Effect of Al and Si in Pt-supported TiO2 on the Competitive Hydrogenation of Benzene and Toluene

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Introduction
It has been demonstrated that the structural and catalytic properties of TiO2 can be modified by the addition of cations [1-3]. The acidity of TiO2 is increased adding small quantities of Al or Si and thereby a promoting effect in the catalytic activity of these materials is observed [1,2]. The improving of the acidity in TiO2-Al2O3 and TiO2-SiO2 mixed oxides has been related to the charge balance between the promoter (Al or Si) and TiO2, and the valence and coordination of promoter have an important role in the promoting effect [2]. On the other hand, the deposition of metals on mixed oxides supports has been used to improve the catalytic performance of the supported active phase. As mentioned above, the physicochemical properties of TiO2 can be modified by the addition of cations to the support, and the catalytic performance of metal supported on TiO2-based mixed oxides would be modified due to the changes in both the metal-support charge transfer and Strong metal-Support Interaction (SMSI) as a function on the nature and content of promoter [3].

In this work, we present a study of the catalytic performance of Pt catalysts supported on TiO2-Al2O3 and TiO2-SiO2 mixed oxides to observed the effect of type and content of promoter cation (Al or Si) in the activity and selectivity on the competitive hydrogenation of benzene and toluene (CHBT).

Materials and Methods

TiO2-Al2O3 and TiO2-SiO2 mixed oxides were synthesized by the sol-gel method. Aluminum tri-sec-butoxide (Aldrich), tetraethyl-ortho-silicate (Aldrich) and titanium butoxide (Aldrich) were diluted in 2-propanol (Baker) in amounts necessary to formulate 1% wt, 3% wt and 10% wt of Al2O3 or SiO2, respectively. The gels were dried at room temperature and the xerogels calcined at 500°C. The Pt catalysts were prepared by wet impregnation with a solution of H2PtCl6 (Aldrich) and calcined at 500°C. The CHBT was carried out in a flow reactor with 50 mg of catalyst reduced at 300°C and 500°C, the reaction temperature was 150°C and the reactor-feed was a mix of hydrogen flows saturated with benzene and toluene. The hydrocarbon composition was controlled by the use of mass-flow meters (Omega). The composition of reaction products was analyzed by GC (Varian 3400).

Results and Discussion

The effect of promoter content and reduction temperature in the kinetic constants per active site in CHBT is shown in Figure 1. Inhibition in the hydrogenation activity of benzene and toluene is observed for Pt/TiO2-Al2O3 catalysts at TRED=300°C as the Al content is increased. This result shows that the addition of Al in support modifies the catalytic performance of Pt, which can be related to changes in the charge transfer between metal and support by the presence of Al. The activity for the Pt/TiO2 catalysts at TRED=500°C is lower than the same catalysts reduced at 300°C due to the SMSI, and the catalytic activity is improved as the Al content increases. Inhibition or promotion of hydrogenation activity is observed for PtTiO2-SiO2 catalysts as a function of the Si contents and reduction temperature. However, the promoting or inhibiting effects of Si are different from those observed for Al-promoted catalysts, showing that the interaction between the TiO2 and promoter depends to the properties of the cation (Al or Si). These results are indicative that both SMSI and metal-support charge transfer can be modified by the presence of cations in the TiO2-based supports.

Significance
The aim of this work is contribute to understand the promoting effects of cations in the TiO2-based supports in hydrogenation catalysis.

References