Chapter 1

Introduction

Most of today's technologically relevant, chemical reactions would not be very efficient or even possible without the use of a catalyst. Some examples for such processes are oil refining, the production of chemicals (e.g. ammonia synthesis) and the cleaning of exhaust gases [1]. The catalyst can be either in the same phase as the reactants (homogeneous catalysis) or in a different phase, e.g. a solid catalyst and gaseous or liquid reactants (heterogeneous catalysis). The latter is usually preferred by industry due to an easier separation of the reactants/products and the catalyst. Here, the discussion will be focused on heterogeneous catalysis with solid catalysts and gaseous reactants. The industrially used, solid catalysts are very complex materials often consisting of a precious transition metal, which is considered as the catalytically active part, dispersed on a cheaper support material (like alumina, silica or carbon). To improve the performance of the catalyst additives like alkali metals or halogens are commonly used. Due to this complexity most of the catalysts used today have been discovered and improved by sophisticated, but in essence *trial-and-error* approaches. Recently, also high-speed screening techniques for searching new heterogeneous catalyst systems have been proposed [2, 3].

A different approach in trying to understand on a microscopic scale, how and why a catalyst works, is the use of model catalysts representing essential properties of the real catalyst. In the field of surface science single crystal surfaces of the catalytically active metals are usually taken as model catalysts and are investigated under the well-defined gas phase conditions of ultra-high vacuum (UHV). Over the last decades much valuable information about the structure and composition of clean and adsorbate covered surfaces could thus be obtained on an atomic scale. However, the transferability of the results to real catalysis is questioned by the so-called *materials gap* between the structurally rather simple model catalysts and the complex real catalysts, and the *pressure gap*, which is many orders of magnitude in pressure between the UHV conditions and conditions applied in industrial heterogeneous catalysis. Under reaction conditions, the entire structure and composition of the catalyst's surface might thus be changed, which might then also influence its catalytic activity.

Focusing on heterogeneous oxidation catalysis, where rather high oxygen partial

pressures are applied, the surface of the transition metal catalyst might e.g. be oxidized, so that the actual catalytically active phase under technologically relevant environmental conditions is not the metal, but rather the oxide. A prominent example for such an effect is the CO oxidation reaction over ruthenium. Here it was found, that under UHV conditions the Ru(0001) surface shows almost no catalytic activity [4], whereas under high oxygen pressures the catalytic activity exceeds even the one of the frequently used palladium and platinum catalysts [5]. This increase in the catalytic activity towards CO oxidation was assigned to the formation of RuO_2 under these gas phase conditions [6–10]. For the ruthenium catalyst there is thus a clear distinction between the active phases, the rather unreactive metal under low oxygen pressures and the highly active oxide under high oxygen pressures. For the more noble metals like palladium, platinum and silver, which are also frequently used as catalysts in oxidation reactions, the situation appears to be somewhat different. Here, already the metal surfaces show a quite good catalytic activity under UHV conditions. In addition, the oxides of the more noble metals are much less stable than in the case of ruthenium, as can be seen from the heat of formation of the different oxides (most apparent, if presented in eV/O: $\Delta H^f_{RuO_2} = -1.60\,\mathrm{eV/O}$, whereas $\Delta H^f_{PdO} = -0.88\,\mathrm{eV/O}$, $\Delta H^f_{PtO_2} = -0.69\,\mathrm{eV/O}$ and $\Delta H^f_{Ag_2O} = -0.34\,\mathrm{eV/O}$ [11, 12]). Hence, the nature of the active surface under reactive conditions is less clear than in the ruthenium case. In addition, on palladium, platinum and silver the formation of so-called *surface oxides* has been observed under ambient oxygen pressures. In the present context a surface oxide refers to a structure, that is already more complex than a simple ordered oxygen adlayer, but still represents only a nanometer thin oxide-like film on the metal surface. The role of these surface oxide structures in oxidation catalysis is still an open question.

For the surface oxide on Ag(111), which has already been reported in the 1970s [13, 14], not even the atomic structure is fully resolved. A very recent study suggests even that under reaction conditions not one defined structure, but a variety of structures (possibly built by common building blocks) might prevail at the surface [15]. The hitherto observed surface oxide structures on platinum and palladium show a similar complexity. However, here at least so far consistent structural models have been proposed for the surface oxides on Pt(110) [16], Pd(111) [17] and Pd(100) [18].

To obtain a deeper, atomic-scale understanding of the catalytically active state under reaction conditions a growing number of so-called *in-situ* experimental techniques is presently being developed to bridge the pressure gap between UHV and ambient pressure conditions, like e.g. scanning tunneling microscopy (STM) [16, 19, 20], surface x-ray diffraction (SXRD) [21–24], transmission electron microscopy (TEM) [25] and photoelectron spectroscopy (PES) [26]. Also from a theoretical point of view new methodologies have to be developed to describe a macroscopically observed function like heterogeneous catalysis on the basis of microscopic understanding. The elementary molecular processes, which take place on microscopic time and length scales and which determine the behavior of the system, can be well described by modern

electronic structure methods (like density-functional theory, DFT). Their statistical interplay, though, which is decisive for the functionalities of a certain compound, only develops in the meso- and macroscopic regime. Also here, methods from statistical mechanics and/or thermodynamics are well established. It is thus the appropriate linking between the different regimes, which becomes decisive. Such an approach is also referred to as *multiscale modeling* [27, 28].

As a model system for heterogeneous catalysis the present work will focus on the CO oxidation on Pd(100). Experimentally, the Pd(100) surface has been widely studied by a variety of UHV surface science techniques, in contact with both an oxygen and CO gas phase. Recently, also some of the above mentioned *in-situ* methods have been applied to investigate the structure and composition of Pd(100) over an extended temperature and pressure range. Using SXRD measurements a (T, p)-diagram showing the detected phases in an oxygen atmosphere over a temperature range of $T = 600 - 1000\,\mathrm{K}$ and pressures of $p_{O_2} = 10^{-9} - 1\,\mathrm{atm}$ could be obtained [23]. Here, also the afore mentioned surface oxide has been measured over an extended (T, p)-range, suggesting that this phase might also appear under catalytic reaction conditions. In reactor STM experiments by Hendriksen and Frenken [29–31] the structure of the Pd(100) surface could directly be monitored during the catalytic oxidation of CO. Here, the surface was exposed to both oxygen and CO at a total pressure of $p_{\mathrm{tot}} \approx 1\,\mathrm{atm}$ and a temperature of $T \approx 400\,\mathrm{K}$. The partial pressures of the reactant gases CO and O_2, as well as the reaction product CO_2, were measured simultaneously with the STM images. Depending on the partial pressures of O_2 and CO Hendriksen and Frenken observed a change in the reaction rate, which was accompanied by a significant change in the morphology of the surface. Starting on a very smooth surface, which was assigned to the clean Pd(100) surface, and decreasing the CO partial pressure, a sudden increase in the reaction rate went together with a roughening of the surface, which was assigned to the formation of some oxidic phase. Increasing the CO pressure led again to a smoothing of the surface and a decrease in the reaction rate. Unfortunately, it has not been possible so far to obtain atomic resolution in the reactor STM experiments, so that the structure of the oxidic phase could not yet be identified.

These experiments clearly indicate, that the formation of an oxidic phase at Pd(100) might well be possible under gas phase conditions applied in industrial CO oxidation catalysis. What remains unknown, is if it is already the bulk oxide or rather a nanometer thin surface oxide structure that forms under these conditions, and if this is then also the actual catalytically active state. In the present work this problem is addressed theoretically by combining DFT calculations (for the microscopic regime) with concepts from thermodynamics and statistical mechanics (for the mesoscopic regime). Applying an *ab initio* atomistic thermodynamics approach, the structure and composition of Pd(100) is investigated in a first step in thermodynamic equilibrium with a pure oxygen gas phase (Chapter 6). It is then possible to compare the stability of the clean metal surface, different oxygen adlayers, the surface oxide and the bulk oxide over a wide range of oxygen gas phase conditions and identify the thermody-

namically most stable phase in a respective (T, p)-range. In a second step, also the CO is taken into account. The stability of different phases containing oxygen and/or CO is compared in a *constrained* equilibrium with an oxygen and CO gas phase in Chapter 7. Here, the formation of CO_2 is still neglected in the gas phase, as well as at the surface. To explicitly include the effects of the on-going catalytic reaction, in a last step, kinetic Monte Carlo (kMC) simulations are applied (Chapter 8). Here, a connection between the micro- and mesoscopic regime is established by deriving the input parameters of the kMC simulations on the basis of DFT results, instead of using fitted or empirical parameters.

In short, it is found that a $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide structure on Pd(100) is actually a stable phase over an extended temperature and pressure range in thermodynamic equilibrium with a pure oxygen gas phase, as well as in a constrained thermodynamic equilibrium with an O_2 and CO gas phase. Its stability region does extend to catalytically relevant gas phase conditions of ambient temperatures and pressures. Including the on-going CO_2 formation at the surface leads to a small decrease in the stability region of the surface oxide, such that slightly oxygen-rich gas phase conditions are needed to stabilize the surface oxide structure. These results suggest that the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide structure might actually form under catalytic reaction conditions and might then also contribute to the active state of the Pd(100) surface in CO oxidation catalysis.