Molecular dynamics kinetic study on zeolite-catalyzed reactions

Kristof De Wispelaere, Samuel Moors, Jeroen Van der Mynsbrugge, Michel Waroquier and Veronique Van Speybroeck
Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium

The methylation of arenes is a key step in the production of hydrocarbons from methanol over acidic zeolites.[1] We performed free energy simulations of the benzene methylation in H-ZSM-5 to determine the factors that influence the reaction kinetics. Earlier kinetic studies, in which static approaches were followed, typically focused on the reaction of one single methanol molecule with benzene.[2,3] However, to mimic realistic industrial methanol-to-olefin (MTO) conditions, one should account for higher methanol loadings. Therefore, the effect of surrounding methanol molecules on the methylation kinetics will be emphasized in this contribution.

It is found that, prior to reaction, multiple methanol molecules tend to form protonated methanol clusters, indicating that the exact location of the Brønsted acid site is not essential for the zeolite-catalyzed methylation reaction.[4] However, methylation reactions from a protonated methanol cluster exhibit higher free energy barriers than a methylation from a single methanol molecule. Finally, comparison with a pure methanol solvent reaction environment indicates that the main role of the zeolite during the methylation of benzene is to provide the acidic proton and to create a polar environment for the reaction.

The metadynamics approach,[5] which is specifically designed to sample rare events, allows exploring new reaction pathways, hereby taking into account the flexibility of the framework and the presence of additional guest molecules in the pores and channels of the zeolite framework. This approach goes beyond the often applied static calculations to determine reaction kinetics, which complement experimental catalytic and spectroscopic data.

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Kristof.DeWispelaere@UGent.be
http://molmod.ugent.be/