Modeling Zeolite Catalysis at Operating Conditions by Combining Advanced Molecular Dynamics and Microkinetic Modeling

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To predict a zeolite catalyst's performance at operating conditions, one needs to account for phenomena at various length- and time scales. In this contribution, we show the necessity and power of microkinetic modeling and advanced molecular techniques to account for realistic operating conditions. In particular, we investigate how temperature, pressure and feed composition affect a zeolite's ability to catalyze crucial reactions steps during the methanol-to-olefins (MTO) conversion.

Introduction

To achieve a major shift in the global energy and chemicals economy to sustainable resources highly efficient catalysts need to be designed and molecular simulations play a major role in this process. While metal surface catalysis obtained a great predictive power enabling model-guided design due to the application of advanced first principles microkinetic modeling techniques [2], the assessment of a nanoporous catalyst's performance is to date often limited to free energy calculations of isolated reaction steps at single active sites. To predict a zeolite catalyst's performance at operating conditions, one also needs to account for phenomena at various length- and time scales including adsorption, reaction, desorption and – if relevant – diffusion. By combining these data into microkinetic models, a catalyst's performance at operating conditions can be simulated. However, the often very complex reaction mechanisms and computational expense for zeolite catalysis hamper its widespread use. While microkinetic models often rely on static Density Functional Theory (DFT) calculations, complex reaction environments might require a dynamic approach [3-5] which is also able to mimic operating conditions. Therefore, we combine insights from advanced MD and microkinetic modeling to map complex transformations in zeolites at operating conditions.

Experimental

In this work DFT based static geometry optimization and molecular dynamics (MD) based simulations have been performed in a 96T ZSM-5 unit cell containing one acid site. While static calculations are ideally suited to calculate the kinetics of a multitude of individual reaction steps, molecular dynamic, metadynamics and umbrella sampling simulations give complementary insights into the behaviour of the system at operating conditions [1]. Static calculations are performed with VASP using the PBE functional, whereas MD simulations are performed with the CP2K software package, using the revPBE functional.

Results and Discussion

Seminal work by Brogaard et al. [6] demonstrated the excellent agreement between DFT based microkinetic models and kinetic measurements for alkene methylations in zeolites. Inspired by that work, DFT calculations on adsorption, reaction and desorption at various types of active sites for relevant methanol-to-hydrocarbon reactions will be collected in microkinetic models. First, we focus on the differences between methanol and dimethyl ether (DME) as methylating agents. By constructing a DFT based microkinetic model including concerted and stepwise methylation reactions, product formation rates can be calculated that can be directly compared to experimental measurements. Methylations with DME are faster than with methanol (Figure 1) and with increasing temperature and decreasing pressure we observe a shift from the concerted towards the stepwise mechanism. Our calculated rates exhibit maximum deviations from experimental values of a factor 4 and the relative

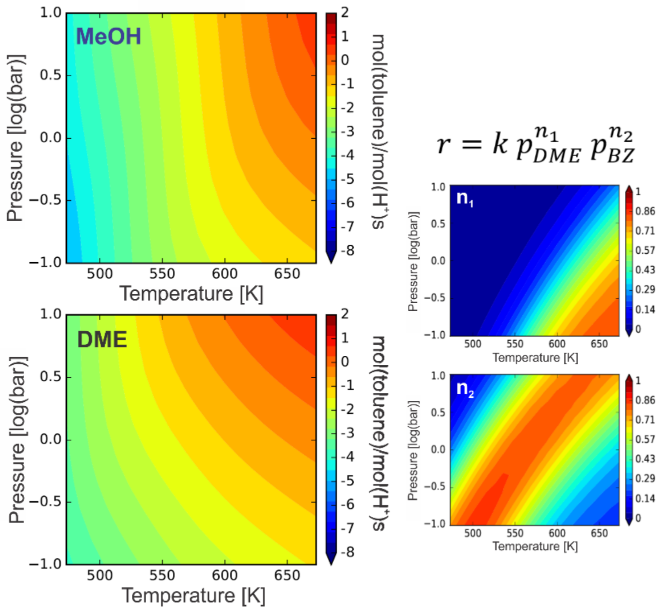

Figure 1: Left - Calculated toluene production rates for benzene methylation in H-ZSM-5 with methanol or dimethyl ether. Right - predicted reaction orders for dimethyl ether and benzene.

rates with DME and methanol are reproduced very well. From our microkinetic model we also compute reactions orders, showing that the widely assumed methylation rate law with a zeroth order in oxygenate partial pressure and first order in hydrocarbon partial pressure [7] is not generally applicable for all combinations of temperature, pressure and feed composition.

Secondly, we investigate alkene cracking reactions as they are an inherent part of the MTO hydrocarbon pool mechanism [7]. Depending on the chain length, temperature and branching of the alkene, it either physisorbs or forms a carbenium ion or alkoxide.[8] To unravel the nature of the alkene intermediates and their preferential cracking pathways at realistic conditions, we use a set of MD based simulations. To predict product selectivities, a detailed microkinetic model is constructed.

Conclusion

By combining insights from advanced molecular dynamics and first principle microkinetic modeling, we obtain detailed insights into the kinetics of complex reaction mechanisms and product selectivities for selected methanol-to-olefins reactions at operating conditions. Temperature, pressure and feed composition are found to significantly impact the governing mechanism and behavior of the catalyst.

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