CROTONALDEHYDE HYDROGENATION OVER BIMETALLIC Pt-Sn CATALYSTS SUPPORTED ON PREGRAPHITIZED CARBON BLACK

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INTRODUCTION

Unsaturated alcohols form a very important group of compounds for the chemical industry, especially for the synthesis of fine chemicals. Hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols is not easy. It is best achieved by using carbon-supported iridium or osmium catalysts; monometallic platinum catalysts usually produce the hydrogenation of the C=C bond instead of the carbonyl bond, and it is necessary to promote the metal to obtain a certain selectivity towards the desired unsaturated alcohol. Support effects [1,2] and addition of a second metal such as tin [3], iron [4] or nickel [5] have been claimed to improve the selectivity of platinum catalysts towards the hydrogenation of the carbonyl bond. Thus, we have recently shown that the use of an activated carbon support containing oxygen surface groups enhances the selectivity towards crotyl alcohol in the gas phase hydrogenation of crotonaldehyde [2]. Also, nylon-supported platinum-tin catalysts have been used in the selective hydrogenation of α,β-unsaturated aldehydes carried out in the liquid phase [3]. In these studies, it has been observed that tin promotes the selective hydrogenation of the carbonyl bond, thus increasing the yield of the unsaturated alcohol.

This communication reports the results obtained on the effect of tin addition on the surface characteristics, and catalytic properties, of platinum supported on a carbonaceous material in the gas phase hydrogenation of crotonaldehyde, at atmospheric pressure.

EXPERIMENTAL

The support was a pregraphitized carbon black prepared from a furnace carbon black (CC-40-220, from Columbian Chemical Co.) by heat treatment in flowing helium at 2273 K for 1 h. It had a BET surface area (N_2, 77 K) of 212 m^2g^{-1} and a micropore volume (CO_2 273 K, Dubinin-Radushkevich) of 0.03 cm^3g^{-1}.

One monometallic Pt/C and three bimetallic Pt-Sn/C catalysts were prepared by first impregnating the support with an aqueous solution of H_2PtCl_6 with the appropriate concentration to obtain a Pt loading of 1 wt% Pt. After drying, the bimetallic catalysts were prepared by impregnation of Pt/C with acidic aqueous solutions of $SnCl_2$ in different concentrations to achieve nominal tin loadings of 0.25, 0.5 and 0.75 wt% (Series B). Three more bimetallic catalysts were prepared by successive impregnations, but reversing the order of precursor addition (i.e. by first introducing $SnCl_2$) (Series C); finally, three samples were obtained by coimpregnation with ethanolic solutions of H_2PtCl_6 and $SnCl_2$ (Series A).

The platinum dispersion was determined by hydrogen and carbon monoxide chemisorption at room temperature, after reduction in flowing hydrogen at 523 K for 12 h. The chemical state of platinum and tin, both in the fresh and reduced catalysts, was studied by X-Ray Photoelectron Spectroscopy (XPS). The catalytic behaviour in the title reaction and in benzene hydrogenation was determined in a glass microreactor at atmospheric pressure and under differential conditions; the reaction products were analyzed by gas chromatography.

RESULTS AND DISCUSSION

The results obtained in the H_2chemisorption measurements at room temperature are plotted in Figure 1. It can be seen that the addition of tin greatly affects the chemisorption capacity of the catalysts, irrespective of the preparation method. These results correlate well with the catalytic activities for benzene hydrogenation at 323 K, which decreases as the amount of tin in the catalyst increases, although the loss of activity is more pronounced, for catalysts with Sn/Pt $\geq$ 0.8, than expected from the chemisorption data.

Formation of metallic tin upon reduction has been evidenced by XPS analysis. Platinum reduction is complete, but a certain amount of oxidized tin remains along with metallic tin, the relative ratio between them depending on the Sn/Pt ratio in the catalyst.

The catalytic activity in the gas phase hydrogenation of crotonaldehyde at 343 K depends both on the Sn/Pt ratio and on the preparation method. There is a maximum in activity for low and medium tin contents, irrespective of the preparation method. When catalysts with the same Sn/Pt ratio but prepared in different ways are compared, the highest activity is obtained by using successive impregnations, adding the tin precursor in the first place.

The selectivities of the different catalysts towards the formation of the unsaturated alcohol (crotyl alcohol) are plotted in Figure 2 as a function of the Sn/Pt atomic ratio. The formation of the unsaturated alcohol increases as the amount of tin increases. Catalysts prepared by succesive impregnations, adding first the tin precursor and then the Pt one, show the highest selectivity, acheiving up to 60% crotyl alcohol with the highest tin loading catalyst.

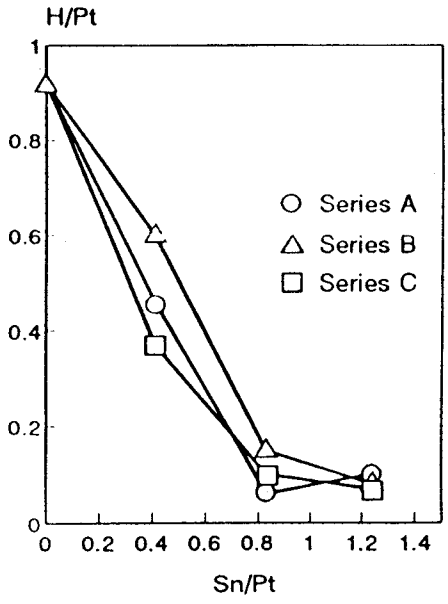

Figure 1. Hydrogen chemisorption at 298 K.

CONCLUSIONS

The addition of tin to carbon-supported platinum catalysts modifies the catalytic properties of platinum. The effect depends on both the preparation method and the Sn/Pt ratio in the catalyst. High tin loadings favour the selective attack on the carbonyl bond in the gas phase hydrogenation of crotonaldehyde, resulting in an enhanced production of the unsaturated alcohol. This can be explained on the grounds of an appropriate surface chemistry of the catalyst, including the presence of oxidized tin species sourrounding metallic platinum, and/or Pt-Sn alloys.

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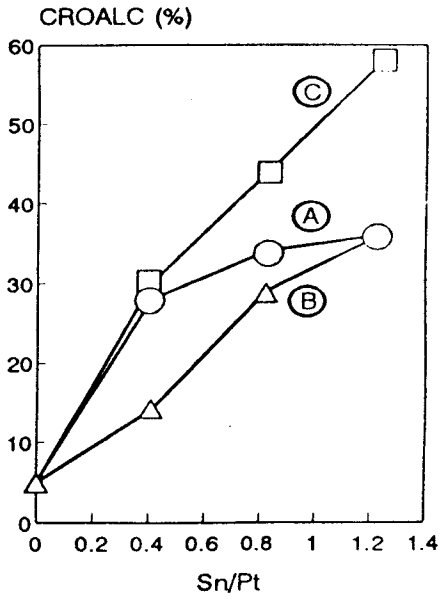

Figure 2. Crotonaldehyde hydrogenation at 343 K. Selectivity towards crotyl alcohol as a function of tin content in catalysts.