# Modeling complex chemical and physical transformations in nanoporous materials at operating conditions

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In this lecture, state of the art molecular modeling techniques will be highlighted to study complex transformations in nanoporous materials, which may either refer to physical and/or chemical transformations. 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 have entered the scene, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). Under realistic operating conditions of temperature, pressure, and guest loadings, these framework materials themselves may be prone to large-amplitude variations in their structure. 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, which allow for the exploration of the free energy surface at operating conditions, may account for the complexity of the transformation in close agreement with experiment. Within this talk, the potential of these techniques to unravel the nature of reactive intermediates for cracking of olefins over acidic zeolites and to unravel prevailing reaction routes within the methanol to hydrocarbons process is illustrated. Similar free energy sampling methods may also be adopted to study physical and chemical transformations in metal-organic frameworks. Due to their open structure, the potential of these materials to break chemical bonds and create local defects is even larger, as will be exemplified in this lecture by highlighting a variety of framework materials ranging from rigid to flexible materials.

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