

One pot preparation of NiO/ZrO₂ sulfated catalysts and its evaluation for the isobutene oligomerization

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Abstract

The synthesis of NiO/ZrO₂ sulfated catalysts prepared by the one pot method (sol–gel) is reported. Specific surface areas comprised between 52 and 108 m²/g were obtained. XRD patterns showed the presence of monoclinic and tetragonal zirconia phases. FTIR-pyridine absorption spectra show the presence of Lewis and Brønsted sites in sulfated zirconia but only Lewis sites in nickel zirconia sulfated catalysts. A good correlation between the amount of adsorbed pyridine and the catalytic activity for the isopropanol dehydration was observed. However, an opposite effect was observed for the isobutene oligomerization, where the catalysts with the lower acidity showed the higher activity. The role of Ni⁺² diminishing the deactivation rate forming π -allylic bonds with the olefins is discussed.

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1. Introduction

The oligomerization of butenes is a reaction with a wide range of important applications in the chemical and petrochemical industry, widely used in order to obtain branched C₈= or C₁₂= olefins; in the case of C₈= olefins, they are employed for the production of gasoline additives [1–4] and as the raw material for the plastic production industry in the case of C₁₂= olefins [5]. Industrially, the oligomerization is carried out by using a catalyst consisting in phosphoric acid supported in a solid [6]. Because of the nature of the catalyst used this process is considered highly pollutant. In addition, the process presents serious deactivation problems at the industrial operation conditions employed (140 °C and atmospheric pressure), caused firstly for the formation of C₁₆= olefins over the catalyst surface [7–10]. The absorbed C₁₆= olefins continue reacting in an uncontrolled polymerization reaction, until the formation of high molecular weight oligomers

[11]. Therefore, one of the challenges in the oligomerization of butenes is the development of catalyst with high selectivity to the formation of the C₈=–C₁₂= fractions, avoiding the formation of C₁₆= olefins or heavier fractions. In this way, there have been reported good results with catalyst of nickel supported in zeolites [12–14]. Sulfated alumina exchanged with nickel has been reported in a recent paper as an active and stable catalyst for the oligomerization of ethylene [15]. The authors propose the formation of Ni⁺¹ as the active centers for this reaction.

Then, it is clear that to carry out the oligomerization reaction a catalyst with strong acidity is necessary, but at the same time with the capacity to control the size of the chain of the olefins obtained.

With this in mind, in the present work the results obtained in the oligomerization of isobutene over NiO/ZrO₂ sulfated catalysts are reported. The catalyst was prepared by the named “one pot” sol–gel procedure, starting from zirconium alkoxide and nickel sulfate.

2. Experimental

The synthesis of the catalysts was carried as follows; 30 ml bi-distilled water and 200 ml of ter-butanol were mixed in glass

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