Unraveling the Reaction Mechanism of Methanol Conversion: the Synergy between Extended Cluster Models and Molecular Dynamics

Kristof De Wispelaere,[1]* Karen Hemelsoet, Samuel Moors, Jeroen Van der Mynsbrugge, Michel Waroquier and Veronique Van Speybroeck
1 Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, (Belgium)
*kristof.dewispelaere@ugent.be

Introduction

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 is the archetypal MTO catalyst and shows a high selectivity toward light olefins due to its specific topology. This nanoporous catalyst exhibits the chabazite topology with spacious elliptic cages connected through 8-membered rings.

The generally accepted reaction mechanism for the MTO process is based on a hydrocarbon pool (HP), in which organic molecules (predominantly polymethylbenzenes) trapped within the anorganic zeolite framework act as co-catalysts.[1] It is believed that these polymethylbenzenes play a crucial role in the olefin elimination reactions in the chabazite topology. However, to date, no decisive answer exists to the question which mechanism is responsible for olefin production in H-SAPO-34.[2] First-principle 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.

Materials and Methods

Static calculations are performed on a large finite 44T cluster representative for the H-SAPO-34 material. Geometries are optimized by using a two-layered ONIOM(B3LYP/6-31+g(d):PM3) approach whereas electronic energies are obtained with B3LYP/6-311+g(d)-D, taking the crucial dispersion interactions into account. Molecular dynamics (MD) simulations take into account periodic boundary conditions and are performed with the revPBE functional. For these simulations both VASP and CP2K software packages are utilized.

Results and Discussion

In the first part of this contribution it is shown that hexamethylbenzene (HMB), the most active HP compound in H-SAPO-34,[3] can subsequently undergo an ipso-methylation, deprotonations and exocylic methylations upon methanol feed. In this fashion side-chains grow, which can be easily split off as ethene or propene (Figure 1). This low-barrier elimination step is in stark contrast with conclusions of earlier studies on this side-chain route.[4,5] Accurate chemical kinetics of all individual reaction steps are presented.[6]

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 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.[7] The knowledge of this free energy profile enables the determination of kinetic coefficients which complement experimental catalytic and spectroscopic data.[8] As a case study the methylation of benzene is studied in different zeolite topologies to assess the influence of a dynamical approach.
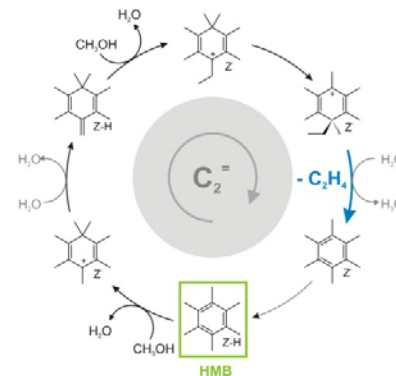
Figure 1. The investigated side-chain cycle for ethene formation in H-SAPO-34.

Significance

A thorough understanding of methanol conversion and its underlying reaction mechanisms enable the optimization of the MTO process. Moreover, a detailed understanding of the influence of the zeolite topology and flexibility on the activity and product selectivity is indispensable to design optimal MTO catalysts.

References

1. Dahl, I. M. and Kolboe, S. *Catal. Let.* 20, 329 (1993); *J. Catal.* 149, 304 (1994); *J. Catal.* 161, 304 (1996)
2. Haw, J.F. and Marcus, D.M. *Top. Catal.* 34, 41 (2005)
3. Van Speybroeck, V., Hemelsoet, K., De Wispelaere, K., Qian, Q., Van der Mynsbrugge, J., De Sterck, B., Weckhuysen, B.M. and Waroquier, M. *ChemCatChem* (2012), DOI: 10.1002/cctc.201200580
4. Lesthaeghe, D., Horre, A., Waroquier, M., Marin, G.B. and Van Speybroeck, V. *Chem. Eur. J*. 15, 10803 (2009)
5. Wang, C. M., Wang, Y. D., Xie, Z. K. and Liu, Z. P. *J. Phys. Chem. C* 113, 4584 (2009)
6. 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)
7. Ensing, B., De Vivo, M., Liu, Z. W., Moore, P. and Klein, M. L. *Accounts Chem. Res.* 39, 73 (2006)
8. Benco, L., Bucko, T. and Hafner, J. *J. Catal.* 277,104 (2011)