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Ga and In promoters in bimetallic Pt based catalysts to improve the performance in the selective hydrogenation of citral

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ABSTRACT

In this paper, bimetallic PtGa and PtIn catalysts supported on multiwall carbon nanotubes and carbon Vulcan were used to study the hydrogenation of citral (α,β-unsaturated aldehyde) in liquid phase to produce nerol and geraniol (unsaturated alcohols, UA). The catalysts were prepared with different metallic loadings by conventional impregnation. All the catalysts contained a Pt loading of 5 wt%. Once reduced under hydrogen flow, the supported catalysts were characterized by test reactions of the metallic phase, H_2 chemisorption, temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Hydrogenation results showed that the addition of a second metal to Pt leads to important modifications of the selectivity to UA. The highest selectivities to UA were reached with different promoter/Pt atomic ratios for Ga and In. The catalyst performances in the citral hydrogenation were related to the characteristics of each supported bimetallic phase. It was found that the PtGa catalysts have a typical behavior of an ionic promoter together with a contribution of the Ga reduced species, reaching high selectivities to UA. On the other hand, PtIn catalysts with a metallic phase composed mainly by zerovalent In species in contact with the metallic phase, also showed high activities and selectivities to UA. The best selectivity value to UA (about 97%) was found for PtIn(2.5 wt%)/CN-P catalyst with an excellent activity.

1. Introduction

Citral is an α,β-unsaturated aldehyde which contains two double conjugated bonds (one carbonyl group and one double bond conjugated with that group), and an isolated double bond. These characteristics make citral an interesting model molecule to study selective hydrogenation reactions, from a scientific point of view to an industrial one [1]. This reaction is a very important one mainly for the preparation of different fine chemicals, for example menthol which is obtained via cyclization and has several uses in pharmaceutical industries [2]. Besides, fine chemicals such as unsaturated alcohols obtained from the citral hydrogenation are intermediary materials for the development of perfumes, flavors and pharmaceutical products [3].

Heterogeneous catalysts have several advantages with respect to homogeneous ones, such as easy separation, handling and recycling of the catalyst. An efficient strategy is to graduate the selectivity using a catalyst of specific characteristics [4]. In fine chemical industry, catalysts based on precious metals and supported on carbonaceous materials are frequently used, giving excellent performances in hydrogenation reactions [5]. However, bimetallic catalysts based on Pt with some p-block metals as promoters (In, Ga) were rarely studied.

Good selectivities to unsaturated alcohols in α,β-unsaturated aldehydes hydrogenation reactions were found using PtSn catalysts supported on different materials [6,7]. In this case the interaction of the ionic Sn species with the oxygen of the carbonyl group could weaken the C=O bond and enhance the carbonyl hydrogenation rate. Besides, it is possible that the presence of metal alloys or a strong metal–promoter interaction leads to an increase of the Pt electron density decreasing the adsorption of the C=C bond. This fact would favor the interaction with the carbonyl group [8,9].

It is known that microporous carbons are normally employed as supports of active metals for the preparation of catalysts to be used in selective hydrogenation reactions, but the use of mesoporous carbons (with lower specific surface area) has been scarcely explored in the literature. In fact few papers about the use of

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Table 1
Surface area (S_{BET}), pore volume (V_{pore}) and isoelectric points (pI) of carbon Vulcan (CV) and carbon nanotubes after purification (CN-P) [9].

Support	S_{BET} ($m^2 g^{-1}$)	V_{pore} ($cm^3 g^{-1}$)	pI
CV	240	0.36	7.4
CN-P	179	0.39	4.7

carbon Vulcan and nanotubes as supports of metals in the selective hydrogenation of citral have been reported [10–13]. Thus, the scientific information about selective hydrogenation of α,β-unsaturated aldehydes using catalysts supported on carbon Vulcan is scarce. Moreover, there are not complete studies about bimetallic catalysts supported on carbon nanotubes. It is known that PtSn catalysts supported on these materials lead to a very high selectivity to unsaturated alcohols (UA: nerol + geraniol) with a very good activity [9]. Other p-block metals, such as Ga and In, are commonly used as promoters in other reactions such as dehydrogenation ones [14–17]. Besides, Ga addition to Pt leads to an important promotion effect in some selective hydrogenation reactions [18–20], but there are no studies of the PtIn couple for the selective hydrogenation of α,β-unsaturated aldehydes. The interaction between the active metal (Pt) and the promoters (Ga or In) is not well-known, so it is not possible to know how these two metals interact to give a favorable promoter effect. Therefore, the characterization and determination of the catalytic behavior of these catalysts would be of great interest. In this paper, PtGa and PtIn bimetallic catalysts supported on two types of carbonaceous materials (carbon Vulcan and multiwall carbon nanotubes) were studied by using different loading of the promoters and evaluated in selective hydrogenation of citral. This work seeks to achieve high production of unsaturated alcohols (geraniol and nerol) from citral hydrogenation, with excellent selectivities to UA.

2. Experimental

Two commercial carbonaceous supports were selected: (i) carbon black Vulcan XC-72 (granular carbon from Cabot Corp., purity >99%), which was called CV; (ii) multiwall carbon nanotubes (MWCN from Sunnano, purity >90%, diameter 10–30 nm, length 1–10 μm), which were called CN. Carbon Vulcan was used in its original form because its impurity levels were very low (0.45%). On the other hand, carbon nanotubes were purified in order to eliminate impurities (about 6%), such as metals and other compounds, that could be negative for the final catalyst. Purified carbon nanotubes were called CN-P. The impurity levels of the supports were determined by EDX and the experimental details of the purification process were given in a previous work [9].

Both supports were previously characterized in order to know their textural properties (S_{BET} and V_{pore}) and their acid character (isoelectric point, pI). These results were reported in a previous work [9] and are shown in Table 1. It was found that the supports present quite similar textural properties, but their acid character, determined by titration, was different. In spite of this, both carbon nanotubes and carbon Vulcan show an amphoteric behavior and display a very good adsorption of the metals during the impregnation step [9,21].

All the bimetallic catalysts were prepared by successive impregnation of the corresponding monometallic ones. Thus, monometallic catalysts were prepared by conventional impregnation of the corresponding support with an aqueous solution of H_2PtCl_6 (Johnson Matthey Inc.) at 25 °C for 6 h. In all cases, the Pt amount used for the impregnation was the appropriate to obtain a Pt content of 5 wt%. In order to achieve uniform contact between the solid and the impregnating solution, a stirring rate of 250 rpm was used and the impregnating volume/support weight ratio was 30 mL g^{-1}. The excess of solution was evaporated at low temperature after impregnation until a paste was formed. Then, the samples were dried overnight at 120 °C and then they were crushed to a powder.

PtGa and PtIn bimetallic catalysts over both supports were prepared by the impregnation of the monometallic Pt one with the corresponding precursor ($Ga(NO_3)_3$, Sigma–Aldrich 99.9% and $In(NO_3)_3$, Alfa Aesar 99.9%) using the same conditions mentioned above for monometallic catalysts. Thus, each portion of monometallic catalyst was impregnated to obtain the corresponding loadings of the second metal (Ga: 0.6, 1.8, 3.12 wt% and In: 0.97, 1.94, 2.5, 2.95 wt%). Finally, all samples were dried overnight at 120 °C and then crushed to a powder. After conventional impregnation, all catalysts were reduced at 350 °C under hydrogen flow for 3 h. In the same way, the monometallic Ga and In catalysts were prepared by conventional impregnation of the supports with the corresponding precursors.

Additionally, some selected catalysts were submitted to further thermal treatment in order to induce sinterization and/or modification of the metallic phase [21]. The thermal treatment was applied after the reduction treatment mentioned before. It consisted on maintaining the selected samples under nitrogen flow at 700 °C for 12 h. These catalysts were referred in the text by the denomination of the corresponding catalysts followed by $—N_2$. Table 2 shows the sample compositions according to the preparation method of the catalysts.

Two test reactions were selected to study the metallic phase of catalytic samples: cyclohexane dehydrogenation (CHD) [22] and cyclopentane hydrogenolysis (CPH) [23,24]. They were performed in a differential continuous flow reactor at 250 and 350 °C, respectively. In both reactions the catalysts were previously reduced “in situ” under H_2 flow at 350 °C for 3 h. The experiments were performed by using H_2/CH and H_2/CP molar ratios equal to 26 and 29, respectively, and a volumetric flow of 600 mL H_2 min^{-1} in both reactions. The catalyst weight used in these test reaction experiments was such as to obtain a conversion lower than 5%, since under these conditions the behavior of the reactor follows a differential flow reactor model that allows the correct measurement of the initial rate and activation energy. The reaction products and the remaining reactants were analyzed by using a gas chromatographic system. The activation energy values for CHD (Ea_{CH}) were calculated by linear regression using the reaction rates measured at three temperatures (250, 240 and 230 °C) and the Arrhenius plot (ln R^0_{CH} vs. $1/T$ (K^{-1})).

The H_2 chemisorption measurements were carried out in a volumetric equipment. The sample weight used in the experiments was 200 mg. All the catalysts were previously reduced in H_2 at 350 °C for 3 h, then outgassed under high vacuum (10^{-5} T). The H_2 adsorption isotherms were performed at room temperature between 25 and 100 T. The isotherms were linear in the range of used pressures and the H_2 chemisorption capacity was calculated by extrapolation of the isotherms to zero pressure [25].

Temperature programmed reduction (TPR) experiments were performed using a reductive mixture of H_2 (5%, v/v)–N_2 with a flow rate of 9 mL min^{-1} in a flow reactor and a sample weight of 200 mg. Samples were heated at 6 °C min^{-1} from 25 up to 800 °C. The exit of the flow reactor was connected to a TCD (thermal conductivity detector) in order to obtain the TPR signal. Before TPR experiments, the dried samples were stabilized with N_2 at room temperature for 1 h.

XPS determinations were carried out in a Multitechnic Specs photoemission electron spectrometer equipped with an X-ray source Mg/Al and a hemispherical analyzer PHOIBOS 150 in the fixed analyzer transmission mode (FAT). The spectrometer operates with an energy power of 100 eV and the spectra were obtained with