Bridging length and time scales in catalysis for C_1 chemistry : from the molecule to the catalyst particle level

Veronique Van Speybroeck[1]*
[1]*Ghent University, Center for Molecular Modeling, Technologiepark 46, 9052 Zwijnaarde, Belgium*
*veronique.vanspeybroeck@ugent.be

Introduction

Catalytic solids used in industrial applications show an intriguing high degree of complexity with phenomena occurring across a wide range of length and time scales, which furthermore highly impacted by operating conditions, i.e. temperature, moisture, presence of water, etc. A prime example of such complex catalysts is found in C_1 catalysis to convert molecules like CO_2, CH_3OH to high-value olefins and other chemical building blocks. For Methanol-to-Olefin catalysis, Brønsted acidic zeolites, which may be modified post-synthetically, are typically used; whereas CO_2 conversion typically employs a mixed multifunctional catalysts combining metallic and zeolite components. Within this talk, I will show new challenges and opportunities in modeling complex catalytic cycles bridging length and time scales starting from the molecular scale with the ambition to reach crystal particle level. This is a highly ambitious task, needing realistic representations of the catalyst at work, accurate methods to sample the free energy surface in a dynamic way and derivation of kinetics of processes in a multi-length-time scale window.

When a feed of molecules is sent over solid catalyst following events take place: first molecules need to enter the crystal particle possibly already experiencing a surface barrier, next they undergo intracrystalline diffusion towards the active sites, where a reaction can take place and afterwards the formed products need to diffuse out of the crystal (Figure 1). All these events are characterized by vastly different length and time scales. Currently transport phenomena are mostly modeled with classical force fields whereas reactions are treated with quantum mechanical (QM) methods. To account for the complexity at the active site, e.g. dynamic changes of active sites under operating conditions, discovery of multiple competing reaction paths, high temperature mobile adsorbates, molecular dynamics (MD) methods at operating conditions are mandatory. First principle MD methods have become a strong vehicle to dynamically explore complexity at the active site, however their routine usage is prohibited by the computational cost and the difficulty in finding interesting reactive paths in phase space.[1] To mitigate this issue, we need methods that allow to evaluate the interatomic forces in a much more computationally efficient way compared to QM, however keeping the same accuracy. In this respect recent avenues on derivation of Machine Learning Potentials (MLPs) derived from underlying QM that can be used in subsequent MD simulations are very promising. A major point of attention is efficient training data generation for the complex catalysts under study. Within this talk, I will show key examples within zeolite catalysis to derive very accurate MLPs, reaching chemical accuracy, which allow to study catalytic events at operating conditions over longer length and time scales.

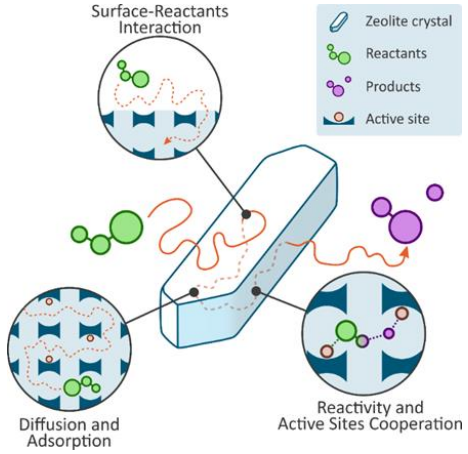

Figure 1. : Illustration of various steps taking place during a zeolite-catalyzed reaction.

To bridge from the molecule to the particle level, one must also consider transport phenomena. I will show that for diffusion of intermediates within the pores of nanoporous frameworks where explicit interactions with active sites can occur, also QM based methods are necessary. Additionally, reaction and diffusion may be entangled. A recent discovery within my group, showed how ketene when traveling through 8-membered rings of H-SAPO-34 in presence of water reacted along the diffusion path. All these findings lead to the conclusion that we need consistent kinetic models from the molecule to the crystal particle level, to unravel the behavior of industrially important catalysts as found in C_1 catalysis. I will show how developments at the intersection of machine learning, enhanced sampling and quantum mechanical based methods open a window of opportunity to bridge length and time scales for modeling complex catalytic cycles at operating conditions.

Materials and Methods

A series of computational methods are used, encompassing periodic Density Functional Theory calculations with VASP and CP2K, enhanced sampling molecular dynamics simulations. Machine learning potentials are derived using equivariant neural networks and active learning procedures implemented in psiflow. Transfer learning is used to refine the energies beyond Density Functional Theory. Furthermore integrated methodologies are developed to simultaneously learn the energies, forces and reactive paths in phase space.

Results and Discussion

Proof of principle for new methods that bridge length and time scales in key steps of C_1 conversion processes will be shown : mechanistic pathways for the first carbon-carbon bond formation in zeolite catalyzed methanol to hydrocarbons, influence of topology and acid site density on transport of ethene, propene, substituted benzenes and reactive intermediates like ketene in zeolites, lifetimes of intermediates like adsorbed alkenes at operating conditions, interaction of guest molecules with the external zeolite surface.

Significance

A fundamental understanding of the multi length/time scale phenomena taking place for industrially relevant zeolites is of utmost importance to understand and design industrial processes such as the conversion of methanol and selective transformation of CO_2 to high-value light olefins over zeolite and bifunctional catalysts.

References

1. Van Speybroeck, V.; Bocus, M.; Cnudde, P.; Vanduyfhuys, L., Operando Modeling of Zeolite-Catalyzed Reactions Using First-Principles Molecular Dynamics Simulations. *ACS Catal* **2023,** *13* (17), 11455-11493.