Chapter 1

Introduction

Modern surface studies are often stimulated by the need of understanding heterogeneous catalysis which constitutes the basis for many chemical technologies employed in nowadays industry. Industrial processes usually operate at high temperatures and pressures (i.e. several atmospheres) and the catalysts are usually made of different components, exhibiting very complex structures. They are generally in the form of highly dispersed powders, usually made of transition metals deposited on high surface area metal-oxide supports which may include small amount of promoters to enhance the efficiency of the catalysts. A better understanding of surface processes in a microscopic or atomistic way is crucial in chemical industries, but the complexity of the real systems preclude a thorough investigation of the physical and chemical phenomena that take place on the surface of commercial catalysts during a reaction.

In order to overcome this problem, model catalysts with well-defined chemical and morphological properties are the subject of surface science studies. Model catalysts can be studied and characterized in detail using surface science techniques. Nevertheless, these systems can not perfectly mimic the complexity of the real catalyst surfaces. This discrepancy is generally known as the *materials gap* between surface science and real catalysis. In order to narrow this gap, earlier surface science studies on defined metal single crystal surfaces (including stepped or defect-rich surfaces) have been recently accompanied and enriched by studies on model supported catalysts. Different supported model systems have been developed, using thin oxide films or oxide single crystals as support for different metal particles. These supported model catalysts better resemble the complexity of real

systems (including particle size effects and support interactions), and they can be still studied using surface science techniques.

Industrial reactions proceed under conditions, e.g. high pressures, which forbid the direct *in-situ* application of typical surface science techniques, leading to the so called *pressure gap*. In fact, many of the surface science techniques commonly used to investigate heterogeneous catalytic systems require ultrahigh vacuum (UHV) or pressures at least ten orders of magnitude lower than the environmental conditions of technical catalysts. Results obtained from surface science studies under UHV can not always directly be employed to explain the complex chemistry of technical catalysts [1,2]. It has been speculated that new adsorbate structures may originate under high pressure (≥1 bar) exceeding the saturation coverage obtained under UHV [3]. Furthermore, at elevated pressure and temperature the catalyst surface may restructure, e.g. when volatile or mobile components such as carbonyls are involved [4].

In recent years, there have been several experimental efforts to bridge this pressure gap by developing surface-sensitive techniques operating under more realistic conditions. Among them are X-ray absorption spectroscopy (XAS) [5,6], high-pressure X-ray photoelectron spectroscopy (HP-XPS) [7,8], sum frequency generation (SFG) spectroscopy [9], polarization-modulation infrared absorption spectroscopy (PM-IRAS) [10], etc. SFG and PM-IRAS are vibrational techniques which are employed in our group to study different reaction systems, being able to detect dynamic surface adsorbate structures both under UHV and under high pressure. The SFG technique has been successfully employed to study Pd(111) single crystal and alumina supported Pd nanoparticles over a wide range of pressures and temperatures. More recently, a PM-IRAS experimental setup was build up as complementary tool to SFG. In fact, PM-IRAS offers some advantages compared to SFG, such as wider spectral range, shorter acquisition time, and lower running cost.

The aim of this thesis was to address both the *materials* and the *pressure gaps.* Beside standard surface science techniques working under UHV (XPS, Low Energy Electron Diffraction, LEED), PM-IRAS and Gas Chromatography (GC) were employed to perform study at elevated pressure. Two different catalysts have been investigated in this work, Pd(111) single crystal and Pd particles deposited on a thin alumina film grown on a NiAl(110) single crystal. Most of the experiments have been performed on the simple but atomically well-defined Pd(111) single crystal surface, which was chosen as starting point to test the new PM-IRAS experimental setup. However, in order to narrow the distance

existing between model systems and real catalysts, recent experiments were performed on the more complex $Pd/Al_2O_3/NiAl(110)$ system. Our approach was to start with a very simple probe molecule, carbon monoxide, CO, to identify and characterize the different adsorption sites first on Pd(111) and then on the $Pd/Al_2O_3/NiAl(110)$ model systems. The behaviour of both catalysts was addressed preliminarily under UHV and subsequently under more relevant conditions (i.e. millibar pressures). Next, the molecular complexity was increased by studying the interaction of both Pd model catalysts with methanol, CH_3OH. Methanol is one of the important raw materials produced from syngas. Commercial catalysts to produce methanol are generally based on $Cu/ZnO/Al_2O_3$-systems [11], but Pd based catalysts have shown a higher selectivity [12]. The decomposition of methanol to carbon monoxide and hydrogen on Pd-based catalysts has also raised much attention, because of its practical importance for methanol-fuelled vehicles and for other heat-recovery systems [13,14 and references therein]. Methanol decomposition may precede *via* dehydrogenation to CO and hydrogen or *via* C-O bond scission to carbonaceous species (CH_x), CH_4 and water. The probability of the two different reaction pathways was investigated under UHV and under more relevant conditions on Pd(111) and supported Pd nanoparticles. Similar behaviour was found for the two systems: under UHV dehydrogenation of methanol dominated, while for higher pressures and temperatures considerable amount of carbon (from methanolic C-O bond scission) was detected. Methanol oxidation was also studied under similar conditions on both Pd model catalysts. The same oxidation products were detected during the reaction at high pressure, but the oxidation state of alumina supported Pd particles changed, showing a partial oxidation of the Pd particle surface. Oxidation of Pd(111) and Pd nanoparticles was also studied under UHV conditions.

The interaction of Pd(111) single crystal with ethylene and 1,3-butadiene was also investigated both under UHV and at mbar pressure. The adsorption and hydrogenation of ethylene on group VIII noble metal surfaces can be regarded as prototypical reactions for longer and more complex olefins. Although ethylene hydrogenation has been extensively studied, there are still some open questions regarding its reaction mechanism and the intermediate species involved. Ethylene adsorption and hydrogenation have been studied on Pd(111) using XPS and PM-IRAS from UHV up to millibar pressure. The butadiene hydrogenation reaction was recently studied in our group on Pd single crystals and on alumina supported Pd particles. High pressure studies using GC were performed, allowing obtaining detailed information about the kinetic behaviour of these catalysts (turn-over-

frequency (TOF), selectivity, activation energy, etc.). In this work butadiene adsorption and butadiene hydrogenation on Pd(111) have been studied using (PM-)IRAS and pre- and post-reaction XPS and LEED to gain information about adsorbate species on the surface during the reaction and to check for possible catalyst deactivation.

The thesis initially introduces the reader to the fundamentals of PM-IRAS and of the main techniques employed in this work, to the experimental setup, and describing as well the preparation and properties of the Pd model catalysts (chapter 2). Chapter 3 deals with the interaction of CO on Pd(111) and on alumina-supported Pd particles. First, CO is studied at low pressure on Pd(111), and subsequently high pressure PM-IRAS measurements are presented. Adsorption of CO on $Pd/Al_2O_3/NiAl(110)$ is discussed, before the debate question of C-O bond scission is finally addressed. In chapter 4 the adsorption, decomposition and oxidation of methanol are presented. The first section deals with the study of methanol on Pd(111) by using PM-IRAS, XPS and gas chromatography (GC). The influence of defects on the catalyst activity is also addressed by comparing results of methanol adsorption and decomposition on smooth Pd(111) and on defect-enriched Pd(111) surfaces. Methanol decomposition on smooth Pd(111) has been studied as well combining XPS, low-energy electron diffraction (LEED) and scanning tunnelling microscopy (STM). Methanol oxidation on Pd(111) under high pressure is then discussed. Afterwards, methanol adsorption, decomposition and oxidation under similar conditions on alumina-supported Pd particles are discussed. The final section of chapter 4 deals with the different oxidation behaviour of different Pd model systems under UHV conditions. PM-IRAS and XPS can also be applied to study more complex molecules, as it is shown in chapter 5, where measurements of ethylene, C_2H_4, and 1,3-butadiene, C_4H_6, on Pd(111) are presented. In the end, the most important results of this work are summarized in chapter 6.