

Skeletal isomerization of linear butenes on ferrierite: Effect of the presence of lower olefins in the feed and of operating conditions

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The skeletal isomerization of linear butene on ferrierite, at atmospheric pressure and 0.15 atm 1-butene partial pressure, was studied by feeding 1-butene streams with different ethene and propene concentrations and exploring several operating conditions. At short time-on-stream (5 min), the strongest acid sites govern the catalytic behavior, independent of the operating conditions in the studied ranges. At longer times, the reaction temperature mainly defines the conversion level. The higher the temperature, the larger the linear butene conversion. Temperature also has a strong influence over the nature of the carbonaceous deposit formed during reaction. At 400 °C, the deposit mainly shows an aromatic nature. The presence of lower olefins as impurities in the feed modifies both catalytic activity and by-product distribution. By decreasing the ethene concentration, the C_4 fraction in the product stream increases and a lower carbonaceous deposit is formed. Using a nitrogen stream saturated with water during both pretreatment and reaction, the catalytic activity increases and the coke amount slightly diminishes, but the isobutene production is unfavored.

KEY WORDS: skeletal isomerization; isobutene; ferrierite; feed impurities; coke

1. Introduction

The skeletal isomerization of linear butenes has gained importance as an alternative route for the production of isobutene, which is used for the methyl *tert*-butyl ether synthesis and in alkylation reactions. That skeletal isomerization reaction takes place on acid catalysts. The ferrierite zeolite shows one of the best catalytic behaviors, as reported by numerous articles in the literature [1–4].

The effect of operating conditions over catalytic behavior of ferrierite during the skeletal isomerization of linear butene has been reported [5,6]. Nevertheless, topics related to ferrierite deactivation have constituted the main focus of interest, especially in order to understand the isobutene selectivity improvement with time-on-stream. This characteristic catalytic behavior of ferrierite has been related to the carbonaceous deposit formation [3,7], to the type of acid sites [5], to the space around the acid site [8], and more recently to the acid site density [9].

The inner pores of ferrierite have been modified by plasma-polymerized propylene in order to identify the role of carbonaceous deposit during the skeletal isomerization of linear butenes [7]. Nevertheless, there are no available data related to the effect of lower olefins present in the butene feed either on catalytic behavior of ferrierite or on its deactivation.

In this paper, we study the effect of the presence of ethene and propene, as impurities of the feed, over both catalytic behavior and deactivation of ferrierite during the skeletal isomerization of linear butene. The ethene concentration in the butene feed is modified by passing the stream through a molecular sieve bed placed before the isomerization reactor. The effect of both the temperature and the presence of water under reaction conditions is also analyzed.

2. Experimental

An ammonium ferrierite sample was provided by TOSOH, Japan (sample HSZ-720NHA). The SiO_2/Al_2O_3 molar ratio was 17.8, Na_2O and K_2O concentrations being below 0.05% and 0.10%, respectively. The crystalline structure was characterized by X-ray diffraction using a Rich-Seifert Iso-Debyelex 2002 diffractometer, the diffraction spectrum range being $0 < 2\theta < 60^\circ$.

The catalytic behavior during 1-butene isomerization was studied in a continuous down-flow, fixed-bed quartz tubular reactor operated at atmospheric pressure, using 500 mg of catalyst sieved to 35–80 mesh. Samples were heated in a nitrogen stream at $17.3^\circ C\ min^{-1}$ from 25 to 550 °C, keeping this temperature for 30 min, thus obtaining samples in the acid form. After heating, samples were cooled to the selected temperature in the nitrogen stream. For catalytic tests, a pure 1-butene stream was co-fed with nitrogen, 0.15 atm 1-butene partial pressure. In order to modify the ethene concentration in the butene

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