

## 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 RuO<sub>2</sub>(101) surface towards CO oxidation was investigated. We provided ample evidence that the active areas of O-rich Ru surfaces consist of RuO<sub>2</sub>. Moreover, a mechanism for the catalytic CO oxidation on RuO<sub>2</sub> 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 RuO<sub>2</sub>.

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 RuO<sub>2</sub> film grows epitaxially on Ru(0001) at O coverages above 2–3 ML, when large amounts of O<sub>2</sub> (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. RuO<sub>2</sub> is oriented with the (110) face along the Ru(0001) surface. The structural characterizations of the RuO<sub>2</sub>(110) film by LEED I/E analysis showed that the RuO<sub>2</sub>(110) surface is terminated by bridging O atoms and cus (coordinatively unsaturated site) Ru atoms. CO and N<sub>2</sub> adsorb on top of the cus Ru atoms. In particular, CO is much more strongly bound on the cus Ru atoms of the RuO<sub>2</sub>(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 RuO<sub>2</sub>(110) surface are more weakly bound (O<sub>br</sub> 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 RuO<sub>2</sub>(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 RuO<sub>2</sub>(110) layers can readily recombine with the lattice O atoms of RuO<sub>2</sub>(110) to CO<sub>2</sub>. The RuO<sub>2</sub>(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 RuO<sub>2</sub>(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 RuO<sub>2</sub>(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 RuO<sub>2</sub> film at least along one direction may be higher. The growth of a RuO<sub>2</sub>(100) film on Ru(10 $\bar{1}$ 0) is expected, because the lattice-mismatch between the RuO<sub>2</sub>(100) and Ru(10 $\bar{1}$ 0) is only 4.5%. In fact, we found that RuO<sub>2</sub> layers are oriented with the (100) face on the Ru(10 $\bar{1}$ 0) surface.

According to a LEED I/E analysis, these RuO<sub>2</sub>(100) layers are terminated by bridging O atoms and cus Ru atoms, similar to the RuO<sub>2</sub>(110) surface. In contrast to the bridging O atoms of RuO<sub>2</sub>(110), which are separated to the cus Ru atoms, the bridging O atoms of RuO<sub>2</sub>(100) are attached to cus Ru atoms. Similarly to the RuO<sub>2</sub>(110) film on Ru(0001), CO can be strongly bound over the cus Ru atoms of RuO<sub>2</sub>(100) layers on Ru(10 $\bar{1}$ 0). CO molecules on the RuO<sub>2</sub>(100) layer can readily recombine with the lattice O of RuO<sub>2</sub>(100) to CO<sub>2</sub> with a CO to CO<sub>2</sub> conversion probability, which is similar to that of RuO<sub>2</sub>(110)/Ru(0001).

CO can also strongly adsorb on the bulk (1 $\times$ 2)-RuO<sub>2</sub>(100), which results in a similar catalytic activity towards CO oxidation as those of the RuO<sub>2</sub>(110) and the RuO<sub>2</sub>(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  $\text{RuO}_2$ .

Through the investigations of the CO oxidation on various  $\text{RuO}_2$  surfaces, a general mechanism for the catalytic CO oxidation on  $\text{RuO}_2$  emerges: CO molecules strongly adsorb on cus Ru atoms of the  $\text{RuO}_2$  surfaces. CO can then react with lattice O atoms at  $\text{RuO}_2$  surfaces to  $\text{CO}_2$ . Under steady-state conditions, the  $\text{RuO}_2$  surface may be continuously restored by  $\text{O}_2$  supply from the gas phase [88].