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This abstract is for a:

☒ **Contributed Talk**

☐ **Poster**

☐ **Either (If I am not accepted for a contributed talk, I would be happy to present a poster)**

Molecular dynamics kinetic study on the zeolite-catalyzed methanol conversion process

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The methanol conversion process is an appealing zeolite-catalyzed process for the production of base chemicals as it relies on alternative carbon rich feedstocks.[1] We performed free energy simulations of key reaction steps – methylations and framework bound methoxy group formation – to determine accurate reaction kinetics. Earlier kinetic studies, following static approaches, typically focused on the reaction of one reactant molecule.[2] However, to mimic industrial methanol-to-olefin (MTO) conditions, one should account for higher reactant loadings. In this contribution, the effect of additional protic molecules like water or methanol on the reaction kinetics will be emphasized. It is found that the role of these surrounding protic molecules is twofold. Prior to reaction, multiple methanol or water molecules tend to form protonated clusters, hereby delocalizing the position of the Brønsted acid site.[3] Moreover, this behaviour highly depends on the loading of the protic molecules in the zeolite's unit cell. Secondly, the free energy barriers and kinetics of methylation and methoxy group formation are significantly affected by the observed proton mobility and cluster formation as these reactions involve the migration of protons. The metadynamics approach was applied, as this technique is specifically designed to sample reaction pathways in complex molecular environments, hereby taking into account the framework flexibility and the presence of additional guest molecules.[4] Additionally, transition path sampling was applied to sample a larger number of possible reaction pathways.[5] The results are in accordance with and complement a set of experimental catalytic and spectroscopic data.

References

1 K. Hemelsoet, J. Van der Mynsbrugge, K. De Wispelaere, M. Waroquier and V. Van Speybroeck, ChemPhysChem, 2013, **14**, 1526.

2 V. Van Speybroeck, J. Van der Mynsbrugge, M. Vandichel, K. Hemelsoet, D. Lesthaeghe, A. Ghysels, G.B. Marin and M. Waroquier, *J. Am. Chem. Soc.*, 2011, **133**, 888.

3 S. Moors, K. De Wispelaere, J. Van der Mynsbrugge, M. Waroquier and V. Van Speybroeck, *ACS Catal.*, 2013, **3**, 2556

4 B. Ensing, M. De Vivo, Z.W. Liu, P. Moore and M. Klein, *Acc. Chem. Res*, 2006, **39**, 73

5 P.G. Bolhuis, D. Chandler, C. Dellago, P.L. Geissler, *Annu. Rev. Phys. Chem.*, 2002, **53**, 291.