

The Mechanism of Methanol Conversion: Insight from Extended Cluster Models and Molecular Dynamics

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Abstract

The methanol-to-olefin (MTO) process is an important alternative for olefin production as waning oil reserves arouse the use of unconventional carbonaceous feedstocks. H-SAPO-34 and H-ZSM-5 are the archetypal MTO catalysts and shows a high selectivity toward light olefins and branched hydrocarbons, respectively.

The generally accepted reaction mechanism for the MTO process is based on a hydrocarbon pool (HP), in which organic molecules – predominantly alkenes and polymethylbenzenes – trapped within the anorganic zeolite framework act as co-catalysts.[1,2] However, to date, no decisive answer exists to the question which mechanism is responsible for olefin production in H-SAPO-34.[3] First-principle DFT calculations can aid the unraveling of the MTO mechanisms and the design of an optimal catalyst. Moreover, this contribution shows an innovative approach wherein static calculations and molecular dynamics simulations complement each other.

In the first part of this contribution it is shown that hexamethylbenzene (HMB), the most active HP compound in H-SAPO-34,[4] can subsequently undergo an ipso-methylation, deprotonations and exocyclic methylations upon methanol feed. In this fashion side-chains grow, which can be easily split off as ethene or propene. This low-barrier elimination step is in stark contrast with conclusions of earlier studies on this side-chain route.[5,6] Accurate chemical kinetics of all individual reaction steps are presented.[7]

In the second part of this contribution the influence of three factors on the chemical kinetics of reactions occurring within the nanoporous host is examined in detail. We distinguish: (1) the confinement imposed by the zeolite, (2) the framework flexibility of the catalyst and (3) the presence of additional solvent molecules. Advanced MD simulations are performed to compute the free energy profile along the reaction coordinates. Methods like metadynamics and thermodynamic integration prove a very useful, yet challenging tool to explore free energy landscapes for chemical reactions.[8] The knowledge of this free energy profile enables the determination of kinetic coefficients which complement experimental catalytic and spectroscopic data.[9] To assess the influence of such a dynamical approach, the methylation of benzene is studied in H-ZSM-5.

References

1. Dahl, I. M. and Kolboe, S. *Catal. Lett.* 20, 329 (1993); *J. Catal.* 149, 304 (1994); *J. Catal.* 161, 304 (1996)
2. Svelle, S., Joensen, F., Nerlov, J., Olsbye, U., Lillerud, K. P., Kolboe, S. and Bjorgen, M. *J. Am. Chem. Soc.* 128, 14770 (2006)
3. Haw, J.F. and Marcus, D.M. *Top. Catal.* 34, 41 (2005)
4. Van Speybroeck, V., Hemelsoet, K., De Wispelaere, K., Qian, Q., Van der Mynsbrugge, J., De Sterck, B., Weckhuysen, B.M. and Waroquier, M. *ChemCatChem* 5(1), 173 (2013)
5. Lesthaeghe, D., Horre, A., Waroquier, M., Marin, G.B. and Van Speybroeck, V. *Chem. - Eur. J.* 15, 10803 (2009)
6. Wang, C. M., Wang, Y. D., Xie, Z. K. and Liu, Z. P. *J. Phys. Chem. C* 113, 4584 (2009)
7. Van Speybroeck, V., Van der Mynsbrugge, J., Vandichel, M., Hemelsoet, K., Lesthaeghe, D., Ghysels, A., Marin, G. B. and Waroquier, M. *J. Am. Chem. Soc.* 133, 888 (2011)
8. Ensing, B., De Vivo, M., Liu, Z. W., Moore, P. and Klein, M. L. *Accounts Chem. Res.* 39, 73 (2006)
9. Benco, L., Bucko, T. and Hafner, J. *J. Catal.* 277,104 (2011)

Biography

Kristof De Wispelaere is currently a PhD fellow at the Center for Molecular Modeling. Before, he obtained his MS degree in chemical engineering at Ghent University, Belgium with highest honour. He did his master thesis at the Center for Molecular Modeling on the deactivation of zeolite and zeotype catalysts in the MTO process wherefore he was rewarded with the Solvay Prize. After graduation he received a PhD fellowship from the Research Foundation - Flanders (FWO). His current research projects focus on the theoretical modeling of olefin production during the MTO process in zeotype materials and the applications of advanced Molecular Dynamics techniques in the field of heterogeneous catalysis.