



Low temperature conversion of linear C₄ olefins with acid ZSM-5 zeolites of homogeneous composition

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ABSTRACT

Conversion of linear butenes over ZSM-5 zeolites leads to a large variety of products, from olefins to aromatics. At low temperature, these products are mainly olefins from C₃⁺ to C₁₃⁺, with a predominance of dimeric products. The analysis of the product stream obtained by the reaction of *n*-butenes over several materials with MFI topology, but with different aluminum content provides evidence for an oligomerization–cracking–realkylation mechanism. The reactions occur predominantly in the catalyst bulk or at the external surface, depending on the amount of coke developed inside the catalyst. This behavior is determined by the concentration of framework Al and associated silanol groups, inducing coking. For Al-rich MFI samples, the amount of hard coke is sufficient to block the access of reactants to internal acid sites. As a result, extra-crystalline catalysis dominates, while the appearance of the individual products is consistent with that predicted by classical carbocation theory. For siliceous samples, hard coke formation is less pronounced, and evidence for shape selective product formation is present. Expected relations among structural, morphological and acidic properties of all MFI materials have been confirmed by XRD, SEM and BET and by ²⁷Al MAS NMR, NH₃-TPD and FTIR.

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1. Introduction

Linear C₄ olefins are low-value products available from oil refining and in particular from light olefin production. They can be transformed catalytically into higher-value molecules, such as aromatics, and in particular *p*-xylene. The latter is used as feedstock for terephthalate, polyester [1] and pharmaceuticals production [2].

Acid ZSM-5-type zeolites have been reported [3] allowing the one step transformation of butenes into *p*-xylene with moderate selectivity and yield. This transformation consists of three major steps, *viz.* *n*-butenes dimerization into octene molecules, cyclization of octene molecules into C₅- and C₆-alkylnaphthenes and hydrogen transfer from the latter to aromatics. The relatively high number of occurring acid-catalyzed reactions, result in limited *p*-xylene selectivity. It is not clear whether with the help of appropriate zeolite modifications, *in casu* specific tailoring/modification of ZSM-5 zeolite crystals, it is possible to affect the reaction network aiming at modifying the selectivity of product groups.

As in such reaction network, the number of consecutive reactions is high, in the present approach it was decided to study

first the different steps separately. In the present paper, the dimerization step of butenes into octenes will be isolated as much as possible. According to classical carbocation chemistry, primary products from *n*-butene dimerization all are isomeric olefins with a 3-methylheptene and 3,4-dimethylhexene carbon skeleton [4].

Low *n*-butenes dimerization activity and fast deactivation detected with ZSM-5 [Si/Al=25] at 423 K [5] were ascribed to micropore filling with coke molecules. The skeleton of product molecules was more linear with MFI materials compared to mesoporous materials. Two activity regions have been distinguished for conversion of small olefins over H-ZSM-5 zeolites according to reaction temperature [6]. Below 500 K, pores are filled with coke molecules and extra-crystalline catalysis becomes dominant. Above 500 K, the rate of the cracking reactions is higher than the oligomerization rate; coke molecules can be cracked and pores remain at least partly accessible; reactions occur (partly) intraporous, while shape-selective products are obtained.

For dimerization of *n*-butenes, it has been reported that the ZSM-5 pore architecture is not a selectivity determining parameter [7], while others [8] reported a good correlation between the yield of trimers and the acidity of the external surface of ZSM-5.

The aim of this work is to study the first steps of the low temperature (220 °C) *n*-butenes conversion over H-ZSM-5 materials. The

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