

## Highly Selective Dimerization of n-butenes Over Promising Ni-modified Al-MCM-41/ZSM-5 Catalyst Systems

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### Abstract

When refining heavy crude oil fractions by catalytic cracking processes large amounts of C4 cut are produced. An opportunity for an extensive use of large parts of the C4 fraction is the dimerization of n-butenes over amorphous NiO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts to C8 olefins of various branching degree in the so-called *OCTOL* process. Especially linear and low-branched dimers can be used as precursors for fabrication of plasticizers and surfactants. Since current catalysts for the *OCTOL* process generate dimer mixtures with an ISO-Index of  $\geq 1.1$ , which appears to be a branching-degree related parameter, further improvement of catalysts performance regarding selectivity is required.

Heterogeneous catalytic oligomerizations occur at coordinative unsaturated nickel sites or at acid sites. The acid-catalyzed carbenium ion mechanism leads to highly branched, long-chain oligomers, caused by hyperconjugation effects during oligomerization.<sup>[1]</sup> To obtain low branched dimers a suppression of the carbenium ion mechanism and favoring the coordinative oligomerization is necessary. Albrecht et al.<sup>[1]</sup> and Rabeah et al.<sup>[2]</sup> have shown that the presence of acid sites plays a crucial role for the formation of active nickel sites. Therefore, several research groups used different acidic support materials, like amorphous aluminosilicates or zeolites loaded with nickel as oligomerization catalysts.<sup>[1]</sup>

Within this work, nickel containing Al-MCM-41/ZSM-5 mixed phase catalyst systems with different aluminum and nickel content were synthesized and catalytic tests have been carried out. As one result, catalysts with varying catalytic activity and selectivity, revealed by ISO-indices ranging between 0.9 and 1.8 were obtained.

Based on the analysis of the product stream, it can be stated that the coordinative reaction mechanism is prevailing for all synthesized catalysts, even for catalysts with high ISO-Indices.

Thus, the first step of process optimization in the course of enhancing coordinative produced amount of linear dimers is achieved.

In the purpose of further process improvement catalysts properties like the electron density of the unsaturated nickel sites and metal-support-interactions, respectively, should be rather considered.

[1] S. Albrecht, D. Kießling, G. Wendt, D. Maschmeyer, F. Nierlich, *Chemie Ingenieur Technik* 2005, 77, 695–709.

[2] J. Rabeah, J. Radnik, V. Briois, D. Maschmeyer, G. Stochniol, S. Peitz, *ACS Catal.* 2016, S. 8224-8228