Theoretical study on the genesis of new hydrocarbon pool compounds during MTO conversion in zeolites

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MTO conversion has been a challenging topic for both experimental and theoretical researchers [1]. Instead of plainly following *direct* routes [2-3], the MTO process has been found to proceed through a *hydrocarbon pool* mechanism, in which organic reaction centers act as co-catalysts inside the zeolite pores [4-6]. However, it remains unclear when and how these co-catalytic hydrocarbon pool compounds are formed either from impurities in the initial methanol feed or from primary MTO products like ethene and propene. Theoretical methods provide an ideal complementary tool to gain initial insights into these poorly understood reactions.

In this work, elementary dimerization reactions between ethene, propene and methanol are modeled within the zeolite framework. In this first assumption, ethene and propene have already been generated out of methanol impurities during the induction period, through the incomplete calcination of templating agents [6], or as primary MTO products from an previously active hydrocarbon pool compound. These dimerization reactions will eventually lead to the formation of new hydrocarbon pool species in nearby channels and cages by cyclization reactions and hydride transfers.

As opposed to previous results by Svelle et al. [7], our calculations show that dimerization of alkenes through a stepwize mechanism (with the intermediate formation of a stable alkoxide species) does not result in the straightforward formation of a higher alkene or alkoxide. We consistantly observe the formation of alkylcyclopropane intermediates instead. A ring breaking step through zeolitic protonation of the cyclopropane structure is needed to obtain a higher alkene. Once enough ethene and/or propene molecules have been subsequently added, a cyclization step would ensure the formation of a new hydrocarbon pool compound.

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