Atomic-Scale Structure and Catalytic Reactivity of the RuO$_2$(110) Surface


The structure of RuO$_2$(110) and the mechanism for catalytic carbon monoxide oxidation on this surface were studied by low-energy electron diffraction, scanning tunneling microscopy, and density-functional calculations. The RuO$_2$(110) surface exposes bridging oxygen atoms and ruthenium atoms not capped by oxygen. The latter act as coordinatively unsaturated sites—a hypothesis introduced long ago to account for the catalytic activity of oxide surfaces—onto which carbon monoxide can chemisorb and from where it can react with neighboring lattice-oxygen to carbon dioxide. Under steady-state conditions, the consumed lattice-oxygen is continuously restored by oxygen uptake from the gas phase. The results provide atomic-scale verification of a general mechanism originally proposed by Mars and van Krevelen in 1954 and are likely to be of general relevance for the mechanism of catalytic reactions at oxide surfaces.

Despite the enormous significance of transition metal oxides as catalysts, little is known about the microscopic properties of their surfaces. With the present system we combine structural information derived from scanning tunneling microscopy (STM) and quantitative low energy electron diffraction (LEED) in conjunction with density-functional theory (DFT) calculations with data for CO adsorption and oxidation to obtain an atomic-scale picture of the reactivity of an oxide surface. The data allow the long-standing concept of coordinatively unsaturated sites (cus) in heterogeneous catalysis to be verified and demonstrate the participation of O atoms as constituents of the oxide lattice in the catalytic reaction.

We prepared the “O-rich” phase by exposing a well-defined Ru(0001) single crystal surface to high doses of O$_2$ (typically about 10$^{-2}$ mbar for several minutes) at 700 K. In this way, a total O$_2$ uptake equivalent to about 10 ML was achieved, as determined by analyzing subsequently taken thermal desorption spectra (TDS). The LEED pattern resulting from such a treatment consists of a superposition of the hexagonal array of diffraction spots with the (1 x 1) periodicity of the Ru(0001) substrate, and additional sharp spots arising from three domain orientations of a lattice with a rectangular mesh with dimensions (6.4 ± 0.3 Å by 3.1 ± 0.2 Å). Within the limits of accuracy, the latter agree with the lattice parameters, (6.38 Å by 3.11 Å), of the (110) plane of bulk RuO$_2$; the following quantitative analysis confirms this assignment.

Exposure to CO at room temperature resulted in changes in the intensities of the LEED spots from the RuO$_2$ structure but not of those with (1 x 1) periodicity of the Ru(0001) substrate. This is a strong indication that the superposition of diffraction spots in the LEED pattern arises from the co-existence of patches of Ru(0001)-(1 x 1)-O (which does not adsorb CO at 300 K) and of RuO$_2$(110) (to which CO is strongly bound as outlined below). This view is confirmed by STM data (Fig. 1).

The LEED and STM data show that a RuO$_2$(110) film is growing epitaxially on the Ru(0001) surface as an incommensurate overlay. A film thickness of about 10 to 20 Å is derived from the STM corrugation when crossing the boundary to an adjacent Ru(0001)-(1 x 1)-O island, in agreement with x-ray reflectivity measurements (10). The RuO$_2$(110) domains are well ordered and exhibit typical dimensions of several hundred angstroms.

Structural analysis was performed by quantitative LEED [the standard technique for surface crystallography (11)] in conjunction with DFT calculations. LEED intensity versus energy data from beams arising from the hexagonal (1 x 1) phase revealed a structure identical to that of the previously analyzed Ru(0001)-(1 x 1)-O phase (4). The structure for the bare RuO$_2$(110) surface is identical to the ideal termination and is reproduced in Fig. 2A.

The electronic structure of RuO$_2$(110) was examined by pseudovalence charge density functional theory calculation. The calculation is based on a local density approximation (LDA) for the exchange-correlation potential. The RuO$_2$(110) film is growing epitaxially on the Ru(0001) substrate. This is a strong indication that the superposition of diffraction spots in the LEED pattern arises from the co-existence of patches of Ru(0001)-(1 x 1)-O (which does not adsorb CO at 300 K) and of RuO$_2$(110) (to which CO is strongly bound as outlined below). This view is confirmed by STM data (Fig. 1).

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RuO$_2$(110) terminated by bridging O atoms.

eV (work function of the “O-rich” Ru surface atomic scale as observed by STM. The stoichiometric surface composition, which shown in Fig. 2A represents a completely calculations are reliable (13). The model shown in Fig. 2A is a completely stoichiometric surface composition, which is supported by the perfect structure on atomic scale as observed by STM. The work function of the “O-rich” Ru surface was experimentally determined to be 5.8 eV (14). DFT calculations for the RuO$_2$(110) surface terminated by bridging O atoms also gave a value of 5.8 eV, whereas without bridging O, the work function was calculated to be 4.12 eV, far too small if compared with the experimental value.

In the bare RuO$_2$(110) structure (Fig. 2A), one Ru atom per unit cell (indicated by Ru$_{\text{cus}}$) is not capped by an O atom and may hence be classified as a coordinatively unsaturated site (cus). According to our DFT calculations (Fig. 3), the cus-Ru atom exposes a kind of dangling bond at the surface, which explains its high reactivity.

To our knowledge, this notion was first introduced by Burwell (9) to account for the gain of activity of Cr$_2$O$_3$ in chemisorption of oxygen or CO or in olefin hydrogenation as a result of heating. It was speculated that coordinatively unsaturated metal ions are responsible for this gain in activity. In the present study this concept could be directly verified: In contrast to the Ru(0001)-(1 x 1)-O surface on which CO is not adsorbed at room temperature, exposure of the RuO$_2$ surface leads to the formation of a chemisorbed species that is detectable in TDS experiments desorbs at around 350 K. This phase was again analyzed by LEED and DFT calculations. In the resulting geometry (Fig. 2B), the CO molecule is attached to a cus-Ru atom through its C atom, with its axis normal to the surface plane. The C–O bond length is 1.13 Å and the Ru–C bond length is 1.95 Å. Both values are similar to those found for CO adsorbed on the bare Ru(0001) surface (15). The agreement between the structural parameters obtained either by experiment (LEED) or theory (DFT) is better than 0.04 Å. DFT calculations gave a CO adsorption energy of about 1.2 eV, consistent with the observed desorption temperature of 350 K (16). The CO binding energy on RuO$_2$ is considerably larger than on other oxide surfaces for which typical energies of about 0.7 eV are reported (7). On the basis of our DFT calculations, we conclude that the bonding mechanism is similar to that described for transition metal surfaces by the so-called Blyholder model (17), namely, by coupling of the CO 5σ orbital to the surface and back-donation of d-electrons from the substrate to the 2π*-derived level of the adsorbate. The strength of the CO adsorption is hence considered as a molecular probe for the d-electron density at the cusp-Ru atom forming the adsorption site.

Figure 4A shows an STM image from the RuO$_2$(110) surface after exposure to 10 L of CO (1 L = 1.3 x 10$^{-6}$ mbar L). The bright, randomly distributed features on the dark rows are identified with adsorbed CO molecules because their density strictly correlates with the gas exposure. Their adsorption site is known (Fig. 2B), and thus the bright strings in this image have to be attributed to the rows of bridging O atoms (18). In view of the fairly low desorption temperature and the small coverage, it is quite surprising that under these conditions individual CO molecules are imaged. Transition metal surfaces are usually energetically
cally rather smooth with regard to CO adsorption so that the activation energy for adsorbate diffusion is typically only on the order of a few tenths of 1 eV. As a consequence, the high mobility of individual CO molecules at room temperature prevents their imaging by STM. In contrast, single CO molecules adsorbed on RuO$_2$(110) are practically immobile at 300 K. This is consistent with the results of DFT calculations, which reveal that the activation barrier for surface diffusion along the troughs is on the order of 1 eV and hence not far away from the energy needed for complete release into the gas phase (1.2 eV).

We believe that this effect also reflects a fundamental difference between metal and oxide surfaces. On a metal surface all substrate atoms are identical, and their wave functions are delocalized so that no strong energy differences are expected if the adsorbate is moved across the unit cell. With an oxide surface, however, the different chemical nature of the atoms causes pronounced localization of the chemisorption bond in the form of dangling bonds (Fig. 3). Nevertheless, in the present case the barrier for lateral displacement of the CO molecules is not too high to prevent reaction with neighboring O atoms. If the CO-covered RuO$_2$(110) surface is briefly heated to 600 K, not only CO but also CO$_2$ comes off the surface, as demonstrated by mass spectrometry. A subsequently recorded STM (Fig. 4B) exhibits the formation of holes in the originally perfect RuO$_2$ surface. This effect is attributed to the partial removal of O atoms from the substrate lattice by reaction with CO to CO$_2$. The bright protrusions are tentatively assigned to small clusters of Ru atoms, which agglomerated after the loss of their O links. Subsequent exposure to O$_2$ at elevated temperatures restores the original defect-free surface structure. Such a redox mechanism was first proposed by Mars and van Krevelen (19) and is verified on atomic scale here.

The high reactivity of the “O-rich” Ru surface in CO oxidation can thus be explained as follows. On the metallic Ru surface, bonding of the O atoms is too strong to allow reaction with CO, which desorbs without reacting (20). This bond becomes weaker with increasing O coverage, but at full monolayer coverage the adsorption energy for CO is in turn too low to ensure appreciable coverages of the second reactant at the elevated reaction temperatures. In contrast, on the RuO$_2$ surface, the strength of CO adsorption (DFT: 1.2 eV) is comparable to that of the bond of the bridging O atoms (DFT: 1.6 eV). Hence, the latter participate in the catalytic reaction and are, on the other hand, continuously restored under steady-state conditions by O$_2$ supply from the gas phase.

**Fig. 4.** (A) STM image (200 Å by 200 Å, U = −1.08 V, I = 0.46 nA, constant current mode) of the RuO$_2$(110) surface after exposure of 10 L CO. The CO molecules are imaged as bright protrusions with an apparent height of 0.5 Å. The CO molecules are sitting between the bright rows. (B) STM image (200 Å by 200 Å, U = −0.82 V, I = 3.34 nA) of the CO-covered RuO$_2$(110) surface of Fig. 3 after annealing to 600 K. The removal of CO molecules is accompanied by the creation of 1.5 Å to 3.0 Å deep holes.

**References and Notes**

13. For the DFT calculations, we used the generalized gradient approximation of J. P. Perdew et al. [Phys. Rev. B 46, 6671 (1992)] for the exchange-correlation functional and used ab initio pseudopotentials created by the scheme of N. Troullier and J. L. Martins [Phys. Rev. B 43, 1991 (1991)] in the fully separable form. The Ru core is taken to consist of all orbitals up to and including 4p states, and O cores consist of the 1s state. The electronic wave functions were expanded in a plane-wave basis set. The surface was modeled by five independent layers of RuO$_2$(110) in a symmetric slab (supercell approach). G. Neugebauer and M. Schefßer, Phys. Rev. B 46, 16067 (1992); by mirror plane operation, nine layers per RuO$_2$(110) slab in total are generated. Consecutive RuO$_2$(110) slabs are separated by a vacuum region of about 16 Å, which was checked to be sufficient to avoid interaction between the RuO$_2$(110) slabs. Calculations were performed with a (1 × 1) surface unit cell with an energy cut-off of 60 Ry. The integral over the Brillouin zone was performed by using a special k-point set by S. L. Cunningham [Phys. Rev. B 10, 4988 (1974), with 8 k-points in the irreducible part of the (1 × 1) Brillouin zone to accelerate the electronic relaxation. Fermi broadening of the occupation numbers was used with a width of 0.1 eV, and the energies were extrapolated to zero temperature. The calculation scheme allowed for the relaxation of the electrons and atoms. We relaxed all O and Ru coordinates, which maintain the planar 2-mm symmetry. Only the positions of the central Ru + O layer lying on the mirror plane of the symmetric RuO$_2$(110) slab were frozen in. The lattice parameters (V = 6.58 Å and c = 3.23 Å) of RuO$_2$(110) determined by DFT optimization of the corresponding bulk RuO$_2$, the values of which compare reasonably well with experimental ones (V = 6.38 Å and c = 3.11 Å). For further details of the program code, see A. P. Seitsonen, thesis, Technical University Berlin (2000) and www.iki.fi/aps/Thesis.html.
16. For CO on Ru(0001) the theoretical value is 1.8 eV. CO desorption takes place at around 480 K [H. Pfnür, P. Feulner, D. Menzel, J. Chem. Phys. 79, 4613 (1983)].
18. This assignment differs from the clean TiO$_2$(110) surface, but it turned out that imaging of bridging O atoms is sensitively affected by the state of the STM tip [U. Diebold et al., Surf. Sci. 411, 137 (1998)].
20. Recent experiments in which a O + CO covered Ru(0001) surface was irradiated by infrared femtosecond laser pulses demonstrated that this obstacle may be overcome by weakening the Ru-O bond through transiently reaching high electron temperatures before CO desorption is completed by phonon excitation [M. Bonn et al., Science, 285, 1042 (1999)].
21. Under similar tunneling conditions, adsorbed O atoms in the Ru(0001).–(2×2)–O phase were previously unequivocally identified with dark spots in the STM image [J. W. Mutterlin et al., Surf. Sci. 394, 159 (1997)].