9 Summary

Among the most studied catalytic reactions, the CO oxidation on platinum single crystals displays a number of interesting kinetic and nonlinear phenomena despite of its conceptual simplicity. The different reaction regimes, characterized by particular sets of control parameters, normally partial pressures and temperature, have been extensively investigated [1]. In addition, with the aim to expand the reaction parameter range, forced oscillations [2] as well as modified catalysts [3] [4] have been recently employed.

In this thesis I have explored different strategies to further extend the above-mentioned regimes of the catalytic CO oxidation on Pt(110) by dynamically influencing the path of the chemical reaction with surface acoustic waves (SAW), time-delayed feedback, and laser irradiation. The results confirm the potential of the methods, give an insight into the influence mechanisms, and are likely to represent a progress towards controlling catalytic reactions at surfaces [5].

A review on the mechanism of the CO oxidation reaction is presented in chapter 1, while the experimental setup is described in chapter 2. Coverage calibration measurements are presented in chapter 3. It is shown that the Photoemission Electron Microscopy (PEEM) integrated intensity of a CO-covered Pt(110) surface can be employed as a new method to determine the adsorbate coverage. From the PEEM isotherms the preexponential factor and the coverage-dependent activation energy of desorption ($7\cdot 10^{17\pm1}$ ML$\cdot$s^{-1} and 40.9 ± 0.5 Kcal$\cdot$mol^{-1} in the zero coverage limit, respectively) were derived. By inserting these kinetic parameters into the theoretical model, it has been possible to bring computer simulations much closer to the experimental conditions.

Chapters 4 and 5 deal with the role of subsurface oxygen and surface reconstruction in the pattern formation during the CO oxidation on Pt(110). The time evolution of an oxygen island, grown on a precovered CO Pt(110) surface, was recorded while increasing the temperature of the sample, following a procedure found to lead to subsurface O formation.

Although a ring-like, bright structure arose between the dark, oxygen-covered and the mainly clean regions, no clear proof for the presence of subsurface oxygen formation was found. In contrast to the expected lowering of the work function induced by the subsurface oxygen, the ring brightness never exceeded the value of the clean surface, obtained by heating the crystal up to 800 K. Concerning the surface reconstruction, it was surprising to observe spiral wave formation in the CO oxidation on an amorphous Pt surface, which does not exhibit identifiable surface rearrangements. An *excitable* or *oscillatory medium*, characterized by at least two independent variables, is needed for spiral formation [6]. Without surface reconstruction only one independent variable is left! If surface reconstruction is neglected also on a microscopic scale, other mechanisms should account for the self-sustained oscillations. In this view, oxide formation, surface carbon deactivation, surface roughening, and subsurface oxygen formation are discussed in chapter 5.

In chapters 6 to 8 the effects of influencing the pathway of a chemical reaction are presented. As a result of PEEM investigations of the CO oxidation on a Pt single-crystal, an increase in the activity upon Surface Acoustic Wave (SAW) excitation was found, caused seemingly by a raised CO desorption. Among the possible explanations of this enhancement, the mere thermal heating of the sample surface has been ruled out. Since dramatic morphological changes of the catalyst film have been observed, mechanical and electric mechanisms that may account for the catalyst destruction were considered. However, none of them alone explains the observed SAW effects convincingly. Regardless of the underlying mechanism, the results presented in this work demonstrate that acoustic excitation is a viable route to increase, at least temporarily, the activity of a catalytic reaction at the gas–solid interface.

Chapter 7 describes an experiment aiming to verify experimentally a *distributed real-time feedback simulation* [7] by means of Laser Induced Thermal Desorption (LITD). The current, still preliminary, EMSI-LITD combined study shows that the CO+O/Pt system is suitable to successfully perform experiments for controlling pattern formation.

In chapter 8 a different control approach, in form of a delayed feedback, is described. By appropriately applying minute perturbations to an accessible parameter of a chaotic system, which is characterized by an extreme sensitivity to perturbations, it is possible to stabilize a selected behavior of the system [8]. In this experiment a stabilization of periodic oscillations in the rate of the CO oxidation in a regime of chaotic oscillations was achieved.

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