



Low temperature conversion of linear C₄ olefins using acid ZSM-5 zeolites with aluminum concentration gradient

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ABSTRACT

Two ZSM-5 materials with high and low overall Si/Al ratio, each with an Al concentration gradient across the crystals (G-samples) have been synthesized, physico-chemically characterized with several techniques (XRD, SEM, N₂ adsorption, ²⁷Al MAS NMR, NH₃-TPD, FT-IR and TOF-SIMS), and catalytically tested in the low-temperature dimerization of n-butenes, paying attention to coke formation. Their acidic properties were found consistent with their framework aluminum content, except for a lower than expected number of Brønsted acid sites as measured by FTIR of adsorbed pyridine. The dimerization – cracking – realkylation mechanism, previously observed for n-butenes dimerization over acid ZSM-5 with homogeneous aluminum distribution, was confirmed over G-type catalysts. The influence of hard coke content, observed in the previous work, on product selectivity and distributions was also found for G-type catalysts. The siliceous G-type catalyst, with low amount of hard coke and micropores partly accessible to reactants, shows shape-selectivity properties consistent with dominating intra-crystalline catalysis. The aluminous G-type catalyst, with high amount of hard coke, and micropores completely filled with aromatic carbonaceous residue, shows thermodynamically equilibrated products selectivity and distributions in agreement with extra-crystalline catalysis.

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1. Introduction

In earlier works [1–5], the low temperature conversion of n-butenes has been reported on H-ZSM-5 zeolites, aiming at isolating C₄⁺ dimerization from the overall network of n-butenes toward p-xylene conversion. A extensive literature study on the subject has been reported recently [6]. According to the classical carbocation mechanism, molecules with 3,4-dimethylhexane or 3-methylhexane skeleton are primary products [1]. Several authors found that dimerization activity is correlated with the acidity exhibited by the external surface area [2–5]. Most recently [6], acid ZSM-5 catalysts with a homogeneous aluminum concentration across the crystal, covering a wide Si/Al framework ratio, were studied in the low temperature conversion of n-butenes. The product distribution was explained by a sequence of dimerization – cracking – realkylation reactions, where cracked molecules such as propene and pentenes, can undergo alkylation with n-butenes [6].

Whereas the dimerization rate follows the framework Al content (FAI), it slows down for higher FAI values because of restrictions in reactant diffusion caused mainly by coke formation in the

micropores [6]. An amount of 3 wt% of hard aromatic coke was found to be sufficient to prevent the access of molecules to ZSM-5 micropores. Higher amounts of hard coke found for aluminous ZSM-5 catalysts, prevent the occurrence of the intraporous catalytic events, product fractions in the n-butene dimerization reaction being characterized by the absence of shape selective effects, indicating that the external crystal surface is the main locus of catalytic activity. Siliceous ZSM-5 catalysts containing lower amounts of hard coke, keep the pores at least partially accessible to reactants. Typical shape-selective properties of ZSM-5 result, viz. higher amount of cracked molecules with reduced degree of branching, higher distribution in the dimers of methyl-branched isomers at the expense of dimethyl-branched ones and of 2-methyl-branched isomers exceeding thermodynamic equilibrium.

In view of the above results, ZSM-5 zeolites with Al depleted crystal rim or with FAI concentration increasing with crystal depth, might change this product picture. The existence of such materials recently has been reviewed [7,8] and their use in n-butene reactions has not been reported.

A possible profile of aluminum enrichment of the zeolite crystal surface [9–11] can be obtained by selective removal of silica from the crystal interior upon alkaline treatment [12–14]. Mechanistically, the formation of this profile is based on the different dissolution behavior of the constituents at high alkalinity. While silicon interacts preferentially during the crystallization process,

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