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Step decoration studied with first-principles statistical mechanics YONGSHENG ZHANG, KARSTEN REUTER, Fritz-Haber-Institut der Max-Planck Gesellschaft — With respect to oxidation catalysis or oxide formation, surface defects like steps, kinks, or vacancies are widely believed to play a decisive role, e.g. in form of active sites or as nucleation centers. Despite this suggested importance, first-principles investigations qualifying this role for gas-phase conditions that are representative of these applications are scarce. This is mostly due to the limitations of electronic-structure calculations in tackling the large system sizes and huge configuration spaces involved. We overcome these limitations with a first-principles statistical mechanics approach coupling density-functional theory (DFT) calculations with grand-canonical Monte Carlo simulations, and apply it to obtain the phase diagram of on-surface O adsorption at a (111) step on a Pd(100) surface. The link between the electronic and mesoscopic techniques is achieved by a lattice-gas Hamiltonian expansion, in which we parameterize the lateral interactions affected by the step from DFT calculations at a Pd(117) vicinal surface, and all remaining lateral interactions from calculations at Pd(100). For a wide range of O gas-phase conditions we find the (111) step to be decorated by a characteristic zig-zag structure. Intriguingly, this structure prevails even up to the elevated temperatures characteristic for catalytic combustion reactions, where only small amounts of disordered oxygen remain at the Pd(100) surface.

Yongsheng Zhang
Fritz-Haber-Institut der Max-Planck Gesellschaft

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