This presentation will summarize some of the work I have done to elucidate the importance of frequently neglected environmental complexities in heterogeneous catalysis, such as the roles of underlying support material and solvent. I will begin by describing the partition function of a heterogeneous catalyst approximated as a mean field lattice. To improve upon the mean field approximation, a thermodynamically consistent model for the lateral interactions between adsorbates will be constructed through the use of a many-body expansion of the lattice energy. We then consider the adsorption of species to the catalyst from solution through a diffusion-limited Langmuir adsorption model. Finally, we incorporate the adsorption of charged species by treating the catalyst-solution interface as a double-layer capacitor, wherein adsorption of anions to the catalyst surface charges the capacitor.

Based on this complex model, we investigate the solution-phase heterogeneous catalytic esterification of 1-propanol to methyl propionate under basic conditions on Pd(111). We find that the propanol substrate adsorbs to the catalyst as the neutral alcohol, not as the deprotonated alkoxide. Under steady state conditions, the catalyst surface has a high H coverage, though not high enough to be considered poisoned, and this results in the destabilization of all other reaction intermediates through lateral interactions. The catalyst activity is ultimately limited by the rate of initial C-H bond scission in the propanol substrate, and by the slow removal of H atoms by oxygen. The mechanistic insight into alcohol esterification afforded by microkinetic modeling helps rationalize the observed activity of the unpromoted palladium catalyst, as well as predict the role of promoter species such as tellurium and bismuth, which are known to improve both the activity and the selectivity for this reaction.