# Theoretical verification of the alkene hydrocarbon pool cycle for MTO conversion in ZSM-5

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To meet the ever increasing demand for oil-based chemicals in spite of waning oil reserves, the development of new technologies based on alternative feedstocks is high on the scientific agenda. One of the most promising emerging technologies is the methanol-to-olefin (MTO) process in acidic zeolites. Despite considerable efforts from both experimental and theoretical research, the reaction mechanism has proven to be extremely difficult to unravel. Experimental results advocate a hydrocarbon pool mechanism, in which organic centers inside the zeolite pores act as co-catalysts.[1,2] Recently, a complete such catalytic cycle has been studied from a theoretical viewpoint.[3] Until now, however, polymethylbenzenes have been commonly regarded as the most important hydrocarbon pool species, independent of the employed zeolite. While this assumption still holds for zeolites with the BEA- or CHA-structure, recent experiments have shown that ZSM-5 (which has the MFI-topology) could be an important exception. Researchers found that the higher methylbenzenes, even though present, are virtually unreactive in the pores of ZSM-5. Ethene appears to be formed solely from the lower methylbenzenes, while propene and higher alkenes would be formed from alkene methylations and interconversions. These observations led to the proposal of a dual cycle mechanism, in which the polymethylbenzene cycle yields predominantly ethene and the alkene cycle yields propene and higher alkenes.[4,5]

In this study, the alkene cycle is modeled using advanced quantum-chemical techniques. We aim to verify whether olefin formation proceeds through this route and whether propene formation is indeed preferred. Since the proposed dual cycle might eventually allow controlling the propene-to-ethene ratio, a thorough understanding of all elementary steps is of utmost importance.

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