Effects of zeolite topology on methylation reactions in the MTO process from a theoretical perspective

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Crude oil prices are rising steadily while the global demand for base chemicals such as ethene and propene still increases every day. To fulfill this need for light olefins, there has been a growing interest in technologies based on other natural resources. Methanol-to-olefin conversion (MTO) catalyzed by acidic zeolites is currently one of the most promising alternatives. MTO has the added advantage that it allows a greater control over ethene-to-propene product ratio, in contrast with traditional steam cracking processes. Although MTO has been studied for over 20 years, the debate on the true nature of the underlying reaction mechanism is still ongoing. [1] Recent insights strongly support an indirect mechanism based on organic molecules acting as co-catalysts inside the zeolite pores. [2] Within this hydrocarbon pool several reaction cycles can occur, depending on the zeolite employed. Whereas polymethylbenzenes were found to be the most important hydrocarbon pool species in the H-SAPO-34 catalyst (which has a CHA topology) [3], recent experimental and theoretical evidence suggest a parallel route based on repeated alkene methylations and cracking steps in the MFI-structured H-ZSM-5. [4,5] In light of these observations, current experimental studies suggest other zeolite materials with different topologies as potential MTO catalysts. [6]

Previous experimental and theoretical studies have shown that methylations of various alkenes are crucial reaction steps. Therefore it is of utmost importance to obtain an in depth understanding of this reaction. In this study methylations of ethene and propene are modeled in different zeolite environments. Reaction barriers and rate constants in cage-like frameworks such as H-SAPO-34 (CHA), H-SSZ-13 (CHA), H-ZSM-58 (DDR) and tunnel-structured H-ZSM-22 (TON), are modeled using accurate quantum chemical calculations on extended clusters. Comparison is made with available barriers from periodic calculations on the CHA topology. [7] The kinetic parameters are mutually compared to assess the influence of topology and acidity on these MTO reactions.

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