First-principles Statistical Mechanics Approach to Step Decoration at Solid Surfaces

von

M. Sc.

Yongsheng Zhang

Erstgutachter: PD Dr. Karsten Reuter

Zweitgutachter: Prof. Eberhard K. U. Gross

Disputationstermin: 14. May 2008

Abstract

As prominent defects at solid surfaces atomic steps are commonly perceived as playing some kind of special, if not decisive role for the surface properties or functions in materials science applications. When aiming to qualify this role at the atomic scale an important first task is to identify the structure and composition at the step edge under realistic gas-phase conditions that are representative for the targeted application. From the modeling side, this requires two ingredients: A reliable description of the energetics at the surface, in other words of the chemical bonds that are formed there. And on the other side a proper treatment of the manifold of processes that can occur, in particular also due to the contact with the gaseous environment at finite temperatures.

In this thesis this problem is addressed with a first-principles statistical mechanics approach, *i.e.* with an approach that is based entirely on a reliable first-principles energetics. Since the evaluations of the partition functions required to at least thermodynamically account for the statistical interplay at finite temperatures would necessitate on unfeasible amount of first-principles total energy calculations, the approach relies on parameterizing as intermediate between the electronic and mesoscopic regime a coarse-grained lattice model, which is then employed in the statistical simulations. The approach is illustrated using the interaction of an oxygen atmosphere with a close-packed (111) step at Pd(100) as example. Apart from the methodological advances that are achieved the major result for this application is then that the specific way how oxygen atoms decorate the step even in environments with pressures of the order atmospheres and elevated temperatures around 1000 K is obtained. Since such gas phase conditions are representative for an important catalytic application like the high-temperatures combustion of methane, this work thus provides first first-principles insight into the structure and composition at a prominent defect at the surface of a working model catalyst.

*For Yuanyuan
and my parents*

Contents

II   Ordering Behavior of Oxygen Atoms at the Pd(100) Surface   53

III   Ordering Behavior of Oxygen Atoms under the Influence of a Step   81

List of Figures

List of Tables