SURFACE REACTIVITY AS A MANY BODY MULTISCALE PROBLEM

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In this talk, we will demonstrate that surface reactivity even of the simplest heterogeneous reactions is a many body problem. The disparity in length and time scales encountered in these processes is tremendous. Phenomena at the fluid-surface interface, at quantum and molecular length and time scales, range from Å to several nanometers and render classical continuum equations, often referred to as mean field equations, inapplicable. Examples of such phenomena include intermolecular forces, nucleation, spinodal decomposition, and quantum reaction effects. On the other hand, reactors are often in the meter length scale with a residence time of seconds to minutes. Application of quantum calculations and molecular simulations, such as Monte Carlo or molecular dynamics, to the entire spectrum of scales is currently impractical.

In this talk, we describe hierarchical multiscale simulations for modeling such reaction systems from first principles. The unity bond index, quadratic exponential potential (UBI-QEP) or bond-order conservation (BOC) of Shustorovich and co-workers is employed as an efficient, semi-empirical means of predicting activation energies of large reaction mechanisms of catalytic reactors with input from experiments or density functional theory. Transition state theory is employed to estimate pre-exponentials, which in conjunction with the energetics, provide an initial set of reaction rate constants for each local arrangement (class) of adsorbates. Density functional theory (DFT) is used to refine the input to the semi-empirical technique and/or to assess self-consistency of the important reaction steps identified via sensitivity analysis Refinement of such reaction rate constants is possible using suitable experimental data and efficient optimization tools. These data are then used as input in lattice Monte Carlo simulations. The latter simulations solve directly a master equation as a Markov process and are properly coupled with continuum, reactor scale simulations. Application of this approach to understanding the chemistry in partial oxidation of methane on Pt and ammonia decomposition on Ru will be presented and contrasted to experiments.

While MC simulations can capture nanometer spatial inhomogeneities, they are too intensive for larger scales. Novel coarse-grained Monte Carlo simulations will be presented and demonstrated to be an important step toward meeting the length scales gap.