447e Multiscale Modeling of Catalytic Activity: from Single Crystals to Defected and Polycrystalline Materials

Soumitra Deshmukh, Abhijit Chatterjee, and Dionisios G. Vlachos

The problem of first principles modeling of more realistic catalysts consisting of many crystallographic planes as well as defects has been a major theoretical and computational challenge. Adsorption, surface diffusion, and surface reaction on the catalyst surface are governed by very separate timescales [1, 2]. This disparity in scales renders prediction of activity of a catalytic process truly challenging. Two separate techniques, namely the quantum mechanical density functional theory (DFT) and the kinetic Monte Carlo (KMC) method are often used to model various aspects of catalytic processes. However, they are both limited to different but still relatively short length and timescales. A recently developed coarse-grained Monte Carlo (CGMC) technique by our group [3, 4] is a useful tool in bridging length and time scales from the quantum to the meso or macroscopic. The technique uses a spatially adaptive lattice to capture the essential features with high resolution and a coarse mesh in relatively inactive regions. It also allows coarse-graining in time to reach realistic scales [5] and to cope with the typical problem of fast diffusion [6].

While the existing CGMC is adequate to handle a single component system, most surface reactions involve many surface species and potentially short range interactions. These issues necessitate extension of the current framework to multicomponent systems and to short potentials. In this talk, a new theoretical framework will be presented to fill in this gap. The resulting model is a microscopic analogue of the well-known Stefan-Maxwell equations but accounts explicitly for interactions, correlations, microscopic mechanisms, etc. in a rigorous, coarse-grained, statistical mechanics-based fashion. Results for microscopic rate processes are obtained from periodic slab DFT simulations using the DACAPO code on model catalysts. In this work, we study the catalytic ammonia synthesis and decomposition, as a benchmark system. Synthesis has been of interest for a long time due to its use in fertilizers, whereas decomposition is currently being explored for CO-free production of hydrogen for fuel cells. Hybrid DFT/CGMC simulations are employed to understand the effect of defects of catalyst surfaces on reactivity of the ammonia chemistry. It will be shown that mean field models fail completely to explain experimental data, whereas our hybrid simulations provide a systematic way toward first principles modeling of defected and polycrystalline catalysts.

[1] S. Raimondeau and D. G. Vlachos, "Recent developments on multiscale, hierarchical modeling of chemical reactors", Chem. Eng. J. 90(1-2), 3-23 (2002).

[2] D. G. Vlachos, "A review of multiscale analysis: Examples from systems biology, materials engineering, and other fluid-surface interacting systems", Adv. Chem. Eng. accepted, invited (2005).

[3] A. Chatterjee, M. A. Katsoulakis, and D. G. Vlachos, "Spatially adaptive grand canonical ensemble Monte Carlo simulations", Phys. Rev. E 710267021-0267026 (2005).

[4] A. Chatterjee, D. G. Vlachos, and M. A. Katsoulakis, "Spatially adaptive lattice coarse-grained Monte Carlo simulations for diffusion of interacting molecules", J. Chem. Phys. 121(22), 11420-11431 (2004).

[5] A. Chatterjee, D. G. Vlachos, and M. A. Katsoulakis, "Binomial distribution based t-leap accelerated stochastic simulation", J. Chem. Phys. 122024112-024111-024116 (2005).

[6] M. A. Snyder, A. Chatterjee, and D. G. Vlachos, "Net-event kinetic Monte Carlo for overcoming stiffness in spatially homogeneous and distributed systems", Comput. Chem. Eng. 29(4), 701-712 (2005).