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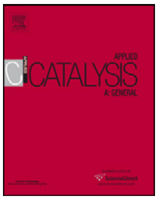

Catalytic performance in selective hydrogenation of citral of bimetallic Pt–Sn catalysts supported on $MgAl_2O_4$ and γ-Al_2O_3

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ABSTRACT

The liquid phase citral hydrogenation, using Pt and PtSn catalysts supported on $MgAl_2O_4$ and γ-Al_2O_3, was studied in a stirred reactor at 70 °C and atmospheric pressure. It was found that the addition of Sn to the Pt catalysts increases the selectivity to double unsaturated alcohols for both catalyst series. Besides, monometallic catalysts hydrogenate the α,β-unsaturation with a high selectivity in absence of cyclization secondary products. The performance of these catalysts in the citral hydrogenation was related with the characteristics of the metallic phase. Results from test reactions – cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH) – H_2 chemisorption, 2-propanol dehydration, temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS), were used to explain the influence of the support and the Sn loading and postulate the models of the catalytic metallic surface. Results indicated that, a fraction of ionic Sn would be deposited near Pt, thus increasing the polarization of the carbonyl group, and a fraction of metallic Sn could form Pt–Sn alloy phases that would hinder the hydrogenation of the olefinic bonds and would be active to the hydrogenation of the carbonyl group. Both effects contribute to a higher selectivity to unsaturated alcohols in bimetallic $PtSn/Al_2O_3$ catalysts than $PtSn/MgAl_2O_4$ ones, which display a low alloy formation.

1. Introduction

The production of α,β-unsaturated alcohols is a very interesting process since it leads to the obtention of very important intermediaries of organic synthesis used in the manufacture of allyl ethers and allyl esters, and final products for Fine Chemistry used in perfumery and pharmacy [1–4]. The selective hydrogenation of unsaturated α,β aldehydes to produce the corresponding unsaturated alcohols is a difficult reaction due to the double olefinic bonds are preferably hydrogenated, both by thermodynamic and kinetic reasons. The use of monometallic catalysts based on Pt, Pd, Ru or Ni supported on non reducible oxides [5–8] leads mainly to the formation of saturated aldehydes. In consequence a modification of the metallic phase is necessary to obtain the desirable products. In order to increase the selectivity of monometallic catalysts in the hydrogenation of carbonyl group, several studies [5,9–14] have been carried out to study the effect of the support, promoter addition, metallic particle size and solvents used in the reaction. In particular, it was found that the addition of Sn, Ge, Fe, and Ga to Pt catalysts [10,15,16] can strongly modify the catalytic properties of the metal active by the presence of geometric and/or electronic effects, which would be responsible for the increment of the selectivity to unsaturated alcohols. In this sense, the behaviour of the PtSn systems has been explained as caused by the promotion effect of oxidized species of Sn (placed near to Pt atoms) that promote the carbonyl hydrogenation [17–22]. In this case the interaction of the oxidized Sn species with the oxygen of the carbonyl group could weaken the C=O bond and hence enhance the carbonyl hydrogenation rate. However, the presence of metallic Sn was found by XPS, XRD and TEM in several studies on selective hydrogenation of unsaturated α,β aldehydes [17,20,23–30] and it was considered as an important parameter of the catalytic activity in PtSn catalysts. The metallic Sn could be forming aggregates which produce a geometric effect on the metallic phase [21,25,29]. Besides, this metallic Sn can be alloyed with Pt, thus avoiding the hydrogenation of the olefinic double bond or showing activity to the hydrogenation of the carbonyl group, and in this way it would increase the selectivity to unsaturated alcohols [17,23,26,28,30–32].

Even though there are several papers on the catalytic behaviour of mono and bimetallic catalyts based on Pt supported on Al_2O_3 [5,23,29,30,33–43] in selective hydrogenation of α,β-unsaturated aldehydes, there is practically no information on mono and bimetallic catalysts based on Pt supported on spinels [44]. Besides, it must be noted that none of these papers report the selective hydrogenation of citral (3,7-dimethyl-2,6-octadienal) to unsaturated alcohols.

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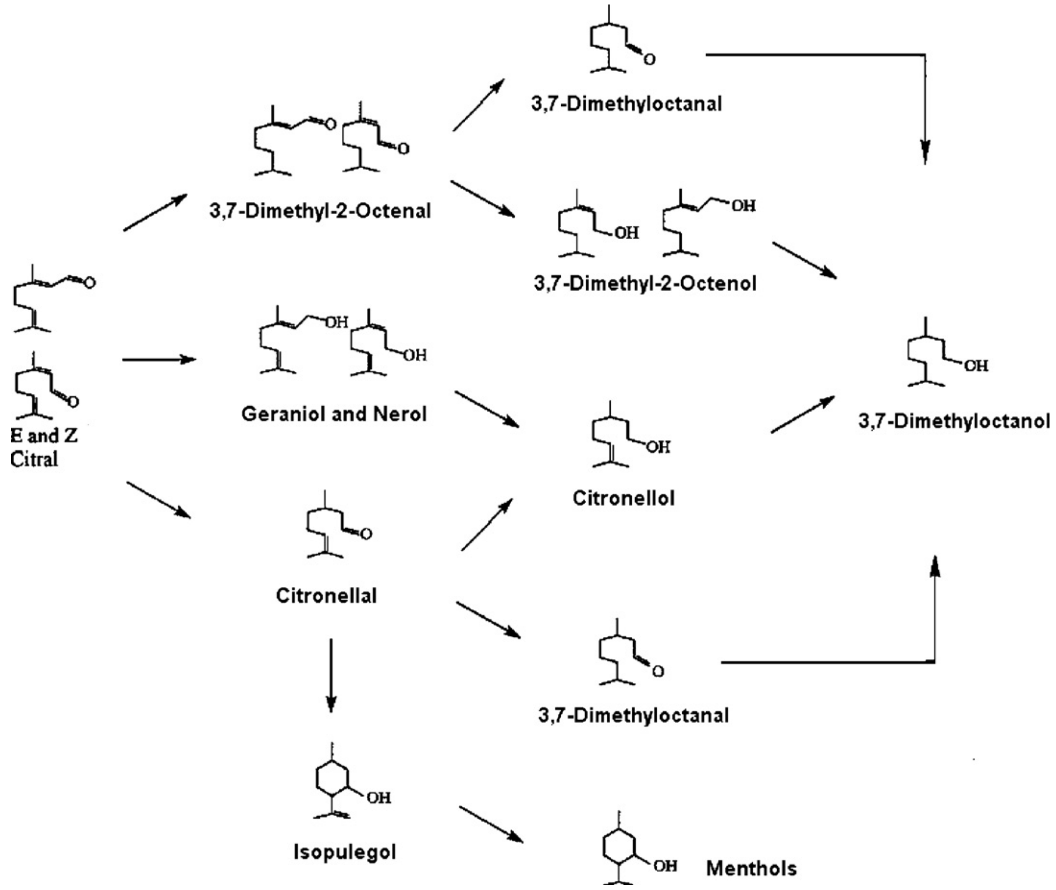

Fig. 1. Main reaction routes in citral hydrogenation.

The objective of this paper is to study the catalytic behaviour in the citral hydrogenation of Pt and PtSn catalysts supported on $MgAl_2O_4$ and Al_2O_3. In this sense the effect of the Sn amount added to a given Pt loading for both supports was investigated. The bimetallic catalysts were prepared by successive impregnation of the corresponding support. The catalysts were submitted to different characterization techniques: test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), H_2 chemisorption, temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS), and the support acidity was examined by 2-propanol dehydration. For this study the citral hydrogenation was selected, because citral is an abundant raw material from the lemongrass oil. Besides, citral is a very interesting molecule model since it has three different unsaturated bonds: a carbonyl group, a double C=C bond conjugated with the carbonyl group and one isolated –C=C– bond. It also exists as cis and trans isomers and it can also be cyclized. Fig. 1 shows the main products which can be obtained by hydrogenation and cyclization.

2. Experimental

2.1. Preparation of the catalysts

Two supports were used: (i) $MgAl_2O_4$ (obtained in the laboratory, $S_{BET} = 108\,m^2\,g^{-1}$) with a spinel structure and equilibrium pH = 8.6, and (ii) commercial γ-Al_2O_3 (CK 300 from Cyanamid Ketjen, $S_{BET} = 180\,m^2\,g^{-1}$) previously calcined at 650 °C. The first support was prepared by using the co-precipitation method [45] from solutions of $Mg(NO_3)_2 \cdot 6H_2O$ (Merck, purity 99%), $Al(NO_3)_3 \cdot 9H_2O$ (Merck, purity 98.5%) and ammonia solution (Merck, 28%, analytical grade). 0.5 M solutions of Al and Mg nitrates with a Al/Mg molar ratio = 2 were used for the preparation of the precursor by slow addition of aqueous solution of ammonia under stirring, until reaching pH = 11 at 40 °C. After its formation, the precursor gel was aged for 1 h at room temperature and then filtered. The gel was washed with an excess of distilled water (volume ratio water/gel = 4) under stirring and filtered again. Additionally, the gel was washed in the same filter paper with distilled water. Then it was dried at 120 °C overnight, and finally calcined at 800 °C for 4 h. Monometallic Pt catalysts (5 wt%) were prepared by impregnation (25 °C for 6 h) of the corresponding support with an aqueous solution of H_2PtCl_6 ($12.6\,g\,L^{-1}$), by using an impregnation volume/mass of support ratio = $4\,mL\,g^{-1}$. After impregnation the samples were dried at 120 °C overnight and then calcined at 500 °C for 3 h. The bimetallic catalysts of Pt(5 wt%)Sn(1, 2, 3 or 4 wt%)/$MgAl_2O_4$ and Pt(5 wt%)Sn(1, 2 or 3 wt%)/Al_2O_3 were prepared by successive impregnation of the monometallic ones. Thus, the precursor of the monometallic catalyst was impregnated for 6 h at room temperature with a hydrochloric solution of $SnCl_2$ by using a Sn concentration such as to obtain 1, 2, 3 or 4 wt% Sn when the support was $MgAl_2O_4$ and 1, 2 or 3 wt% when the support was Al_2O_3. It was used a volume of impregnation/mass of support ratio of $1.4\,mL\,g^{-1}$ for catalysts with 1 and 2% of Sn. The impregnating volume/support weight ratios were 2 and $3\,mL\,g^{-1}$ for 3 and 4 wt% Sn loading, respectively. Finally the samples were dried at 120 °C overnight and then calcined at 500 °C for 3 h.

2.2. Hydrogenation of citral

The different catalysts were tested in the citral hydrogenation at 70 °C and atmospheric pressure in a discontinuous reactor with a device for sampling the reaction products. In each experiments