

Chapter 7 Conclusion

Recently, O-rich Ru(0001) surfaces have been shown to be very active for the catalytic CO oxidation reactions [23, 24]. Throughout this work, the structural characterizations of the bare and the CO covered O-rich Ru surfaces were carried out by employing LEED I/E analysis. In addition, the catalytic activity of the bulk RuO₂(101) surface towards CO oxidation was investigated. We provided ample evidence that the active areas of O-rich Ru surfaces consist of RuO₂. Moreover, a mechanism for the catalytic CO oxidation on RuO₂ is proposed, which should be quite general for the whole class of oxidation reactions over oxide surfaces and which is independent of the surface orientation of RuO₂.

At an O coverage of 0.75 ML, the (2×2)-3O overlayer forms on Ru(0001). The atomic structure of this phase was determined by quantitative LEED. The (2×2)-3O phase shows a (2×2) vacancy structure (an unoccupied hcp site of the (1×1)-O is described as a vacancy). CO does not adsorb in the (2×2)-3O phase at sample temperatures between 100 K and 300 K. This result is in a good agreement with recent ab-initio DFT calculations, which estimated an activation barrier of 0.3 eV for the CO adsorption on the (2×2)-3O phase.

An incommensurate RuO₂ film grows epitaxially on Ru(0001) at O coverages above 2–3 ML, when large amounts of O₂ (such as 60000 L using the gas shower system) are exposed to Ru single crystal surfaces at sample temperatures between 600 K and 800 K. RuO₂ is oriented with the (110) face along the Ru(0001) surface. The structural characterizations of the RuO₂(110) film by LEED I/E analysis showed that the RuO₂(110) surface is terminated by bridging O atoms and cus (coordinatively unsaturated site) Ru atoms. CO and N₂ adsorb on top of the cus Ru atoms. In particular, CO is much more strongly bound on the cus Ru atoms of the RuO₂(110) layers (CO binding energy from DFT = 1.2 eV [88]) in comparison with other common oxides (CO binding energy below 0.7 eV [103]). On the other hand, the bridging O atoms of the RuO₂(110) surface are more weakly bound (O_{br} binding energy from DFT = 1.6 eV [88]) than the O atoms of (1×1)-O (O binding

energy = 2.05 eV). These results imply that the RuO₂(110) layer can efficiently catalyze the CO oxidation, since high binding energies of CO and low binding energies of O on the surface are important factors for the catalytic activity of the CO oxidation via the Langmuir-Hinshelwood mechanism. In fact, LEED and STM [88] investigations revealed that CO on the RuO₂(110) layers can readily recombine with the lattice O atoms of RuO₂(110) to CO₂. The RuO₂(110) formation is responsible for the extraordinarily high activity of the O-rich Ru(0001) surfaces for the CO oxidation.

We also investigated the structure of weakly bound oxygen on RuO₂(110)/Ru(0001), which can provide an even more efficient reaction path of the catalytic CO oxidation at 350 K [109]. We determined by quantitative LEED the weakly bound oxygen to be atomic O, which adsorbs on top of the cus Ru atom.

The incommensurability of RuO₂(110) layers on Ru(0001) suggests that the oxide film is almost unstrained. This can be rationalized in terms of the low-corrugation energy potential surface of Ru(0001). In going to a more corrugated surface such as that of Ru(10 $\bar{1}$ 0), the propensity to form a lattice-matched RuO₂ film at least along one direction may be higher. The growth of a RuO₂(100) film on Ru(10 $\bar{1}$ 0) is expected, because the lattice-mismatch between the RuO₂(100) and Ru(10 $\bar{1}$ 0) is only 4.5%. In fact, we found that RuO₂ layers are oriented with the (100) face on the Ru(10 $\bar{1}$ 0) surface.

According to a LEED I/E analysis, these RuO₂(100) layers are terminated by bridging O atoms and cus Ru atoms, similar to the RuO₂(110) surface. In contrast to the bridging O atoms of RuO₂(110), which are separated to the cus Ru atoms, the bridging O atoms of RuO₂(100) are attached to cus Ru atoms. Similarly to the RuO₂(110) film on Ru(0001), CO can be strongly bound over the cus Ru atoms of RuO₂(100) layers on Ru(10 $\bar{1}$ 0). CO molecules on the RuO₂(100) layer can readily recombine with the lattice O of RuO₂(100) to CO₂ with a CO to CO₂ conversion probability, which is similar to that of RuO₂(110)/Ru(0001).

CO can also strongly adsorb on the bulk (1 \times 2)-RuO₂(100), which results in a similar catalytic activity towards CO oxidation as those of the RuO₂(110) and the RuO₂(100) film. This may imply that cus Ru atoms are exposed on bulk (1 \times 2)-

$\text{RuO}_2(100)$ as on the (110) and (100) planes of RuO_2 .

Through the investigations of the CO oxidation on various RuO_2 surfaces, a general mechanism for the catalytic CO oxidation on RuO_2 emerges: CO molecules strongly adsorb on cus Ru atoms of the RuO_2 surfaces. CO can then react with lattice O atoms at RuO_2 surfaces to CO_2 . Under steady-state conditions, the RuO_2 surface may be continuously restored by O_2 supply from the gas phase [88].