

Chapter 6 CO oxidation on RuO₂(101)

6.1 Introduction

In this chapter, we will pay attention to the CO adsorption on bulk RuO₂(101) and its activity in the CO oxidation. The objective is to probe experimentally, if the RuO₂ crystal itself reveals the high activity for CO oxidation, or only RuO₂ supported on metallic Ru makes an efficient catalyst for CO oxidation.

RuO₂ is an important material in various fields. In electrochemistry, RuO₂ is used as anode for H₂O and HCl dissociation, because RuO₂ is conductive and corrosion resistant [123]. Its overpotential is low, and therefore, less energy is required to use RuO₂ as an electrode in industrial processes. For the photodecomposition of water, RuO₂ can be a promotor on TiO₂ [124]. RuO₂ can be a catalyst in the oxidation of methane to synthesis gas [125].

RuO₂ plays a very important role in some electronic devices. It is used, e.g., as a part of supercapacitor [126,127] and new-generation contacts/ interconnects in Si devices [128].

Although one can find the application of RuO₂ in many fields as a catalyst or as an electronic element, fundamental studies of the geometric structure, electronic structure and reactivity of single crystal RuO₂ under UHV conditions are scarce, because the RuO₂ single crystals are not commercially available. RuO₂ single crystals can be grown by the method of chemical vapor transport in a flowing O₂ system [129], and we had the pleasure to start a collaboration with Prof. G. Krabbes, Dresden, who grew RuO₂ single crystals used in this work.

6.2 Preparation of RuO₂(101)

The reactive agents Cl₂, TeCl₄, or O₂ are known to carry the components Ru and O in the gas phase, forming RuCl₃, RuCl₄, RuO₃, RuO_nCl_n etc. with sufficient partial pressure (50 mbar and higher) [130,131]. To produce the crystal used in this work, O₂ was used as transporting agent. This bears the advantage that only the constituents of Ru oxides are in the reactor, minimizing the impurity level in the grown RuO₂ crystals. Oxygen flow (1 bar) is passed over polycrystalline RuO₂ at 400 K which results in a (equilibrium) mixture of RuO₃/RuO₄ in the gas phase:



The size of the crystal used in this work was about 4 mm×4 mm, and it showed a blue-black color, which is typical for RuO₂ crystals. Because the sample was too small and fragile, it could not be fixed directly between W wires. Instead, we fixed the RuO₂(101) sample on a Mo plate with small steel clips. Slits were made on both sides of the Mo plate, and this plate was clamped by two W wires with a diameter of 0.25 mm. The W wires were then spot-welded on the Ta rods. The thermocouple was spot-welded behind the Mo plate. Therefore, the accurate sample temperature could not be measured. We assumed that the RuO₂(101) and the Mo plate are always in thermal equilibrium.

Before the sample cleaning was carried out, no pattern at all was visible in LEED, indicating that the surface is very rough or disordered. With AES, the relative amount of O to Ru turned out to be about 0.2. For comparison, a O/Ru value of about 2.0 is expected for the perfect stoichiometric RuO₂ surface.

The sample was annealed at 800 K in 8×10^{-6} mbar of O₂ atmosphere for 1 hour. After this procedure, a (1×2) structure of RuO₂(101) could be observed (Fig. 6.1 b). Along one axis every second beam is missing, which is indicative of the existence of a glide plane [30]. With AES, the O/Ru ratio reached 1.87, as determined by Ru (273 eV) peak and O (512 eV) peak intensities. Oxidation of additional 2 hours did not change either the LEED pattern or the AES spectrum.

In bulk RuO₂(110) and bulk RuO₂(100), (1×1) non-reconstructed surfaces can first be prepared, which are then converted to the (1×2) or the c(2×2) surfaces by annealing to above 700 K [111]. We could not prepare a non-reconstructed (1×1) structure of RuO₂(101).

In Fig. 6.1a), the ideal (1×1)-RuO₂(101) surface structure is shown which is terminated by a Ru layer; the glide plane is indicated.

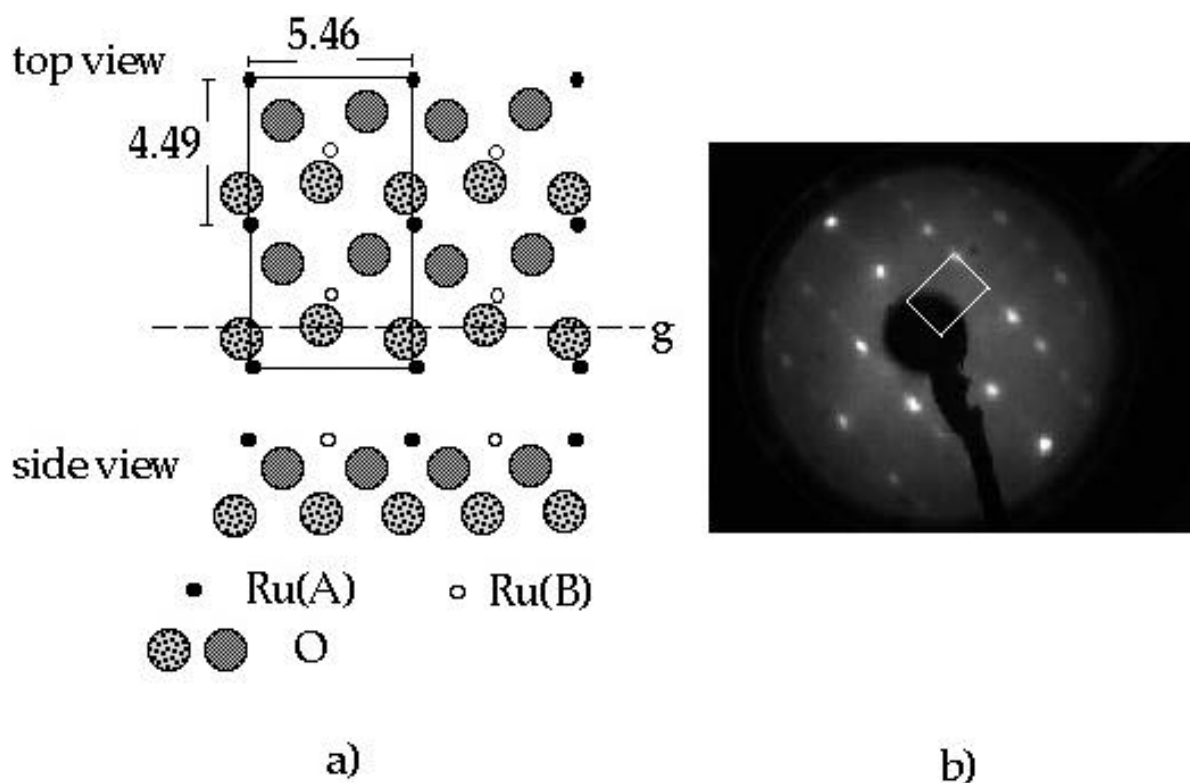


Fig. 6.1. a) Surface structure of the Ru terminated (1x1)-RuO₂(101). b) LEED pattern of the (1x2) reconstructed RuO₂(101) surface. The electron energy was 63 eV. The sample temperature was 350 K.

6.3 CO adsorption on RuO₂(101)

In order to check, if CO adsorbs on the (1x2)-RuO₂(101) surface, the I/E curves were measured before and after dosing 30 L of CO at 130 K. The results are reproduced in Fig. 6.2. The form of the I/E curves does not change after dosing CO. However, the absolute intensities of the integer-order and fractional-order beams become weaker after CO exposure. The LEED pattern indicated an overall increase of the background intensities upon CO exposure. We conclude therefore that CO molecules do adsorb on RuO₂(101).

Generally, thermal desorption spectroscopy is used to estimate the binding energy of CO. In this work, CO thermal desorption experiments could not be performed. The sample was too small, and the plate that held the sample was too large. Since the whole plate had to be heated to increase the sample temperature, the real CO desorption signal from the sample could not be discriminated from the

background signals originating from the sample holder.

To estimate the binding energy of CO on RuO₂(101), we measured the beam intensity of an integer order beam (1,0), with and without CO adsorbed as a function of the sample temperature (Fig. 6.3). When the clean sample is heated with a constant heating rate, the beam intensity decays. At higher temperatures the atomic position becomes more disordered due to larger lattice vibrations. The decrease of the beam intensity is described by the Debye-Waller factor [30].

The behavior of the I/T curves (intensity versus temperature) from the CO-precovered surfaces is different from that of the clean surface. The beam intensity is almost constant (after exposing to 10 L of CO) or increases slightly (after exposing to 1 L of CO) up to 380 K. Beyond 380 K, the behavior of the I/T curves is almost identical to that of the clean surface, indicating that all CO molecules have

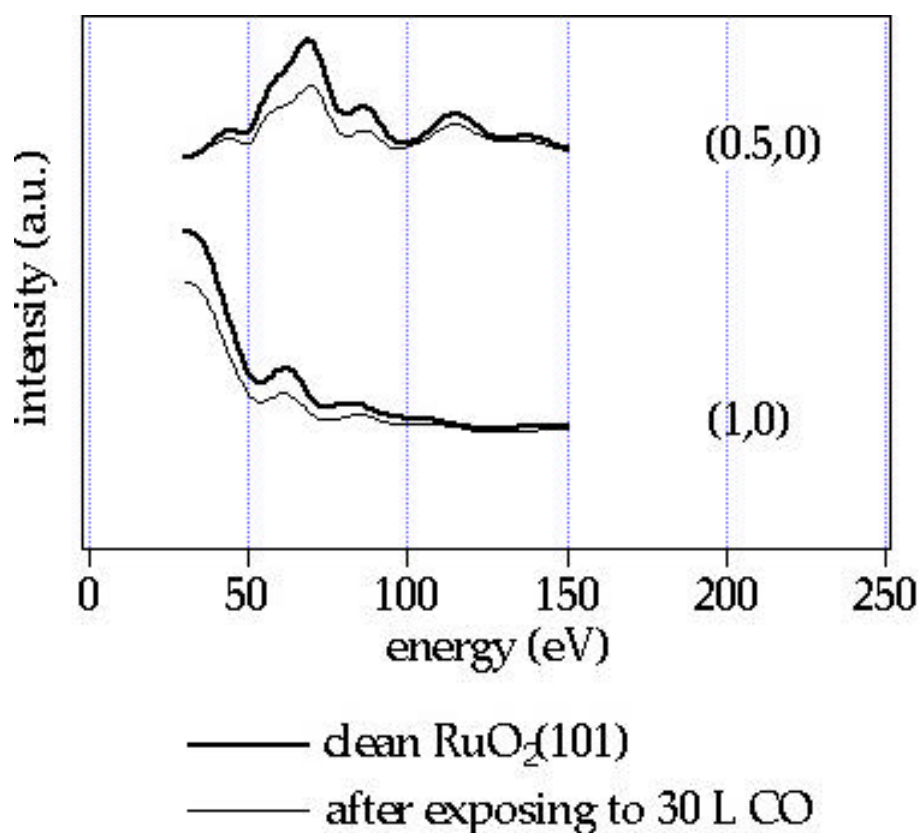


Fig. 6.2. I/E curves of RuO₂(101) before and after dosing 30 L of CO ($R_p = 0.03$).

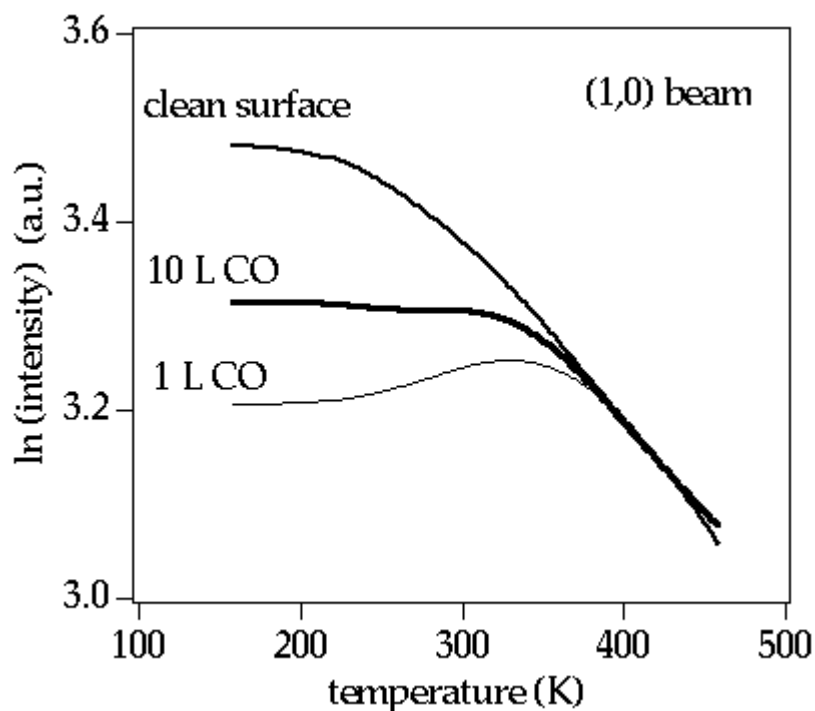


Fig. 6.3. a) The intensity variation of the (1,0) beam during heating the clean and the CO-precovered $\text{RuO}_2(101)$ with a constant heating rate (1.1 K/s). The CO exposures at 130 K are indicated.

already left the surface. This result indicates that CO desorption takes place between 200 K and 380 K. The desorption temperature is much higher than on the other oxide surfaces such as TiO_2 [90], NiO [91, 92] and MgO [93, 94], where CO desorption is completed below 200 K.

We observed that CO molecules are strongly bound on the cus Ru atoms of the $\text{RuO}_2(110)$ and $\text{RuO}_2(100)$ films. Because the adsorption energy of CO on $(1\times 2)\text{-RuO}_2(101)$ is comparable to those of $\text{RuO}_2(110)$ and $\text{RuO}_2(100)$, it is reasonable to assume that CO may be adsorbed on the cus Ru atom of $(1\times 2)\text{-RuO}_2(101)$. In contrast to the (110) and the (100) plane of RuO_2 , CO adsorption on $(1\times 2)\text{-RuO}_2(101)$ does not cause any change of the shape of the I/E curves. Only absolute intensities decrease after CO exposure. This may indicate that two cus Ru atoms are present in a (1×1) unit cell of $\text{RuO}_2(101)$ (e.g., in Fig 6.1a, Ru(A) and Ru(B) atoms are present in a (1×1) -unit cell). CO molecules may occupy both cus Ru atoms forming a $c(0.5\times 0.5)$ overlayer, which may not alter the shape of the I/E curves of

the (0.5,0) and the (1,0) beam.

The stability of CO on the surface is an important factor to determine the high activity towards CO oxidation. Because of the high desorption temperature of CO from (1×2)-RuO₂(101) we expect that the (1×2)-RuO₂(101) is also very active for CO oxidation

6.4 Reactivity of RuO₂(101) for CO oxidation

To investigate the catalytic activity of this surface, we dosed CO in a step of 100 L at 500 K and estimated the surface composition in between with AES so that the amount of O reacted off by CO could be estimated. A temperature of 500 K was chosen, since the reactivity of the CO oxidation on the RuO₂/Ru system was the highest at about this temperature. In Fig. 6.4, the results of the reactivity measurements are summarized. At the beginning, the O/Ru AES ratio amounts to 1.87. The relative

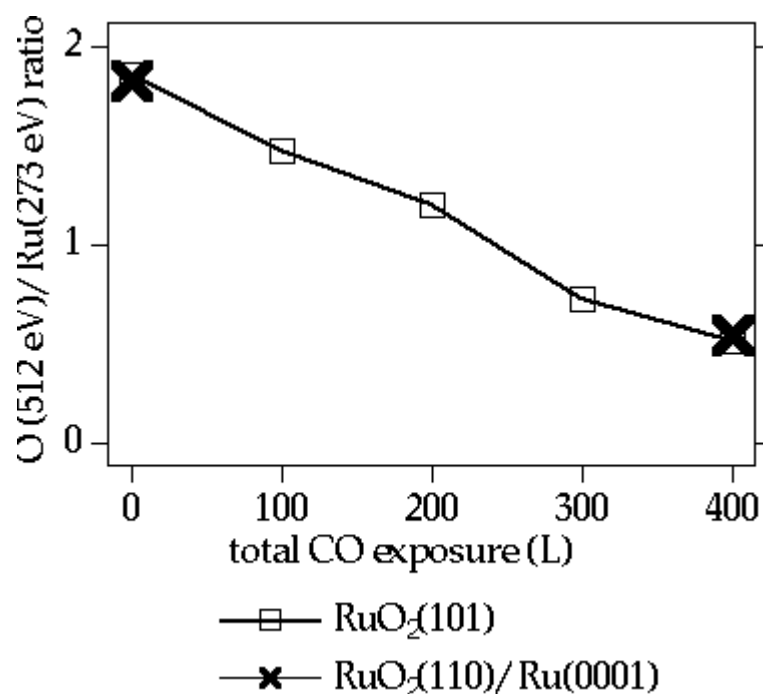


Fig. 6.4. a) AES O/Ru measurements after stepwise dosing of CO in 100 L on RuO₂(101), and AES O/Ru measurements before and after 400 L CO exposure on RuO₂(110)/Ru(0001) at 500 K are compared.

amount of O decreases almost linearly upon CO exposure. Apparently, the lattice O atoms of RuO₂(101) participate in the CO oxidation process. After exposing 400 L of CO, the O/Ru peak ratio is only 0.54. For comparison, the same experiments were performed with the RuO₂(110)/ Ru(0001) system. First, '60000 L' of O₂ was dosed to Ru(0001) at a sample temperature of 800 K so that only the RuO₂(110) derived spots are visible in LEED; the (1×1)-O domain is absent. The O/Ru ratio of this surface was 1.83, similar to that of the well-ordered bulk (1×2)-RuO₂(101) surface. After exposing 400 L of CO at a sample temperature of 500 K, the O/Ru ratio is reduced to 0.5. This result is identical to those of the bulk RuO₂(101). Consequently, the reactivities of RuO₂(110)/Ru(0001) and (1×2)-RuO₂(101) are very much alike. In other words, RuO₂(101) is also an efficient catalyst for CO oxidation.