

**Stability, Composition and Function of
Palladium Surfaces in Oxidizing
Environments:
A First-Principles Statistical Mechanics
Approach**

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Abstract

The catalytic oxidation using transition metals (TM) as the active material is an important technological process, which is still not fully understood. Recently, there has been an increasing awareness that the surface of the TM catalysts employed might be oxidized under the oxygen-rich conditions of the catalytic reaction (ambient pressures of O₂ and other reactant gases). The resulting changes in the composition and structure of the surface can then also strongly influence the catalytic activity of the material.

In the present work the catalytic CO oxidation over the Pd(100) surface is studied as a model system. Recent experimental results for this system suggest that the Pd(100) surface might actually be oxidized under conditions as applied in industrial oxidation catalysis. However, it is still being discussed, if the observed oxidic phase is already a thick, bulk-like oxide film or a nanometer thin surface oxide layer, and if the actual active state of the catalyst under reaction conditions is then mainly dominated by a metallic or an oxidic phase.

To address this topic from a theoretical point of view a multiscale modeling approach has been employed in this work. To describe the system quantitatively on an atomic (microscopic) level density-functional theory (DFT) has been used. The results of the DFT calculations have then been combined with concepts from thermodynamics and statistical mechanics to transfer the information obtained in the microscopic regime to meso- and macroscopic length and time scales.

In a first step the atomistic thermodynamics approach is used to obtain a large scale picture about the thermodynamic stability of different phases in a *constrained* thermodynamic equilibrium with an O₂ and CO gas phase (i.e. the formation of CO₂ is not considered). Focussing on temperature and pressure conditions representative of technological oxidation catalysis it is found that a thin surface oxide structure or a CO covered metal surface are the relevant system states under these conditions. In a second refining step the stability of the surface oxide structure under steady-state conditions is then investigated using kinetic Monte Carlo (kMC) simulations, now explicitly taking into account the on-going CO₂ formation. The result is that despite the catalytic CO oxidation reaction the surface oxide on Pd(100) is still stable under stoichiometric $p_{\text{O}_2}/p_{\text{CO}}$ ratios in the gas phase at elevated temperatures. This indicates the importance of this surface oxide and calls for detailed studies evaluating its contribution to the overall catalytic activity.

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