

First-principles, atomistic thermodynamics for oxidation catalysis

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Present knowledge of surface properties and the function of materials is largely based on studies (experimental and theoretical) that are performed at low temperatures and ultra-low pressures. However, the majority of everyday applications, like e.g. catalysis, operate at atmospheric pressures and at temperatures often higher than 300K. Analyzing this gap, I will outline how a combination of density-functional theory and thermodynamics can be employed to construct a phase diagram of the most stable surface structures in the whole experimentally accessible (T, p) -space from ultra-high vacuum to technically-relevant pressures and temperatures.¹ The crucial importance of such phase diagrams will be emphasized: Only when gas phase parameters are changed without crossing from one phase in (T, p) -space to another one, the "pressure gap" can be bridged and corresponding low-pressure studies may be used to model high-pressure applications. I also stress that phase coexistence, that arises in regions in the phase diagram close to a boundary between different stable structures and where then an enhanced dynamics can be expected, might be particularly important for catalytic applications.² The example of CO oxidation over a RuO₂(110) model catalyst will be used to illustrate the concepts and conclusions that can be derived from such a *first-principles atomistic thermodynamics* surface phase diagram.

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¹ K. Reuter and M. Scheffler, Phys. Rev. B **65**, 035406 (2002).

² K. Reuter and M. Scheffler, Phys. Rev. Lett. (*submitted*), cond-mat/0211602.