Active olefin producing reaction cycles during methanol conversion in H-SAPO-34: an ab initio study

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The quest for chemical processes based on alternative feedstock was initiated by the depletion of oil reserves and the rapidly increasing demand for base chemicals such as ethylene and propylene. The methanol-to-olefin process (MTO), using natural gas, coal or biomass as raw material, is one of the most important alternatives for olefin production. MTO conversion occurs in acidic zeolites or zeotype catalysts. H-SAPO-34, the archetypal MTO catalyst exhibiting the chabazite topology with a 3-dimensional 8-ring channel structure with elliptic cages at the channel intersections, shows the best performance for industrial applications and the highest selectivity toward light olefins.[1] The generally accepted reaction mechanism for MTO is based on a hydrocarbon pool (HP), in which organic molecules (predominantly polymethylbenzenes) trapped within the anorganic zeolite framework act as co-catalysts.[2] It is believed that these polymethylbenzenes play a crucial role in the olefin elimination reactions.[3] To date, no decisive answer exists to the question which mechanism is responsible for olefin production in H-SAPO-34.[4,5]

In this study a variety of reactions involving hexamethylbenzene are investigated by means of advanced molecular modeling techniques to elucidate possible reaction pathways toward olefin formation in H-SAPO-34 during methanol conversion. Hereby side chain methylation as well as paring like reactions are considered. The experimentally observed carbon label scrambling is essential and provides clues about the involved reaction intermediates. This work focuses on the accurate computation of chemical kinetics of all individual reactions, enabling to determine the rate-determining steps in the proposed catalytic cycles. This type of information cannot be obtained experimentally, due to the occurrence of simultaneous side reactions, and hence theoretical data are indispensable. To elucidate the influence of the framework flexibility and the role of solvent molecules like methanol and water on the olefin producing reaction cycles, further work will also include molecular dynamics simulations.

[1] Chen, J.Q., Bozzano, A., Glover, B., Fuglerud, T. and Kvisle, S., Catal. Today 106 (2005) 103.
[2] Li, J.Z., Wei, Y.X., Qi, Y., Tian, P., Li, B., He, Y.L., Chang, F.X., Sun, X.D. and Liu, Z.M., Catal. Today 164 (2011) 288
[3] Lesthaeghe, D., Horre, A., Waroquier, M., Marin, G.B. and Van Speybroeck, V., Chem. Eur. J. 15 (2009) 10803
[4] Song, W.G., Fu, H. and Haw, J.F., J. Phys. Chem. B 105 (2001) 12839
[5] Haw, J.F. and Marcus, D.M., Top. Catal. 34 (2005) 41