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Effect of the sequence of impregnation on the activity and sulfur resistance of Pt–Ni/γ-Al_2O_3 bimetallic catalysts for the selective hydrogenation of styrene

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ABSTRACT

The influence of the preparation of bimetallic Pt–Ni catalysts on their activity and sulfur resistance during styrene semi-hydrogenation was studied. The preparation variables assessed were the sequence of impregnation and the kind of nickel precursor used. The catalysts were tested with the styrene hydrogenation reaction and further characterized by ICP, TPR, XPS and pyridine TPD.

All catalysts showed high selectivities to ethylbenzene (>98%). The bimetallic catalysts were more active than monometallic Pt and the following activity order was found: Pt ≅ NiClPt ≤ NiNPt < PtNiCl < PtNiN. After poisoning with 300 ppm of thiophene the following order of sulfur resistance was found: PtNiCl < Pt ≪ PtNiN ≅ NiClPt ≅ NiNPt.

Differences in activity and sulfur resistance between the catalysts were attributed to electronic effects, in turn related to the presence of different electron-rich and electron-deficient surface species of Pt and Ni interacting between themselves and with the support. The bimetallic catalyst with the highest Cl/Pt atomic ratio on the surface (as obtained by XPS) proved to be the most sulfur resistant; this higher poison resistance was rationalized in terms of both steric and electronic effects.

1. Introduction

The reactions of selective hydrogenation of vinyllic bonds that keep unaltered the aromatic ring and that proceed through heterogeneous catalysis are of great interest and usefulness for the petrochemical, fine chemistry and specialty chemicals industries.

Benzene, toluene and xylenes, commonly known as the BTX fraction, are useful solvents and intermediate. One important source of BTX in the cracking of different petroleum cuts [1–3]. These streams can have up to 1000 ppm of sulfur compounds, thiophene being among the most common ones [1,2]. These sulfur compounds are the main cause of the loss of activity and selectivity of metal catalysts in several refinery processes [4,5].

In the petrochemical industry gasoline and BTX streams coming from the cracking of petroleum cuts must be purified in order to minimize the concentration of olefins and diolefins. The widespread method of purification is the selective hydrogenation of vinyllic compounds, keeping the aromatic rings unaltered [6–8]. The employed catalysts must have a great resistance to different sulfur compounds. A particular type of supported catalysts is that of the highly dispersed bimetallic catalysts, that have properties clearly different from those of the monometallic catalysts [9]. They have a higher activity and selectivity and a greater resistance to the poisoning by sulfur compounds. Many studies on bimetallic catalysts for selective hydrogenation have been performed using both surface characterization techniques and catalytic activity/selectivity tests [9–11]. The greater part of these studies has involved bimetallic catalysts in reactions of selective hydrogenation of hydrocarbons of low molecular mass.

In recent works our group has studied the effect of the precursor salt and the temperature of reduction on the activity and poison resistance of monometallic catalysts for the selective hydrogenation of styrene [12,13]. The objective of this work is to extend this research to the reaction system of the bimetallic Pt–Ni/γ-alumina catalyst and the model feedstock of styrene contaminated with thiophene. The preparation parameters varied are the kind of nickel precursors and the sequence of impregnation of the metal salts. Properties especially assessed are the activity, selectivity and sulfur resistance.

2. Experimental

2.1. Catalysts preparation

Bimetallic catalysts were prepared by means of successive impregnations over a previously calcined γ-Al_2O_3 support

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