



Cooperation between the surface hydroxyl groups of the support and organic additives in the highly selective hydrogenation of citral

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ABSTRACT

A Ru/AlO(OH) catalyst was prepared by co-precipitation and characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermo-gravimetry (TG), and Fourier transform infrared spectroscopy (FT-IR). Its catalytic performance was tested in the selective hydrogenation of citral. The results showed that the combination of Ru/AlO(OH) and water obviously improved the catalyst activity and its selectivity to geraniol and nerol. Introducing organic additives increased the hydrophilicity of metal particles, which favoured the adsorption of the citral C=O bond over the adsorption of the conjugated C=C bond, improving the selectivity to and inhibiting the further hydrogenation of geraniol and nerol. The maximum yield of geraniol and nerol (81%) was achieved in water with ethylenediamine as an additive.

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1. Introduction

Because α,β -unsaturated alcohols are important fine chemicals and pharmaceutical intermediates, the selective hydrogenation of α,β -unsaturated aldehydes to the corresponding α,β -unsaturated alcohols has aroused significant attention. The hydrogenation of the C=O group is less thermodynamically and kinetically favoured than the hydrogenation of the conjugated C=C bond. Thus, the highly selective hydrogenation of α,β -unsaturated aldehydes to the corresponding α,β -unsaturated alcohols remains still a challenge. Generally, citral is extremely difficult to selectively hydrogenate into α,β -unsaturated alcohol. Its hydrogenation pathway in the liquid phase is shown in Scheme 1. Noble-metal-based catalysts [1–4] have been widely studied for the selective hydrogenation of citral, but they generally give low selectivities towards the specific hydrogenation of the C=O bond. In an attempt to improve the selective hydrogenation of C=O bond, significant advances were made over the past several decades in terms of selecting active metals [3–12], tuning the metal particle size [13], and introducing a second metal component [14–20]. Ru-based catalysts have been found to be more effective in the selective hydrogenation of C=O bonds than Ni, Pt, Rh, or Pd [3]. However, the selective hydrogenation of citral over supported Ru catalysts does not give satisfactory geraniol and nerol yields [3,4,7,8,10,13,17]. For instance, Galvagno et al. [13] found

that larger metal particles were more favourable for the selective hydrogenation of citral to geraniol and nerol with Ru/Al₂O₃ as catalyst but obtained a maximum yield of 25%. Zhao et al. [10] obtained a yield of 77.6% over Ru/TPP in 12 MPa of supercritical CO₂ (scCO₂). The highest yield achieved to date is 93.9%, achieved over RuFe/C in methanol/trimethylamine [21]; however, the activity of this catalyst was extremely low and required a reaction time of 400 h.

In this paper, we observed cooperation between water and the surface hydroxyl groups of the support for the selective hydrogenation of citral. Furthermore, the use of some organic additives could greatly improve the catalytic activity of this system and its selectivity to geraniol and nerol. A possible mechanism was proposed.

2. Experimental

2.1. Materials

Materials were purchased from the following suppliers: aluminium sec-butoxide (95%, packaged under argon in sealable ChemSeal bottles), Alfa Aesar; RuCl₃·xH₂O, Kuming Precious Metals (China); and activated carbon (AC), γ -Al₂O₃, and SiO₂ from Kelong Chemical Company (China). All reagents, i.e., NH₃·H₂O (AR), ethanol (AR), ethylene glycol (AR), n-butanol (AR), 1-octanol (AR), 1,3-propanediol (AR), methylamine (AR), ethylamine (AR), propylamine (AR), n-hexylamine (AR), dodecylamine (AR), ethylenediamine (AR), ethanolamine (AR), diethanolamine (AR), and 1,6-hexanediamine (AR), were used as received without further purification.

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