Chapter 1   Introduction

One of the most important goals in surface science is to understand elementary steps in heterogeneously catalyzed reactions on solid surfaces. In fact, a lot of catalytic reactions on solid surfaces are closely related to our daily life. For example, the oxidation of CO and the reduction of NO are important reactions in environmental science. The oxidative coupling of methane or the partial oxidation of alcohols can provide important intermediates that can be converted to more useful products in industrial processes. These reactions take place at solid surfaces, which play therefore a pivotal role in heterogeneous catalysis [1].

Efforts to discover better catalysts were started before recording history [2]. The medieval alchemists tried to find suitable materials to transform one substance to another one. They called it 'philosopher's stone', which is the same concept as 'catalyst' today. Several catalytic reactions were already reported before the beginning of the 20th century. Davy discovered that a warm Pt gauze would spontaneously glow when exposed to the mixture of gases in an 1820s coal mine even though no flame was present [3]. CO oxidation and hydrogen oxidation to water on the Pt gauze were found to be responsible for this phenomenon. In the second half of the 19th century, the Phillips company patented the catalytic oxidation of SO_2 to sulfuric acid [2]. At the beginning of the 20th century, Fritz Haber discovered an efficient catalyst for ammonia synthesis [4]. However, in the 19 th century, the role of the catalysts in these reactions was not clear. It was Van't Hoff and Ostwald, however, who showed that catalysts just lower activation energies of reactions [5]. Ample studies were focused on the interaction between gas molecules and catalysts. Sabatier suggested that an unstable intermediate be formed on the catalyst, which then reacts to a product [2, 6]. This concept of 'unstable intermediate' is what we call now 'adsorption state'. General models for the adsorption and catalytic reactions were suggested by Langmuir [7-9].

Since the 1950s, the development of vacuum techniques and surface analysis instruments enabled thorough investigations of adsorption and catalytic reactions under well-defined conditions. Surface scientists perform experiments under UHV conditions to reduce the influence of residual gas molecules during the investigation of clean solid surfaces or adsorption properties of particular gas molecules. Under UHV conditions one can keep the experimental parameters as simple as possible so that one can hope to correlate elementary steps as trapping, adsorption, diffusion, reaction and desorption with catalytic activity.

UHV studies are extremely useful as long as conclusions based on UHV models are transferable to reactions under real conditions, i.e., at high pressures. In fact, UHV results for many reactions such as ammonia synthesis turned out to be equally valid in the high pressure regime [10]. However, for some reactions such as CO and CO_2 hydrogenation [11], one should scrutinize UHV data to extrapolate them over a wide pressure range, because high pressure conditions frequently stabilize chemical species that can play a crucial role for catalytic reactions, but cannot be prepared with sufficient concentration under UHV conditions. The ultimate goal of modern surface science is to identify microscopic steps of catalytic reactions, which are relevant over a wide pressure range. Pioneering works to bridge this 'gap' between UHV results and real catalytic reactions have been performed by some surface scientists such as Somorjai [12] and Goodman [13], who combined UHV chambers and high pressure reactors in order to characterize catalysts before, during and after reactions at high pressures.

In the present work, we discuss the CO oxidation over Ru, for which UHV models and high pressure results are conflicting. Ru is a poor catalyst under UHV conditions [14, 15], while it is more reactive than the other Pt group metals at high pressures [16, 17]. For the catalytic CO oxidation reactions, O_2 has to adsorb dissociatively on the surface, while CO adsorbs molecularly. CO and chemisorbed atomic O recombine to CO_2 on the surface. To obtain a high activity for CO oxidation, the atomic O should not be too strongly bound on the metal surface.

Under UHV conditions, the apparent saturation coverage of O is 0.5 ML on Ru(0001) by O_2 exposure at 300 K [18, 19]. At O coverages below 0.5 ML, the binding energy of O on Ru is much higher than those of Pt, Pd, Ir and Rh, which are efficient catalysts for CO oxidation [15]. The higher binding energy of O on Ru inhibits the thermal activation of O atoms on the surface and thus lowers the rate for CO oxidation.

However, the reason for the high activity of Ru for the CO oxidation under high pressure conditions is not understood yet. Peden and coworkers demonstrated that in the high pressure range, an O phase with coverage of 1.0 ML can be formed, which is related to the high activity of Ru towards CO oxidation in the high pressure regime [20–22]. However, the pronounced enhancement of the CO oxidation rate by more than two orders of magnitude with respect to a Ru(0001) surface with an O coverage of 1.0 ML was reported for the O-rich Ru(0001) surfaces, which contained an O amount equivalent to at least 3 ML [23, 24]. From these results, one can infer that the increase of the O coverage in the high pressure regime should be closely related to the high catalytic activity of Ru.

The objective of this work is to shed light on the high activity of Ru for the CO oxidation at high O coverages in terms of structural properties by employing LEED, TDS and AES. At an O coverage of 1.0 ML, a (1×1)-O phase is formed on the Ru(0001) surface [25, 26]. In chapter 3, a (2×2)-3O phase at an O coverage of 0.75 ML is discussed. The detailed surface structure of this phase was determined by quantitative LEED I/E analysis. The O-rich phases with O coverages above 1 ML were investigated by LEED, and the results are presented in chapters 4 and 5. We show that extended RuO_2(110) islands are formed on the Ru(0001) surface, while RuO_2(100) grows on Ru(10$\bar{1}$0). The atomic structures of RuO_2 on the Ru single crystals were determined by LEED I/E analysis. The atomic adsorption geometry of CO on RuO_2 domains is also reported. We have identified RuO_2 to be responsible for the high activity of the CO oxidation in O-rich phases. In chapter 6, results about the CO oxidation over the bulk RuO_2(101) is presented.

We demonstrate in the present work that the variation of catalytic activity is closely related to the structural change from chemisorbed O overlayer to RuO_2 upon increasing O coverages. In addition, the catalytic activities of the CO oxidation on RuO_2 surfaces with different orientations are studied, which allows discussing surface structure sensitivity of the CO oxidation over the RuO_2. We discovered that the surfaces of RuO_2 expose the cus (coordinatively unsaturated sites) Ru atoms, which explains the similar catalytic activities of various RuO_2 surfaces.