# Understanding zeolite-catalyzed reactions at operating conditions from first principle microkinetic modeling

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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,[1] 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. Moreover, the growing interest in multifunctional catalysts to convert non-conventional feedstocks requires the ability to model complex active sites.[2] To predict a multifunctional 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. Only by combining these data into microkinetic models, a catalyst's performance at operating conditions can be simulated. The often very complex reaction mechanisms and computational expense for zeolite catalysis hamper its widespread use. Moreover, active sites in zeolites are often inequivalent, requiring solving the microkinetic models with a much more complex kinetic Monte Carlo approach instead of a mean-field approximation.

Seminal work by Brogaard et al.[3] 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. We will particularly 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 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 [4] is not generally applicable for all combinations of temperature, pressure and feed composition.

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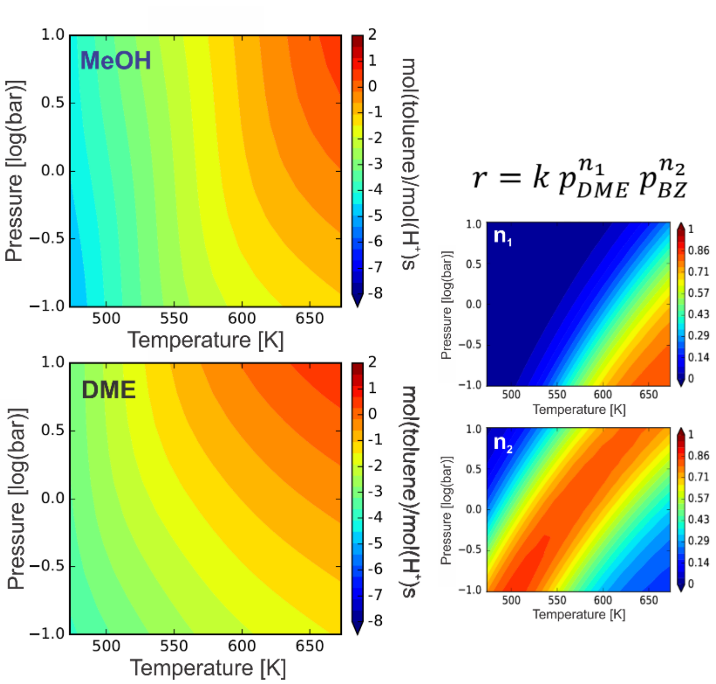

Figure 1. Left: Calculated toluene production rates for benzene methylation in H-ZSM-5 with methanol or dimethyl ether. Right: predicted reaction orders for dimethyl ether and benzene.

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