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## 0 Outline

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The definition of a catalyst is the ability to increase the rate of a chemical reaction without being consumed. Since the easiness of products' separation is a highly desired feature, heterogeneous catalytic systems, for which the catalyst phase is in different from the one of the reaction mixtures, play a particularly important role [1]. Catalysis-based industrial products, especially in the petroleum and pharmaceutical sectors, are worth 18% of the world's total industrial output.

The history of the modern heterogeneous catalysis is likely to have been inaugurated with the experimental and theoretical work of Sabatier and Langmuir. Sabatier [2] realized the correct sequence of a catalytic reaction: chemisorption and *transformation* of the reactants, and desorption of reaction products. By applying the concepts of the crystal structure arising from the work of W.H. and W.L. Bragg, Langmuir was the first to formulate the notion of "adsorption" and develop a mechanism and a mathematical description of the catalytic *action* [3]. The research on catalysis has since then taken different routes. The *surface science* approach, used in the present work, takes advantage of the large set of experimental techniques that are available to investigate elemental reactions at well-characterized surfaces under high vacuum, by minimizing the effect of contaminants and maintaining isothermal conditions. Unfortunately, as pointed out by Jensen and coworkers [4], many results in this regime cannot be extrapolated to industrial applications where mainly supported catalysts in high-pressure atmospheres are employed. To bridge these *material* and *pressure* gaps, more complex model catalysts and high-pressure-compatible techniques have been developed [5].

Among the most studied catalytic reactions, the CO oxidation on platinum single crystals, although conceptually rather simple, displays a number of interesting phenomena like asymmetric adsorption inhibition, adsorbate-driven substrate reconstruction, and product rate oscillations. The different reaction regimes, corresponding to different choices of the control parameter values, which are typically reactant partial pressures and temperature, have been extensively characterized [6]. Moreover, in order to extend the parameter range allowed for the reaction to take place, forced oscillations have been applied [7] as well as modified catalysts have been employed [8] [9].

In this thesis I have explored different strategies to further extend the aforementioned regimes of the catalytic CO oxidation on platinum 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 on the influence mechanisms, and are likely to represent a progress towards controlling catalytic reactions at surfaces [10].

The thesis is organized in the following way.

A review on the mechanism of the CO oxidation reaction is presented in chapter 1. The experimental setup is described in chapter 2. Coverage calibration measurements are presented and discussed in chapter 3. Chapters 4 and 5 contain experimental results concerning two open questions: subsurface oxygen on Pt(110) and the spiral formation on an amorphous Pt sample. In chapters 6 to 8 the effects of influencing the pathway of a chemical reaction are illustrated by reporting the results of three sets of experiments, in which surface acoustic waves excitation, delayed coverage signal feedback, and laser irradiation have been used. In chapter 9 concluding remarks and perspectives are given. A list of acronyms and the acknowledgments are as well included.

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