

Tungsten-ferrierite catalysts prepared by impregnation and ion-exchange: Characterization and activity during the skeletal isomerization of linear butenes

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Tungsten-ferrierite catalysts were prepared by impregnation and ion exchange. Potassium (KF), ammonium (AF), and protonic (HF) ferrierites were used as starting materials. Characterization of impregnated catalysts shows reduction peaks characteristic of tungsten species, whereas the absence of a peak in the corresponding profiles of the exchanged material indicates such species were incorporated into the framework. For impregnated materials, the tungsten species-surface interaction is not strong. Catalytic performance during the linear butene skeletal isomerization at 300 °C and at atmospheric pressure was measured. Exchanged materials reach both conversion and isobutene yield larger than the impregnated ones. Samples prepared from AF and HF practically display the same catalytic behavior at 5 min, being associated with the presence of strong acid sites. Tungsten-impregnated KF does not reach a high activity at a short time-on-stream (TOS), showing a particular by-product distribution related to the absence of strong acid sites. Even though exchanged samples starting from KF show the HF characteristic behavior, differences at 5 min appear. By-product distributions allow us to consider their formation from dimers and/or oligomers. At 5 min, the C₃⁺ fraction is the main one, following propene, propane, and butane in similar proportions. Over the “clean” surface, propene could be involved in other reactions considering its high reactivity. At a long TOS, both the C₃⁺ fraction and propane decrease, whereas propene increases, verifying the bimolecular mechanism.

KEY WORDS: tungsten ferrierite; impregnation; ion-exchange; skeletal isomerization; isobutene.

1. Introduction

Ferrierite shows one of the best catalytic performances during the skeletal isomerization of linear butenes [1]. The characteristic behavior of this zeolite shows a high activity with low isobutene selectivity at a short TOS; then, conversion decreases and selectivity increases with TOS. This behavior has been related to the carbonaceous deposit formation [2,3], the type of acid sites [4], the space around the acid site [5], and the acid-site density [6]. The reaction mechanism of linear butene skeletal isomerization on ferrierite remains under discussion. Nevertheless, the fresh material is accepted as non-selective, whereas the aged one is considered selective. Topics related to ferrierite deactivation have constituted the main interest, especially in order to understand the isobutene selectivity improvement with TOS. An exhaustive analysis of deactivation of solid acid catalysts, including ferrierite, during the linear butene skeletal isomerization has recently been published [7].

Catalytic improvement of KF and AF by tungsten-species impregnation, following the incipient-wetness technique and using both tungstic acid and ammonium

metatungstate as tungsten precursors, was previously reported [8]. The presence of tungsten species on ferrierite improves the catalytic behavior without modifying acidity profiles corresponding to the unpromoted materials [9]. Tungsten species impregnated on KF promotes catalytic activity, but without reaching a high conversion at a short TOS. Then the zeolite form used as starting material in catalyst preparation could be an important parameter. In order to characterize exchange sites in the ferrierite framework, the location of Cu cations in the dehydrated copper ion-exchanged ferrierite [10] and Ni ion sites in hydrated and dehydrated forms of nickel-exchanged ferrierite [11] were analyzed. 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 [5]. More recently, the catalytic properties of ferrierite exchanged with alkaline earth metals in the *n*-butene skeletal isomerization [12] and the selective formation of alkenes through the *n*-heptane cracking on Ca-exchanged ferrierite [13] were reported. Nevertheless, there are no available data on the influence of the catalyst preparation technique on its catalytic performance.

The effect of the preparation technique of tungsten-ferrierite catalysts on their behavior during the linear butene skeletal isomerization is studied in this paper.

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