MAR06-2005-000365

Abstract for an Invited Paper
for the MAR06 Meeting of
the American Physical Society

First-principles statistical mechanics for heterogeneous catalysis

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We present a first-principles approach to heterogeneous catalysis that quantitatively describes the activity over a wide range of realistic environmental situations of varying temperatures and pressures. Within a first-principles statistical mechanics setup [1], density-functional theory is first used together with transition state theory to accurately obtain the energetics of all relevant processes. Subsequently the statistical mechanics problem is solved by kinetic Monte Carlo simulations. This two-step approach enables us to gain microscopic insight into the system, following its full dynamics from picoseconds up to seconds and explicitly considering the detailed statistical interplay of all elementary processes, i.e., by fully accounting for the correlations, fluctuations and spatial distributions of the chemicals at the catalyst surface. In the application to CO oxidation at a $RuO_2(110)$ model catalyst, we compute the composition and structure of the catalyst surface in reactive environments ranging from ultra- high vacuum to technologically relevant conditions with pressures of the order of atmospheres and elevated temperatures [2]. For all these conditions the obtained conversion rates are in unprecedented quantitative agreement with existing experimental data. The catalytic activity is narrowly peaked in environments, where the surface kinetics builds a disordered and dynamic adsorbate composition at the surface. In the full concert of the large number of processes occurring in this active state, the chemical reaction with the most favorable energy barrier contributes only little to the overall CO_2 production.

[1] K. Reuter, D. Frenkel, and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004).
[2] K. Reuter and M. Scheffler, Phys. Rev. B, submitted.