Chapter 9

Summary And Outlook

New developments within material science will eventually rely on a microscopic understanding of the desired functionalities. An important field, where such a predictive modeling or rational design would be priceless, is heterogeneous catalysis. The results presented in this work aim to provide a step towards a better understanding of the processes taking place in heterogeneous oxidation catalysis from a microscopic point of view. As a model system the CO oxidation reaction on the Pd(100) surface has been investigated. Recent experimental results for this system suggest that under conditions of ambient oxygen pressures, as applied in industrial oxidation catalysis, the Pd(100) surface might actually be oxidized. The nature of the oxidic phase (a thick bulk oxide or a monolayer thin surface oxide), though, as well as the active state of the Pd(100) surface under reaction conditions (metal or oxidic phase) is still being discussed.

In the present work a multiscale modeling approach has been employed to address this topic. Density-functional theory (DFT) has been used to quantitatively describe the elementary processes occurring on electronic and atomic length and time scales (fs–ps, Å). To assure the required high accuracy in the underlying energetics the full-potential-(L)APW+lo method has been used, and all surface calculations were performed within the supercell approach. The DFT results are then combined with concepts from thermodynamics and statistical mechanics to achieve an appropriate linking to the meso-/macroscopic regime covering length scales large enough to capture the statistical interplay among the manifold of elementary processes, as well as covering times up to seconds or longer. Since the here applied methods do not rely on any empirical or fitted parameters, they are referred to as *first-principles* (or *ab initio*) methods.

In a first step within the here employed multiscale modeling hierarchy, the Pd(100) surface has been investigated in contact with a pure oxygen gas phase. The *ab initio* atomistic thermodynamics approach has been used to compare the stability of the clean metal surface, different oxygen adlayers, the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide and the bulk oxide in thermodynamic equilibrium with the oxygen gas phase. Within this approach it was possible to cover the entire range of possible gas phase conditions,

ranging from UHV to ambient pressures. It was found that a $c(2 \times 2)$ adlayer experimentally observed under UHV conditions does not appear as a stable phase under any temperature and pressure conditions of the oxygen gas phase. This suggests that the $c(2 \times 2)$ structure is only a meta-stable phase, which forms due to the adsorption kinetics in the UHV experiments. The $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide structure, on the other hand, turns out to be stable over an extended temperature and pressure range, forming a new phase aside from simple oxygen adlayers and thick bulk-like oxide films. These findings are in excellent agreement with recent surface x-ray diffraction (SXRD) measurements. It could be shown that these conclusions are not influenced by the remaining uncertainties underlying the DFT calculations (computational setup, approximate exchange-correlation functional), as well as the atomistic thermodynamics approach (approximations to the Gibbs free energy). However, the exact temperature and pressure conditions for the transition between the different phases does strongly depend on the choice of the employed exchange-correlation functional. Comparing to the SXRD measurements the accuracy of the PBE exchange-correlation functional appears to be superior to the RPBE and LDA in this respect.

Under very oxygen-rich conditions the PdO bulk oxide is eventually the most stable phase. Also experimentally the formation of PdO on Pd(100) is observed with increasing oxygen content in the gas phase, which is accompanied by a roughening of the surface, suggesting that the growth of PdO proceeds via the formation of small, three-dimensional crystallites. To obtain a first insight into the shape of these crystallites, the stability of all low-index PdO surfaces has been investigated to set up a Wulff construction representing the equilibrium shape of a single crystal. It was found that the determined shape is rather independent of the chosen exchange-correlation functional. The main limitation of this approach is the restricted configurational space sampled in this study. Surface reconstructions, which could lower the surface energy and thus influence the equilibrium shape, could not explicitly be considered at this point. However, estimates on their effects allow the conclusion that reconstructions on the (111) facet are most likely most efficient in affecting the deduced equilibrium shape. It could further be shown that the stability of the oxide surfaces is not determined by their polarity as expected from a traditional electrostatic point of view. It is rather the coordination of the surface oxygen atoms that appears to be decisive for the stability of the different surface terminations.

Increasing the complexity in the here employed hierarchical approach, the Pd(100) system has been studied in a second step in contact with a two component gas phase containing both reactants, the O_2 and the CO. The atomistic thermodynamics approach has been used to investigate the Pd(100) surface in a *constrained* thermodynamic equilibrium with an oxygen and CO gas phase. In this approach the formation of CO_2 in the gas phase and at the surface is not considered, and the effect of the surrounding gas phase on the surface structure and composition is modeled to a first approximation through the contact with independent reservoirs representing the reactants. The resulting surface phase diagram, presenting the possibly most stable structures for the entire range of possible temperature and pressure conditions of the

O_2 and CO gas phase, can be divided into three parts. In one part of the surface phase diagram simple adlayer structures of O or CO on the Pd(100) surface are stable, in a second part structures involving the reconstructed $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide structure are stable, and the third part marks the stability region of thick bulk-like oxide films. It could be shown that ordered co-adsorbed layers of O and CO on the Pd(100) surface are not stable under any of the investigated temperature and pressure conditions, due to strongly repulsive interactions between the two adsorbed species. This is in good agreement with experimental results, where it was found that O and CO prefer to form separate domains on Pd(100). The additional adsorption of CO on the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide does, however, lead to stable structures. Focusing on gas phase conditions representative for technological oxidation catalysis $(T = 300 - 600\,\text{K}, p \approx 1\,\text{atm})$ it was found that within the constrained atomistic thermodynamics approach it is either the surface oxide structure or a CO covered Pd(100) surface that is stable under such conditions. The stability region of the bulk oxide, on the other hand, does not extend to these gas phase conditions. Again these conclusions are not affected by the choice of the exchange-correlation functional. Using different exchange-correlation functionals shifts the boundaries between the different phases in the phase diagram to some extent. For all three employed functionals (PBE, RPBE and LDA), though, the catalytically relevant gas phase conditions are always right at the boundary between the surface oxide structure and the CO covered Pd(100) surface, whereas the bulk oxide is not important. This suggests the monolayer thin surface oxide structure as a most relevant structure for the CO oxidation reaction on Pd(100). It has to be considered, though, that within the constrained atomistic thermodynamics approach, as it has been applied in this work, configurational entropy is not included. At finite temperatures a first effect of configurational entropy would be to smear out the phase boundaries in the phase diagram and create coexistence regions, where e.g. parts of the Pd(100) surface are covered by CO whereas other parts exhibit the reconstructed surface oxide structure. Additionally, the kinetics of the on-going catalytic CO_2 formation might significantly change the stability of the different phases as obtained in the constrained equilibrium approach.

Building on the knowledge obtained in the previous modeling steps, in a last refining step this study has therefore been focussed on the relevant (T, p)-range to investigate the stability of the surface oxide with first-principles kinetic Monte Carlo (kMC) simulations, i.e. by now explicitly including the on-going CO_2 formation. Since at present a lattice-free first-principles kMC simulation to describe the transition between structurally different phases would require some more conceptional developments and in addition would still be computationally prohibitive to perform, a suitable lattice model had to be developed. To avoid the explicit and involved modeling of the actual decomposition of the surface oxide structure, the modeling is concentrated on the onset of the decomposition process. Starting under temperature and pressure conditions, where the surface oxide is certainly the most stable phase in the thermodynamic surface phase diagram, this onset of the surface oxide decomposition under reaction conditions (i.e. including the CO_2 formation) was followed with increasing

133

CO content in the gas phase by evaluating the presence of surface oxygen species in the oxide lattice. Compared to the results obtained in the constrained atomistic thermodynamics approach the on-going catalytic reaction at the surface is found to slightly decrease the stability region of the surface oxide for $T = 400\,\text{K}$. It could be shown, though, that for a pressure ratio of $p_{O_2}/p_{CO} \approx 10$, i.e. slightly oxygen-rich conditions, the surface oxide structure is stabilized even despite the CO_2 formation. This is in excellent agreement with recent reactor-STM experiments performed under very similar (T, p)-conditions. For a temperature of $T = 600\,\text{K}$ the stability of the surface oxide is even more enhanced. Here, the simulation results predict that the surface oxide is stable even for a pressure ratio of $p_{O_2}/p_{CO} = 1$, i.e. for gas phase conditions representative of technological CO oxidation catalysis.

Employing a multiscale modeling approach it was thus possible to obtain a first insight into the structure and composition of the Pd(100) surface under reaction conditions based on a microscopic understanding. It could be shown that under temperature and pressure conditions as typically applied in industrial catalytic CO oxidation it is well possible that the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide contributes to the active state of the Pd(100) surface. The results suggest furthermore that there might actually be a coexistence between patches of metallic Pd(100) covered by CO, and patches of the surface oxide (possibly also with adsorbed CO). Under steady-state conditions this could then lead to a continuous formation and decomposition of the oxidic phase. Such oscillations in the morphology of the catalyst's surface could again significantly influence the catalytic behavior of this surface. A full understanding of the catalytic function of this surface can therefore not be obtained by either concentrating on the metallic or on the oxidic phase alone.

Experimentally, this would require further developments in the field of so-called *in-situ* techniques allowing to investigate the surface under reaction conditions, and thus providing information about the catalyst in its active state. From a theoretical point of view following the results obtained in this work, the description of the transition between the metallic and oxidic phase would become necessary in a next step in order to achieve first a quantitative modeling of the possibly heterogeneous surface structure and composition in the reactive environment, and then also of the corresponding catalytic activity.