

## Low-barrier route for the MTO reaction in H-SAPO-34: insight from extended cluster models and molecular dynamics

*Kristof De Wispelaere, Karen Hemelsoet, Samuel Moors, Michel Waroquier and Veronique Van Speybroeck*

*Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium*

The methanol-to-olefin (MTO) process is an important alternative for olefin production as waning oil reserves arouse the use of unconventional carbonaceous feedstocks. The archetypal MTO catalyst is H-SAPO-34, exhibiting a high selectivity towards light olefins due to its chabazite topology. It is generally accepted that the MTO process is based on a hydrocarbon pool (HP) with highly methylated benzene compounds as the most active species in H-SAPO-34.[1] Despite the numerous experimental and theoretical studies performed during the last decades, no decisive information exists on the reaction mechanism(s) responsible for olefin production in H-SAPO-34.

In a first part of this contribution it is shown that hexamethylbenzene, the most active HP compound in H-SAPO-34, can subsequently undergo an ipso-methylation, deprotonations and exocyclic methylations upon methanol feed. In this fashion side-chains grow, which can be split off as ethene, propene or isobutene. This low-barrier elimination step is in stark contrast with conclusions of earlier studies on this side-chain route.[2-3] The focus lies on the computation of accurate chemical kinetics of all individual reaction steps using a large finite 44T cluster representative for the H-SAPO-34 material.[4]

A second aspect of this contribution relates to the influence of the flexible zeolite environment on the chemical kinetics of reactions occurring within the nanoporous host. Molecular dynamics simulations are performed to determine the free energy profile along the reaction coordinate of the reactions under study. Methods like metadynamics prove a very useful, yet challenging tool to explore free energy landscapes for chemical reactions.[5] The knowledge of this free energy profile also enables the determination of kinetic coefficients which complement experimental catalytic and spectroscopic data.[6]

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