First-principle kinetic study of butene cracking on H-ZSM-5

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Over the last decades, the methanol-to-olefins process (MTO) has become one of the most promising alternatives for the production of base chemicals such as ethylene and propylene. The versatility of this process is mainly attributed to the different raw materials from which methanol can be synthesized, ranging from biomass over coal to natural gas. Methanol is converted over acidic zeolites, e.g., H-ZSM-5. Cracking of alkenes plays an important role in the product selectivity for this catalyst.[1] Depending on the implementation, a separate H-ZSM-5-based cracking process can be coupled to the MTO unit. In this process, the C_{4+} fraction of the MTO product, consisting mainly of butenes, is converted into light olefins to increase the overall propylene to ethylene ratio. H-ZSM-5 provides an optimal balance between conversion, selectivity towards light olefins and catalyst deactivation.[2] The cracking process occurs via a complex network of carbenium ion intermediates. Recent studies have indicated that butenes tend to form dimers before cracking reactions can occur.[3,4] However, a thorough understanding of the elementary reaction steps and the nature of the pre-activated complexes is still lacking.

In this study, several possible reaction pathways for the cracking of a butene mixture are investigated using DFT methods on a large finite cluster model. Chemical kinetics at operating conditions are calculated based on transition state theory. We aim to identify feasible reaction paths by comparing bimolecular and monomolecular cracking mechanisms. A profound insight into the prevailing mechanism is the key to achieving optimal control over the product distribution in the overall process.

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