The steady-state of catalysis
studied by first-principles statistical mechanics

Karsten Reuter[a,b,*], Daan Frenkel[b], and Matthias Scheffler[a]

[a] Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Germany)
[b] FOM-Institut for Atomic and Molecular Physics,
Kruislaan 407, SJ1098 Amsterdam (The Netherlands)

* reuter@fhi-berlin.mpg.de

A quantitative modeling of catalytic activity requires a high accuracy in the description of each of the manifold of involved elementary processes, as well as a correct statistical mechanics treatment of the interplay between them. We attempt such a modeling by first-principles kinetic Monte-Carlo simulations, i.e. using rates derived from density-functional theory as input. Modeling the CO oxidation over $RuO_2(110)$ we obtain a full (T, p_{O2}, p_{CO}) turnover frequency diagram, which agrees well with all available experimental data. The surface configurations actuating catalysis are found to be strongly influenced by kinetic effects, most prominently under gas phase conditions where the system is close to a surface phase transition. The highest steady-state turnover rates are obtained for the resulting phase coexistence at the surface, which enables specific reaction mechanisms that do not operate at other temperature and pressure conditions including ultra-high vacuum.