Theoretical elucidation of the reaction mechanism of methanol-to-olefin conversion in acidic zeolites

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Introduction

The ever increasing demand for oil-based chemicals in spite of waning oil reserves calls for the development of new technologies based on alternative feedstock. Among these emerging alternatives, the methanol-to-olefin process (MTO) in acidic zeolites is one of the most promising, since methanol can be made from practically any gasifiable carbonaceous species. However, unraveling the reaction mechanism of MTO conversion has been a challenging task for over 30 years [1], from both experimental and theoretical viewpoint. This presentation will mainly focus on the theoretical contributions towards the recent elucidation of the MTO mechanism, which are strongly linked to experimental observations.

Theoretical

All geometries were optimized at the ONIOM(B3LYP/6-31+g(d):MNDO) level of theory on a large 8T:46T ZSM-5 cluster with the Gaussian03 software. Subsequently single-point calculations at the ONIOM(B3LYP/6-31+g(d):HF/6-31+g(d)) level of theory were performed. These energies were further refined by including van der Waals corrections at the B3LYP-D level of theory with the Orca software package. Kinetic coefficients were obtained using classical TST and the PHVA method.

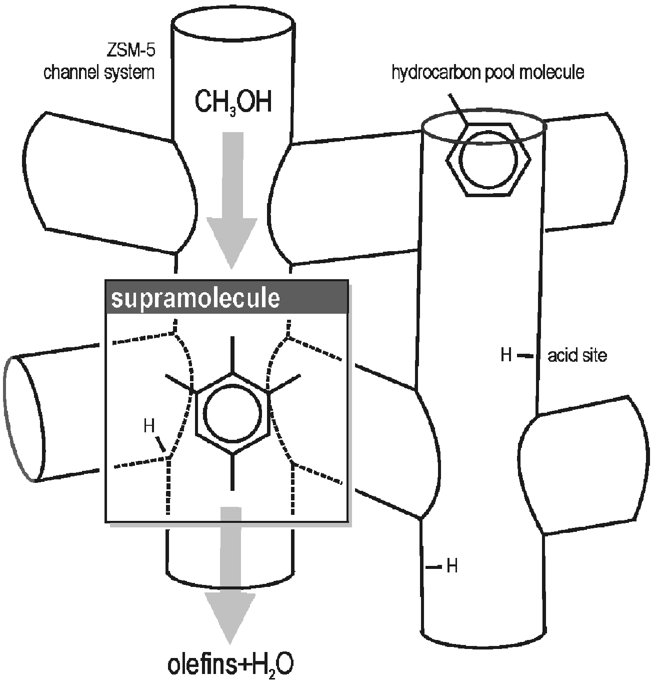

Figure 1. Supramolecular catalyst consisting of organic hydrocarbon pool molecule, zeolite environment and acid site.

Results and discussion

Initially, increasing evidence was reported on the failure of MTO conversion along the often proposed ‘direct’ routes, in which methanol and methanol derivates alone form the olefins with assistance of a Brønsted acid site [2-3]. Instead, a ‘hydrocarbon pool’ hypothesis has emerged, in which organic reaction centers act as homogeneous co-catalysts inside the heterogeneous zeolite catalyst, adding a whole new level of complexity to this issue [4-5], as shown in Figure 1. To obtain additional proof and insight, a complete supramolecular complex of both the zeolite framework and the co-catalytic hydrocarbon pool species was modeled through multi-layer quantum chemical techniques [6-8]. This approach provided a more detailed understanding of the crucial interactions between the zeolite framework and its contents, which form the driving forces for successful methanol-to-olefin conversion.

Conclusions

Full catalytic routes to ethene, propene and isobutene have been found in full accordance with experimental results. The ZSM-5 framework plays a crucial role on reaction kinetics, through electrostatic stabilization and shape selectivity.

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