

Skeletal Isomerization of Linear Butenes on Boron Promoted Ferrierite: Effect of the Catalyst Preparation Technique

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Abstract Potassium and acid ferrierites were impregnated with boron species by wet and incipient wetness techniques. All samples display a medium-intensity band at $3,450\text{--}3,470\text{ cm}^{-1}$ associated to Si–OH...O groups corresponding to boron-containing units. The $1,398\text{--}1,404\text{ cm}^{-1}$ band assigned to the B–O stretching in BO_3 units does not appear on boron–potassium–ferrierite prepared by wet impregnation. Catalytic performance during the linear butene skeletal isomerization was measured. At $300\text{ }^\circ\text{C}$, boron impregnated by incipient wetness technique on acid ferrierite reduces both linear butene conversion at a short time and isobutene yield in all time range. Boron potassium–ferrierite prepared by wet impregnation has a suitable acidity to promote isobutene production. At $450\text{ }^\circ\text{C}$, this sample shows the best performance, being the isobutene yield 1.7 times higher than the acid-ferrierite one and reaching the highest isobutene selectivity (92%). This performance is maintained with time. Both isobutene yield and by-product distribution are strongly affected by temperature; dimer intermediates are formed. Finally, both kinds of hydroxyl groups corresponding to $3,466$ and $3,635\text{ cm}^{-1}$ bands influence the isobutene production whereas BO_3 sites are inactive for this reaction.

Keywords Boron–ferrierite · Isobutene · Skeletal isomerization · Wet impregnation

1 Introduction

The skeletal isomerization of linear butenes is an alternative route for the production of isobutene, which is used for the methyl *tert*-butyl ether synthesis, the polyisobutene production, and in alkylation reactions. The skeletal isomerization reaction takes place on acid catalysts and demands a stronger acidity than the double bond isomerization, but a strong acidity also favors undesirable side reactions such as dimerization–oligomerization, cracking, disproportion, and hydrogen transfer. In order to improve the isobutene selectivity, an ideal skeletal isomerization catalyst should have an adequate acidity strong enough for the isomerization reaction but not too strong for undesirable side reactions.

Ferrierite, a zeolite with a bidimensional pore structure of ten-membered rings ($4.2 \times 5.4\text{ \AA}$) intersected by eight-membered rings ($3.5 \times 4.8\text{ \AA}$), shows one of the best catalytic performances during the skeletal isomerization of linear butenes [1]. The characteristic behavior of this zeolite is a high activity with low isobutene selectivity at a short time-on-stream; then, conversion decreases and selectivity increases after some minutes under reaction conditions [1, 2]. This behavior has been related to the type of acid sites [3], the space around the acid site [4], the acid site density [5], and the carbonaceous deposit formation [2, 6]. Among several catalysts, Li- and Cs-exchanged ferrierite was evaluated to investigate the effect of the presence of acid sites on the external surface, the acid site density, and the space around the site over the isobutene selectivity [4]. Catalytic properties of ferrierite exchanged with alkaline earth metals during the linear butene skeletal isomerization were reported [7]. ZSM-5 and ZSM-11 were synthesized with different contents of aluminum and boron, suggesting there are synergistic effects between framework boron and aluminum to enhance the butene skeletal

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