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Recent theoretical insights into the role of the zeolite framework on methanol-to-olefin conversion

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Abstract

The two major conflicting proposals in the methanol-to-olefin process are thoroughly investigated and compared using hybrid multi-level modeling techniques. This investigation leads to the absolute rejection of the intensively studied direct mechanisms and provides a successful alternative catalytic cycle as well as additional insight into the hydrocarbon pool proposal.

Keywords: ab initio, hydrocarbon pool, methanol-to-olefins, ONIOM, ZSM-5

1. Introduction

The rapidly increasing demand of oil-based chemicals calls for the development of new technologies based on alternative natural sources. Among these, the methanol-to-olefins (MTO) technology is one of the most promising. However, for over 30 years the actual mechanism of the MTO process in acidic zeolites has been the source of considerable debate, fueled by countless and often conflicting propositions [1].

The trickiest step to elucidate has always been the formation of the first carbon-carbon bond, for which more than 20 distinct mechanisms have been proposed. Early speculation mainly centered on mechanisms based on the 'direct' formation of small olefins from C1-species only, e.g. the oxonium ylide route [1]. More recent developments suggest an alternative 'hydrocarbon pool' model, in which impurities in the mixture undergo repeated methylation and olefin elimination [2]. Our goal is to unequivocally determine the underlying mechanism of the MTO process from a theoretical viewpoint, as experimental methods are often impractical for evaluating individual reaction steps.

2. Computational Section

Density functional theory (DFT) calculations using the B3LYP functional were performed within the Gaussian03 software package. Both the small cluster approach and the two-layered QM/QM embedded ONIOM method were employed. This more advanced method allows for inclusion of the zeolite framework at moderate additional computational cost. Inclusion of the framework is vital when studying the hydrocarbon pool route, which is space-demanding and based on carbenium-ion intermediates that require stabilization by the surrounding framework.

Calculations were performed on alumino-silicates with three industrially and/or academically important topologies: MFI, BEA and CHA. Generally speaking, the zeolite framework can contain parallel or intersecting channels (like the MFI topology of HZSM-5), cages interconnected by small windows (like the CHA topology of HSAPO-34) or a combination of both cages and channels (like the BEA topology in HBeta).

3. Results and Discussion

We started by tackling the vast number of direct mechanisms by setting up an extensive reaction scheme (Figure 1), tying together a large variety of possible direct reactions, even including several previously overlooked pathways [3]. Based on this scheme, we found all direct mechanisms to fail at one point or another.
For certain concerted C-C coupling reactions during which a zeolite basic oxygen site activates a C-H bond, the energy barrier is too high to overcome because of the limited basicity. For other routes, the oxonium ylide proposal in particular, the failure is based on the high instability of the ylides, even when zeolite framework effects are explicitly taken into account [4]. Our theoretical results imply that no complete direct pathway from methanol leading all the way to ethylene (or to any intermediate containing a carbon-carbon bond) exists.

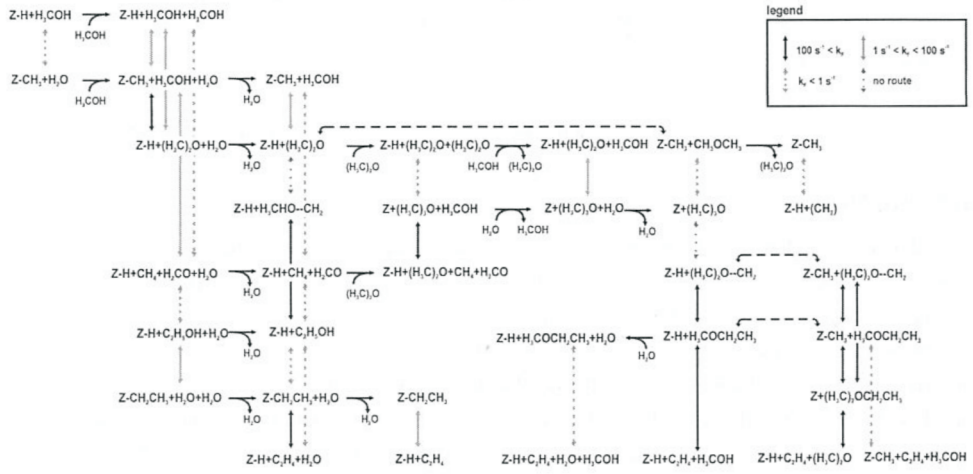

Figure 1. Full scheme containing all investigated direct reaction routes from methanol to ethylene.

The hydrocarbon pool alternative, on the other hand, seems to offer an even more complex challenge. We have recently constructed a complete catalytic cycle, combining both theoretical and experimental results [5], as shown in Figure 2. Even though there are many other hydrocarbon pool cycles all operating simultaneously, this particular cycle is strongly linked to experimental observations. It fully explains the significant production of isobutene in ZSM-5, it includes the scrambling of labeled carbon atoms into the ring and it contains the two crucial cationic intermediates which were observed through NMR.

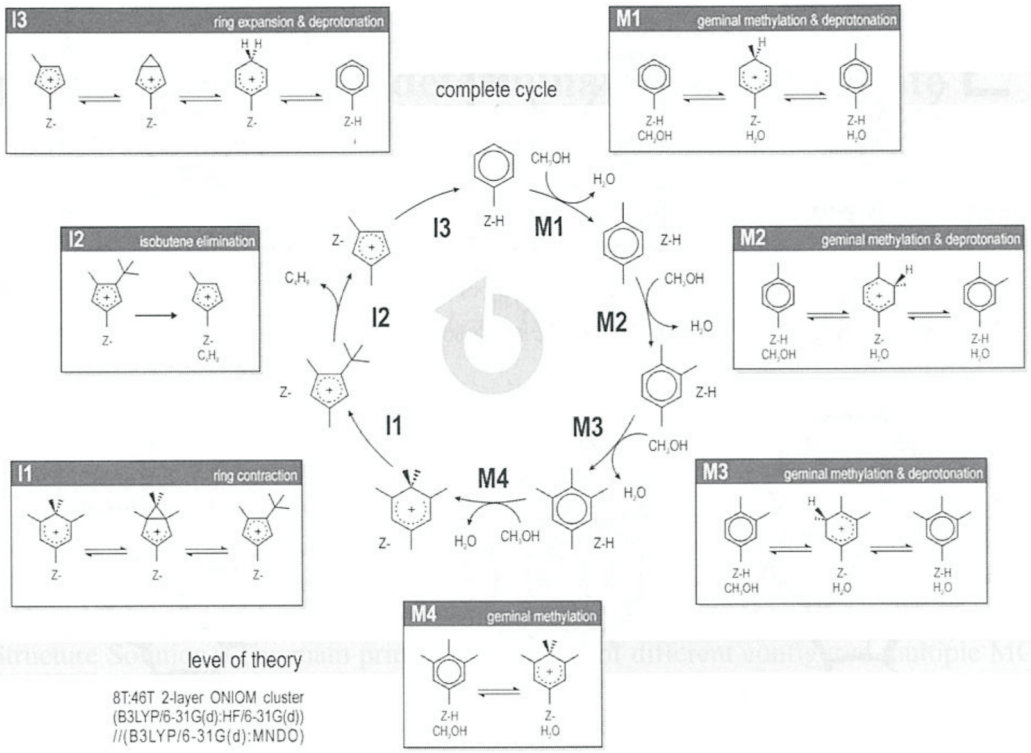

Figure 2. Full catalytic cycle for isobutene formation in ZSM-5, including carbon atom scrambling into a methylbenzene ring and NMR-observed cationic intermediates.

The slowest steps in this cycle are the *gem*-methylation steps (M1-M3), leading to a higher methylbenzene. Once such an additional methylation occurs on an already methylated position (M4), much faster intramolecular rearrangements occur, such as contraction to a 5-ring (I1), splitting off of isobutene (I2) and expansion to a 6-ring (I3). For the crucial M4 *gem*-methylation step our simulations show that the organic hydrocarbon pool species and the inorganic zeolite framework cooperate as a supramolecular catalyst towards low-energy alternative pathways [6]. We find that both hydrocarbon pool species and zeolite topology play a crucial role in the reaction kinetics for the first C-C bond formation, to the extent that there might not be just one methanol-to-olefin mechanism, but several separate mechanisms tailored to each different zeotype material [7]. If the available space is too small (like in the MFI structure of ZSM-5), transition state shape selectivity will result in a higher activity of the lower methylbenzenes, rather than the higher methylbenzenes. If the space is too big (like in the BEA structure), there is inadequate electrostatic stabilization of the cationic intermediate. The role of the zeolite framework on this particular step is illustrated in Figure 3.

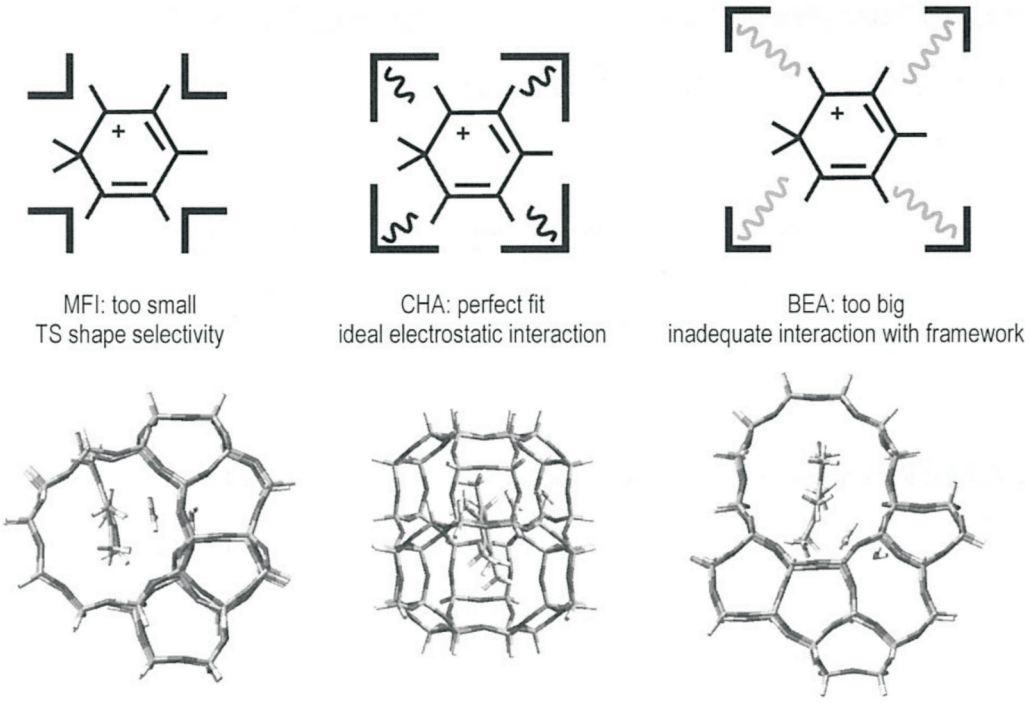

Figure 3. Importance of the electrostatic effect of the zeolite topology on the carbenium ion product (top row) and transition state shape selectivity (bottom row) for gem-methylation of hexamethylbenzene.

4. Conclusion

Theoretical simulations have demonstrated that the numerously suggested direct mechanisms all fail in the formation of the first C-C bond. The hydrocarbon pool model provides an alternative route, for which C-C bond formation will successfully occur in agreement with both experimental and theoretical results. For the crucial *gem*-methylation step this success is due to the stabilizing effect of the surrounding zeolite framework on crucial cationic intermediates.

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