

BIMETALLIC PT-ZN CATALYSTS SUPPORTED ON ACTIVATED CARBON

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Introduction

The modification of the catalytic behavior of a noble metal through the addition of a second non-active metal able to form alloy phases or intermetallic compounds with the former is an interesting field in heterogeneous catalysis. As an example, the platinum-tin system supported on alumina is widely used in naphtha reforming and alkane dehydrogenation reactions, where it shows higher activity and stability than the monometallic platinum catalysts [1]. Other important applications of bimetallic Pt-Sn catalysts include the dehydrogenation of light alkanes [2], the oxidation of carbon monoxide [3] and the selective hydrogenation of α,β -unsaturated aldehydes (acrolein, crotonaldehyde, etc.) to yield saturated alcohols [4,5]. For this latter reaction it has been shown that the catalytic performance depends on the Sn/Pt atomic ratio, the preparation method and, mostly, on the interaction between platinum and tin species, both in the metallic and in oxidized states.

The Pt-Zn system resembles in some aspects the Pt-Sn system. Platinum and zinc can also form alloy phases of different stoichiometries (PtZn, Pt₃Zn, among others). In fact, promising results have been obtained with bimetallic Pt-Zn catalysts in reactions such as selective hydrogenation [6]. This communication reports the preparation, characterization and catalytic performance of bimetallic Pt-Zn catalysts with high zinc content supported on activated carbon. Carbonaceous materials are being more and more frequently used as catalyst supports; besides the beneficial contribution of their high surface area, their chemical inertness favors the interaction between the two metallic phases in bimetallic systems as the one under study.

Experimental

The support was a commercial activated carbon (Norit RX-3, from Norit) with a BET surface area (N₂, 77 K) of 1350 m²·g⁻¹. Three bimetallic Pt-Zn catalysts were prepared by sequential impregnation. Firstly, the support was impregnated with an aqueous solution of zinc (II) nitrate; samples with nominal contents of 1, 3, and 5 wt% Zn were prepared. After drying, a second impregnation was carried out with an acetone solution of H₂PtCl₆ of the appropriate concentration to load 0.5 wt% Pt. A monometallic Pt catalyst was prepared in a similar way for the sake of comparison.

The catalysts were characterized by temperature-programmed reduction (TPR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy (AES) after *in situ* reduction at different temperatures. The effects of the Zn/Pt atomic ratio and of the reduction treatments on their catalytic behavior have been studied in the vapor phase hydrogenation of crotonaldehyde (2-butenal), as well as in iso-butane dehydrogenation to iso-butene.

Results and Discussion

The TPR profiles show much higher hydrogen consumption for the bimetallic catalysts, what is assigned to the reduction of zinc (II) species. This reduction takes place in two stages (at about 530 K and at 800 K), this indicating the presence of isolated Zn species which are reduced at high temperature, together with other species in close interaction with Pt, which favors their reduction at lower temperatures. These results correlate with those obtained by Auger spectroscopy, which show that a given amount of Zn is already reduced after the treatment at 523 K. The presence of these metallic Zn particles close to platinum centers makes likely the formation of Pt-Zn alloy particles, with a distinctive catalytic behavior.

The results obtained in the vapor phase hydrogenation of crotonaldehyde over the bimetallic catalysts indicate an important effect of the presence of zinc and of the Zn/Pt ratio. The reaction has been studied at 353 K, with the catalysts reduced at 773 K. Under these conditions, the catalyst with 1wt% Zn shows the highest initial activity, $810 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{gPt}^{-1}$. The monometallic Pt catalyst and also the other bimetallic samples show initial activities of about $450 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{gPt}^{-1}$. However, the most active catalyst is also the one with the highest deactivation rate, in such a way that after 60 min on stream its catalytic activity had decreased to $200 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{gPt}^{-1}$ whereas that of the Pt/C sample remained at about $310 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{gPt}^{-1}$. Thus, although more active sites have been created by the presence of Zn, they are also quickly deactivated under the reaction conditions.

Crotonaldehyde hydrogenation can yield different products as a function of the preferential hydrogenation of the C=C bond (butanal) or of the C=O bond (crotyl alcohol). Also, the hydrogenation can go further to butanol or even light hydrocarbons. Thus, selectivity becomes an important item in the study and development of catalysts for this reaction. In this way, results obtained with the bimetallic PtZn/C catalysts have shown that the presence of Zn increases the catalytic selectivity towards the preferential hydrogenation of the carbonyl bond to yield the unsaturated alcohol (crotyl alcohol), which is the desired product from the industrial point of view. Whereas the monometallic Pt/C catalyst produces only butanal (hydrogenation of the C=C bond), the selectivity to crotyl alcohol increases up to 24 % for the bimetallic catalysts. These results can be explained by the beneficial effect of the Pt-Zn interaction, with the creation of new sites able to promote the hydrogenation of the C=O double bond.

The bimetallic PtZn/C catalysts have been also tested in iso-butane dehydrogenation to yield iso-butene. The beneficial effect of Zn on the catalytic behavior has been also

evidenced, as the bimetallic catalysts showed less deactivation and a nearly complete (100%) selectivity to the desired product.

Conclusions

The results reported in this communication indicate that presence of Zn strongly modifies the catalytic behavior of platinum in bimetallic PtZn catalyst supported on activated carbon. For the selective hydrogenation of crotonaldehyde, the bimetallic catalysts contain new catalytic centers that are more active and selective towards the hydrogenation of the carbonyl bond to yield the unsaturated alcohol. For iso-butane dehydrogenation, the bimetallic catalysts are more resistant to deactivation and also more selective towards the production of iso-butene than the monometallic Pt/C catalyst. These results can be explained on the basis of a strong interaction between metallic Pt and Zn centers, which may form alloy phases. This interaction is favored by the use of an inert support as activated carbon.

References

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