Advanced molecular simulations of elementary steps in zeolite catalysis

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Zeolites are prominent heterogeneous catalysts with numerous applications in today's chemical industry. The number of zeolite structures and their catalytic applications still increases in view of alternative feedstocks, e.g. in the area of biomass upgrading. Nonetheless, many features of zeolite catalysis are only superficially understood. Herein we show that state-of-the-art advanced molecular dynamics (MD) techniques are able to describe the influence of catalyst and process related parameters, being feed composition, reaction temperature, catalyst topology and Brønsted acidity (Figure 1). As a case study, the methylation of benzene and propene are considered as these are model compounds for the typical hydrocarbon pool species acting as co-catalysts during methanol conversion [1]. It has been reported that these reactions occur in a concerted or stepwise fashion, i.e. methanol directly transfers its methyl group to a hydrocarbon or the reaction goes through a framework-bound methoxide intermediate (Figure 1).

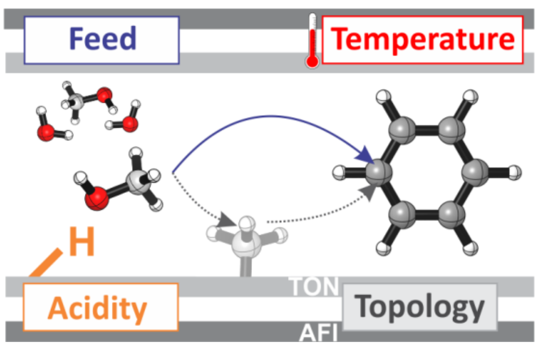

Figure 1 Overview of the catalyst and process related factors included in our MD study.

In our MD study, we focus on four factors that have a distinct impact on the reaction mechanism and kinetics of zeolite-catalyzed reactions. With such dynamical approach, we are able to mimic true reactions conditions as close as possible, hereby explicitly sampling the competition between two competing methylation mechanisms, which was shown to be entropy driven.[2,3] First, by varying the temperature and the number of methanol and water molecules in the system, the influence of feed composition and temperature are assessed. Furthermore, we evaluate the influence of zeolite topology and acidity by comparing results for the unidirectional AFI-structured H-SSZ-24 and TON-structured H-ZSM-22 materials. This study shows the importance and strength of an MD-based approach when modeling zeolite-catalyzed reactions under true reaction conditions.

Acknowledgements - We thank ERC (grant agreement no. 647755 – DYNPOR (2015 – 2020)), the Stevin HPC infrastructure and the Flemish Supercomputer Center (VSC).

[1] Hemelsoet, K. et al. ChemPhysChem 14 (2013) 1526.
[2] Brogaard, R. Y. et al. J. Catal. 314 (2014) 159-169.
[3] De Wispelaere, K. et al. Chem. Eur. J. 21 (2015) 9385.

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