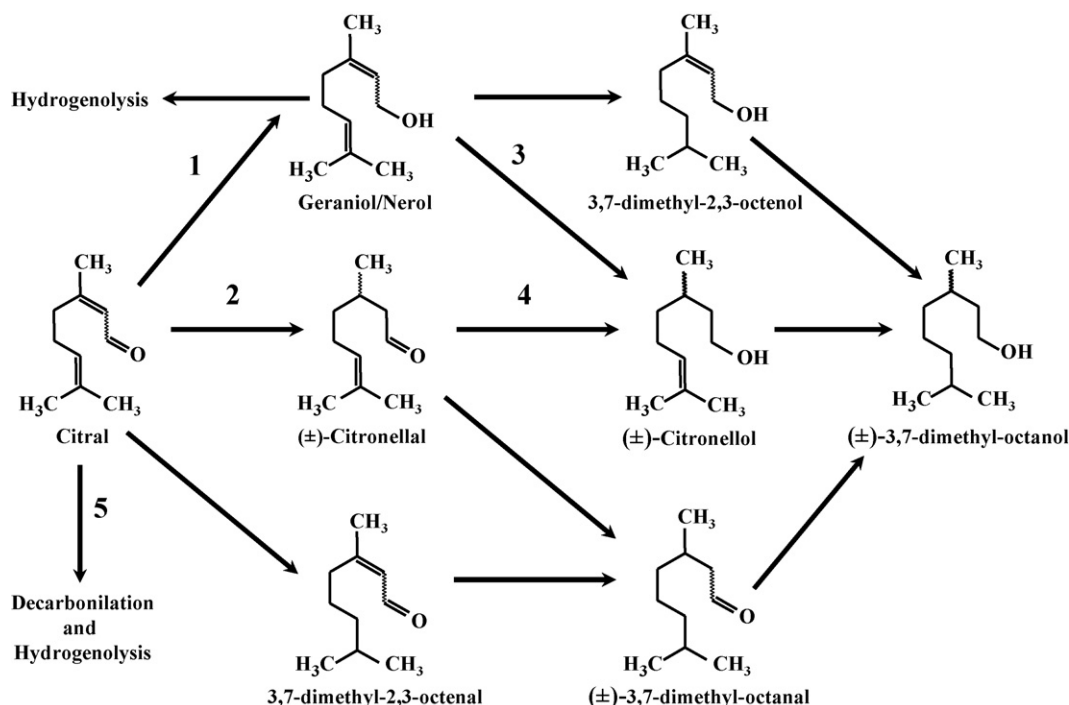
The selective hydrogenation of unsaturated α,β aldehydes to the corresponding unsaturated alcohols is of considerable interest due to the numerous applications of those alcohols in Fine Chemistry. The selective hydrogenation of citral to geraniol/nerol is of particular importance. These unsaturated alcohols are monoterpenoids that have been employed in the production of flavours, fragrances, insect repellants and in the synthesis of other compounds such as acetate and isobutyrate derivatives [1]. Other products of interest are citronellal and citronellol, used in soaps, detergents, perfumes and insect repellants [1–3]. Citronellal is also important due to its application in topical antifungal compositions for the skin [4]. Besides, it can be hydrated to hydroxycitronellal, which is widely used in fragrances due to its lily-of-the-valley aroma [1]. It can also be isomerized to isopulegol, an intermediary

product used in the synthesis of (\pm)-menthol [5–7]. It can also be used in the production of other compounds employed in fragrances, such as the citronellyl acetate. The geraniol/nerol, citronellal and citronellol mixtures, in adequate proportions, are also employed in fragrances [1], antifungal compositions [8–10], insect repellants [3], bactericide formulations [11] and microbiocidal formulations [12].

The reaction network, considering all the possible hydrogenations starting from citral, is shown in Scheme 1. The geraniol–nerol isomers are obtained by selectively hydrogenating the citral C=O functional group, while citronellal is obtained by the selective hydrogenation of the conjugated C=C bond. In turn, citronellol can be obtained by the selective hydrogenation of the citronellal C=O group or from the C=C bond of geraniol–nerol. The hydrogenation of the isolated C=C bond is not desirable since compounds such as 3,7-dimethyl-octanal and 3,7-dimethyl-octanol give an unpleasant odour to the geraniol–nerol, citronellal and citronellol mixtures.

The selective hydrogenation of citral in liquid phase has been widely studied [13]. In general, catalysts based on noble metals show low activity and/or selectivity in the hydrogenation of unsaturated α,β aldehydes. The activity and selectivity of these

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Scheme 1. Reaction network for citral hydrogenation over metal catalysts.

metals can be improved by means of special reduction techniques at low temperature [14–16], interaction of the metallic phase with special supports [17–22] and formation of bimetallic compounds [16,22–33]. In particular, Pt–Co bimetallic catalysts showed a better catalytic performance than those corresponding to Pt monometallic catalysts [16,24,33]. In the liquid-phase hydrogenation of cinnamaldehyde, it was found that Pt–Co catalysts on carbon nanotubes [16] and commercial activated charcoal [24] were more selective to cinnamic alcohol than monometallic catalysts of Pt and Co. Li et al. [16] studied the influence of the preparation method on selectivity, maintaining the Pt/(Pt + Co) ratio. Fouilloux et al. [24] presented the results obtained for different Pt/(Pt + Co) ratios, but he did not account for the high selectivity to cinnamic alcohol observed with Pt–Co bimetallic catalysts. In turn, Borgna et al. [33] studied the hydrogenation of crotonaldehyde at atmospheric pressure over Pt–Co/SiO₂ catalysts, prepared by spin-coating technique. The addition of Co increased the selectivity to crotyl alcohol up to about 25%. From the results obtained by near-edge X-ray adsorption fine structure (NEXAFS), it was proposed that the Pt catalytic performance is modified by the electron transfer from Co. Besides, it is important to bear in mind that the substituting group of the unsaturated α,β aldehyde molecule [34], the type of support, the catalyst preparation method and the reaction conditions [13], can exert a strong influence on the global activity and selectivity in the hydrogenation of this type of compounds.

In this work, we study the catalytic performance of mono-metallic and bimetallic catalysts of Pt and Co, supported over an activated carbon of high specific surface, in the selective liquid-phase hydrogenation of citral. The goal is to (1) obtain an evidence about the formation of Pt–Co bimetallic compounds; (2) determine the influence that these bimetallic compounds and the Pt/(Pt + Co) ratio have over the hydrogenation of citral in liquid phase. Based on the sample characterization and a pseudo-homogeneous kinetic study, a mechanistic model to explain the experimental results is proposed. This model was built considering both the geometrical and the electronic effect between platinum and cobalt on bimetallic samples.

2. Experimental

2.1. Catalyst preparation

Monometallic Pt/C and Co/C and bimetallic Pt–Co/C catalysts were prepared by wet impregnation and co-impregnation, respectively, employing sub-bituminous carbon of high specific surface (1300 m²/g) as support. In all the samples, the total metal load in the final catalyst was around 2%. This impregnation was carried out at room temperature for 24 h, using platinum bis(acetylacetonate), Pt(C₅H₇O₂)₂, and cobalt tris(acetylacetonate), Co(C₅H₇O₂)₃, as impregnating agents. After evaporating the solvent, the precursors obtained were dried under vacuum at 393 K. Finally, the samples were activated *ex situ* in H₂ flow (30 ml/min) at different temperatures between 423 K and 773 K, with no previous calcination, heating them from ambient temperature to reduction temperature at 2 K/min. Samples were kept at the final reduction temperature for 6 h. Mixed oxide elemental compositions were measured by absorption atomic spectrometry (AAS) and the results are shown in Table 1.

2.2. Catalyst characterization

Samples were characterized by temperature-programmed reduction (TPR) and X-ray absorption spectroscopy (XAS).

Temperature-programmed reduction experiments were carried out in a flow system equipped with a quartz microreactor, a temperature controller-programmer and a Balzers GSD 300 mass spectrometer. These experiments were performed with a heating rate of 10 K/min, passing about 30 ml/min of a H₂(5%)/Ar mixture through a dried impregnated sample bed. During programmed heating, *m/e* ratios corresponding to the more important fragments of hydrogen, carbon monoxide, carbon dioxide, water, methane, acetaldehyde and propyne were monitored and registered.

XAS measurements were performed at the Lure synchrotron center (ORSAY, France) using a beam line with an energy of 1.85 GeV. All the measurements were performed on the XAFS3

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