

Isomerization and Dimerization – A Mechanistic Discrimination of Two Competitive Reactions Occurring on Highly Dispersed Ni²⁺ Catalysts

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Abstract

Introduction. Butene is a side product from fluid catalytic cracking (FCC), used in the synthesis of linear and monobranched octenes, a crucial step in the synthesis of PVC plasticizers. Currently, butene dimerization is catalyzed with nickel nanoparticles supported on silica-alumina, leading to nanoparticle agglomeration and its deactivation. Thus, the dispersion of Ni²⁺ in zeolites, compensating two negative charges in the aluminosilicate framework, can enhance the catalyst lifetime. The exchange of the protons with co-cations, e.g. Ca²⁺, increases the selectivity towards linear octenes. Here, we will discuss the role of the Ni²⁺ active site and its contribution in the mechanism to form linear octenes.

Experimental procedure. Commercial samples of the zeolite Ca-LTA were exchanged with various amounts of nickel nitrate (Ni-Ca-LTA) and tested for 1-butene oligomerization at 50 bar and 150-160 °C, using a plug flow reactor system. Adsorption of 1-butene on the Ni-Ca-LTA was monitored via infrared spectroscopy to study the formation of surface intermediates.

Results and Discussion. 1-Butene dimerization on a Ni-Ca-LTA, was highly selective to 3-methylheptene and linear octene, with selectivities of 38-55 and 62-40 %, respectively, in the conversion range up to 35 %. The main dimerization pathway is proposed to take place via initial 1'-adsorption of 1-butene on Ni and subsequent 1- or 2-insertion of a second butene molecule. This explains the high selectivity to methylheptene and linear octene dimers. Dimethylhexene is formed via an initial 2'-adsorption, but to a minor extent. Double bond isomerization plays an important role in the activity and selectivity of butene dimerization. Higher concentrations of 2-butene favor the 2'-insertion into 1'-adsorbed species, for which the selectivity to methylheptene is increased. Moreover, 2'-adsorption is the only possible adsorption mode for internal olefins, which leads to a higher concentration of 2'-adsorbed species on the surface, and hence to the formation of mono- and dibranched dimers. Double bond isomerization equilibrium was reached at about 30-35 % butene conversion and turned out to limit the conversion rate to dimers in that range, independent of increasing space time. IR spectroscopy points to the formation of Ni-allyl and Ni-alkyl complexes as surface active sites for isomerization and dimerization, respectively. Isomerization is suggested to happen via adsorption-desorption with the allylic transition state, while dimerization follows a stepwise Cossee-Arlmann type mechanism. After the primary Ni-alkyl complex has been formed, the second butene molecule is adsorbed in a π -complex. The subsequent C-C coupling turned out to be the rate determining step, as it has been proposed before. These findings demonstrate the unique role of Lewis acid Ni sites upon olefin dimerization with both terminal and internal carbons, leading to the formation of linear or branched dimers.