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Molecular Modeling in Methanol to Olefins reaction

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Outline keynote lecture

The Methanol-To-Olefin (MTO) process is one of the most prominent technologies nowadays to bypass crude oil. It has experimentally been developed in the past 3-4 decades and is currently being industrialized. [1] Starting from a methanol source, light olefins are produced such as ethene, propene but also some medium weight hydrocarbons (C4,C5, C6 olefins and heavier compounds) (Figure 1). MTO chemistry is performed using a zeotype catalyst with a Brønsted acidic site.[2] The mechanism has been much disputed. For more than 30 years it was believed that two C_1 species couple directly to form the first carbon-carbon bond, however currently there is a consensus that a hydrocarbon pool mechanism operates in which an organic center is trapped in the zeolite pores and acts as co-catalyst (Figure 1). The hydrocarbon pool may be of aromatic type but also alkenes itself can take up this role. In some materials a dual cycle operates depending on the operating conditions. In that case alkenes itself may be successively methylated after which by cracking lower olefins are produced.

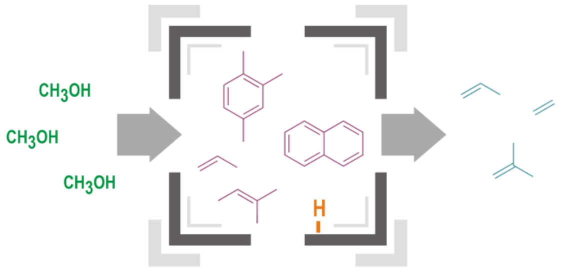

Figure 1. Schematic representation of the supramolecular nature and framework flexibility of the MTO catalyst.

Molecular level understanding of the catalytic process is crucial in developing the catalyst and the process conditions to optimize the product selectivity and increase the lifetime of the catalyst.[3] However modeling efforts need to account for realistic working conditions such as the true nature of the feedstock, framework flexibility, temperature and pressure effects, competitive pathways,… Our approach consists in simulating complex chemical transformations in nanoporous materials using first principle molecular dynamics methods at real operating conditions, capturing the full complexity of the free energy surface.[4] In this lecture, some selected examples within the MTO process are illustrated, where we show the importance of the catalyst topology, acid strength, reaction temperature, feed composition on the governing reaction mechanism. The subtle interplay between various factors enable to enhance the product selectivity or to suppress or enhance the aromatic cycle leading to more or less propene formation. Recently it was shown that post-synthetic incorporation of alkaline earth metals in H-ZSM-5 may also enhance olefin selectivity. [5] It is an example of how meticulously tuning the active site may impact the lifetime of the catalyst and product selectivity. Herein we give molecular level understanding in the nature of the active sites. Throughout the lecture we show to importance of modeling techniques that account for realistic working conditions. The approach followed here may greatly impact catalysis science and reveal insights that were undiscovered so far.

References

1. U. Olsbye, S. Svelle, M. Bjorgen, P. Beato, T. V. W. Janssens, F. Joensen, S. Bordiga and K. P. Lillerud, *Angew. Chem.-Int. Edit*., **2012,** *51*, 5810-5831.
2. K. Hemelsoet, J. Van der Mynsbrugge, K. De Wispelaere, M. Waroquier and V. Van Speybroeck, *Chemphyschem*, **2013**, *14*, 1526-1545.
3. V. Van Speybroeck, K. De Wispelaere, J. Van der Mynsbrugge, M. Vandichel, K. Hemelsoet and M. Waroquier, *Chemical Society Reviews*, **2014**, *43*, 7326-7357.
4. K. De Wispelaere, S. Bailleul, V. Van Speybroeck , *Catalysis Science & Technology* , **2016**, *6*, 2686 – 2705.
5. I. Yarulina, S. Bailleul, A. Pustovarenko, J. Ruiz-Martinez, K. De Wispelaere, J. Hajek, B.M. Weckhuysen, K. Houben, M. Baldus, V. Van Speybroeck, F. Kapteijn, J. Gascon , *ChemCatChem* , **2016**, *8* (19), 3057–3063.

Short CV

Veronique Van Speybroeck is full professor at the Ghent University and head of the Center for Molecular Modeling. She graduated as an engineer in physics in 2007 and obtained her PhD in 2001 from the Ghent University. After her PhD she received a postdoctoral fellowship from the National Fund for Scientific Research Flanders and had the possibility to travel to various foreign institutes for short periods. She is one of the founders of the Center for Molecular Modeling, which is a research center currently composed of about 35 researchers and which focuses on multidisciplinary research between physics, chemistry and engineering with the aim to design molecules, materials, processes at the nanoscale.

Veronique Van Speybroeck built up a large expertise in first principle kinetics in nanoporous materials in the frame of an ERC starting grant, awarded in 2010 on a subject dealing with accurate prediction of chemical kinetics of catalytic reactions taking place in nanoporous materials. Within the framework of this research she showed that theoretical methods have matured to a level where rate coefficients of elementary reactions can now be calculated with near chemical accuracy provided the reaction takes place at a well defined active site and provided the mechanism is known.

Her current research interests focus on first principle molecular dynamics simulations of complex chemical transformation in nanoporous materials, for which she received an ERC Consolidator grant in 2015. With a team of physicist, chemists and engineers, she is studying catalysis in zeolites, metal organic frameworks and covalent organic frameworks using advanced molecular dynamics techniques to mimic experimental conditions as close as possible with theoretical methods.

She is also an elected member of the Royal (Flemish) Academy for Science and the Arts of Belgium.