

Bridging the pressure gap in theoretical models of gas-solid adsorption

Carson J. Mize, Lonnie D. Crosby, and Sharani Roy

Akin to the pressure gap between laboratory surface-science experiments performed under ultrahigh vacuum and industrial surface chemistry conducted under high gas pressures, theoretical models of gas-solid interfacial chemistry are often developed for low gas concentrations yet applied to surface phenomena that occur under high gas concentrations. The primary reason for this discrepancy is the steep cost of computing chemical properties at high surface concentrations (or coverages) of the gas using electronic structure methods. To address this challenge and to study the percolation of gases just beneath the surface, i.e., into the subsurface, at high coverages, we have developed lattice-gas adsorption models that include surface as well as subsurface sites in a crystalline solid and are fully parameterized using density functional theory (DFT). We have applied the models to study the adsorption of atomic oxygen on the Ag(111) surface, first as functions of coverage and temperature using canonical Monte Carlo simulations, and next as functions of pressure and temperature using grand-canonical Monte Carlo simulations. The simulations show the conditions under which subsurface adsorption occurs and provide insight into how subsurface adsorbates might participate in catalytic partial oxidation on silver surfaces. The probable adsorption geometries predicted by Monte Carlo are further investigated by DFT to understand their electronic properties, such as the projected density of states, core-electron binding energies, and subsurface-to-surface diffusion pathways. Overall, the lattice-gas adsorption model provides a simple and transferable theoretical framework to explore the competition between surface and subsurface adsorption in gas-surface systems.