Unraveling complex chemical and physical transformations in nanoporous materials at operating conditions

Prof. Veronique Van Speybroeck

Center for Molecular Modeling, Ghent University, Technologiepark 46, 9052 Zwijnaarde, Belgium
veronique.vanspeybroeck@ugent.be

In this lecture, the power of first principles molecular dynamics simulations to study complex transformations in nanoporous materials, which may refer to either physical and/or chemical transformations, will be highlighted. Chemical conversions in nanoporous materials are omnipresent in heterogeneous catalysis. Within this respect, zeolites are today's workhorses in industrial catalysis. However, in the last decades, also other intriguing materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have entered the scene. Given the relative softness of these materials, the frameworks themselves may be prone to large-amplitude variations in their structure under realistic operating conditions of temperature, pressure, and guest loadings. While these variations may preserve the chemical integrity, they can also lead to the breaking of chemical bonds and the introduction of structural defects in these materials at operating conditions. The altered framework environment introduced by these defects may hereby act as a favorable interaction site, such that chemical and physical transformations are sometimes closely intertwined in these materials.

Earlier simulation techniques at the nanoscale were often restricted to rather idealistic representations of the materials, for example by considering perfectly crystalline, defect-free materials. Furthermore, chemical reactions were often explored based only on knowledge of the potential energy surface at 0 K and information on one single transition state. At real operating conditions, however, the nature of chemical transformations taking place at the nanometer is much more complex due to the interplay of several factors such as the number of particles present in the pores of the material, inherent framework flexibility, competitive pathways, and entropy effects. In such cases, the textbook concept of a single transition state is far too simplistic. Moreover, due to the inherently multiscale nature of the observed function of the material, the whole complexity of the underlying chemical phenomena can no longer be captured by a single computational technique. As a result, awareness has grown that more complex theoretical models are necessary to bridge the gap between experimental observations and theoretical predictions.

This lecture highlights the power of advanced molecular dynamics techniques to sample the free energy surface at operating conditions of temperature, pressure, and guest loading. These advanced sampling molecular techniques account for the complexity of the transformation in close agreement with experiment. Examples are taken from zeolite catalysis as well as physical and chemical transformations within metal-organic frameworks.

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