

ACTIVITY AND SELECTIVITY OF Pt-/SiO₂, Pt/SiO₂-ZrO₂ AND Pt/SiO₂-TiO₂ FOR THE LIQUID PHASE HYDROGENATION OF CITRAL

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Introduction

Heterogeneous catalysts play an important role in many industrial processes, such as hydrogenation. Platinum on SiO₂ is a well established catalyst in the selective hydrogenation process. Silica is a naturally occurring material in minerals, such as quartz, and in plants such as bamboo, rice and barley. The properties of silica have been extensively studied by many authors, due to its wide range of applications [1,2]. Combinations of silica with a large number of other oxides have been reported [3]. Pure ZrO₂ and TiO₂ carriers have very small specific surface area, low thermal stability and high price, which make them unsuitable for industrial applications. In order to overcome these drawbacks, increasing attentions has been paid to the development of mixed oxide supports by combining the higher surface areas and thermal stability of silica with the unique acidic properties of ZrO₂ and TiO₂ [4]. Mixed titania-silica and zirconia-silica materials are potentially useful in a number of technological applications, including catalyst. More particularly, preparation of catalyst platinum usually comprises pore-volume impregnation of the support with solutions containing the precursor species. Typically, the aim of citral hydrogenation is to maximize the yield of citronellal or citronellol, in this work we explore the possibility of selective hydrogenation of citral as a probe reaction on Pt/SiO₂-TiO₂ and Pt/SiO₂-ZrO₂ to investigate their effects on the hydrogenation activity of α , β -unsaturated aldehydes. Most studies of selective hydrogenation of α , β -unsaturated aldehydes have been carried out on supported group VIII metal catalysts by investigating the influence of different factors that promote the formation of the desirable unsaturated alcohols. Nature citral is nearly always a mixture of the two isomers. It occurs in lemongrass oil (up to 85%), and in small amounts in many other essential oils. Citral is an α , β -unsaturated aldehyde with an additional double bond, it is highly reactive and may undergo reactions such as cyclization and polymerization. Citral is very important for aroma compositions such as citrus flavors. In perfumery it can be used only in neutral media due to its tendency to undergo discoloration, oxidation and polymerization. It is used as a starting material in the synthesis of ionones and methylionones particularly β -ionone, which is an intermediate in vitamin A synthesis. The Figure 1 shows the main reaction pathways that can occur during citral hydrogenation. The reduction of citral can lead to a variety of products. A first step is the reduction of either the C=O or the conjugated C=C bond to produce geraniol and nerol or citronellal, respectively. Consecutive hydrogenation leads to citronellol and finally to 3,7-dimethyloctanol.

Materials and Methods

Mixed and supported oxides of SiO₂-ZrO₂ and SiO₂-TiO₂ were prepared by sol-gel method and calcined at 773K for 24 h prior to impregnation. The Pt catalysts were prepared with hydrogen hexachloroplatinatate (IV) hydrate (H₂PtCl₆, Aldrich 99.995%) as a precursor using the incipient wetness technique (0.5 wt % and 1 wt %). The solids were reduced in H₂ at 773K for 2 h and cooled at room temperature in flowing H₂. The liquid phase hydrogenation was carried out at atmospheric pressure in a 150 ml stirred autoclave at 343K. Pre-reduced

catalyst (1 g) was immersed into 45 ml of solvent (hexane). Then a mixture of substrate (citral) and solvent was loaded into the autoclave and the temperature was raised. Liquid samples were analyzed by gas chromatography on a Varian 3400 chromatograph provided with an FID detector and a capillary column Ultra 2 (25m, 0.20 mm i.d.) using helium as carrier gas.

Results and Discussion

Fig. 1 presents the reaction pathways that can occur during citral hydrogenation. The reduction of citral can lead to a variety of products. Since a mixture of isomers E and Z of citral has been used, the corresponding isomeric α , β -unsaturated alcohols, were obtained through the hydrogenation of the carbonyl group. The parallel route via hydrogenation of the conjugated double bond leads to the partially saturated aldehyde (citronellal). For example under the experimental conditions used in the present study, the main products observed were the unsaturated alcohols (geraniol y nerol) when Pt/SiO₂ is used. Figure 2 shows the influence of the support on the performance of Pt/SiO₂ for the hydrogenation of citral at room temperature.

Significance

We report here for the first time the hydrogenation of citral using mesoporous catalyst of Pt over silica-zirconia and silica-titania, which involves an attractive material in the synthesis of fine chemicals due to their textural and acidic properties.

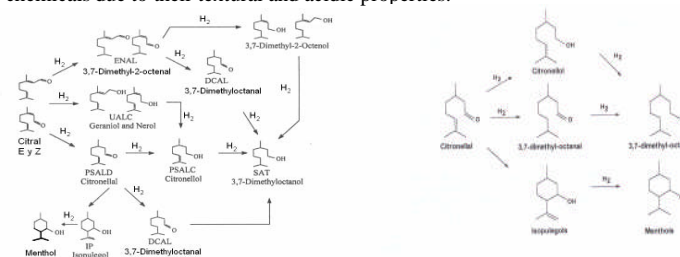


Figure 1. Scheme of the products of citral reduction A) A1:Citral (E), A2:Citral (Z), B:Citronellal, C:Citronellol, D:Dihydrocitronellal, E:3,7 dimetil-octanol F1:Geraniol, F2:Nerol, G:Isopulegol, H:Menthol.

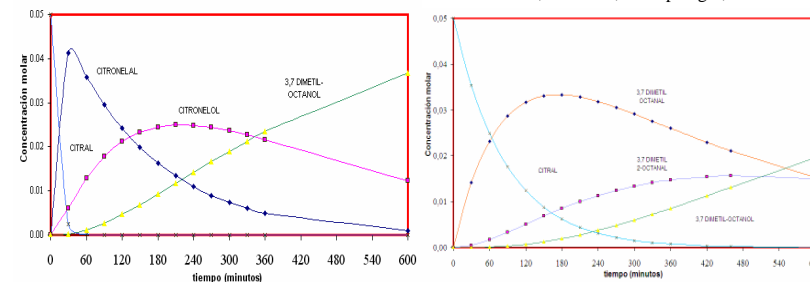


Figure 2. Hydrogenation of citral over Pt in SiO₂-ZrO₂ and SiO₂ pure.

References

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