Atomic-Scale Structure and Catalytic Reactivity of the $RuO_2(110)$ Surface

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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.

Information about the elementary processes involved in heterogeneous catalysis may be obtained from studies with well-defined single crystal surfaces by using techniques from surface physics. In contrast to the conditions of "real" catalysis, such investigations are, however, usually restricted to low gas pressures. A striking example of the problems introduced by this "pressure gap" is presented by the seemingly simple oxidation of CO on some of the Pt group metals. Ru is a poor catalyst at low-pressure conditions (*1*), but turns out to be superior to Pt and Pd if operated in excess O_2 at atmospheric pressure (*2*). The original suggestion that this enhanced activity has to be attributed to the presence of a complete monolayer (ML) of O atoms chemisorbed on the Ru surface (*3*) could not be confirmed. Instead it was found that the latter phase [forming a (1 × 1)-O overlayer on a Ru(0001) single crystal surface (*4*)] is quite inactive, and that the high reactivity is only reached if the total O_2 concentration exceeds the equivalent of about 3 ML (*5, 6*). It will be demonstrated that the active part of this "O-rich" ruthenium phase is RuO_2, which grows epitaxially with its (110) plane parallel to the Ru(0001) surface at high O_2 exposures and elevated temperatures.

Despite the enormous significance of transition metal oxides as catalysts (*7, 8*), 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 (*9*) 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 × 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 × 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 coexistence of patches of Ru(0001)-(1 × 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 overlayer. 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 × 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 × 1) phase revealed a structure identical to that of the previously analyzed Ru(0001)-(1 × 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

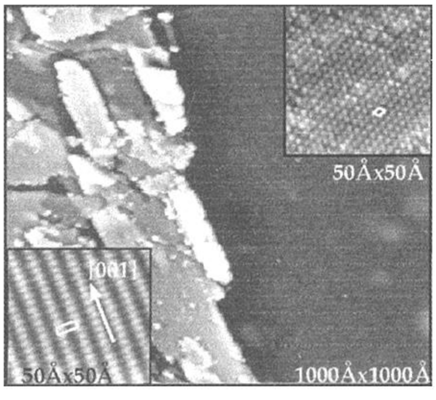

Fig. 1. Large-scale STM (1000 Å by 1000 Å) image together with enlargements (50 Å by 50 Å) as insets. The right side represents a domain of the Ru(0001)-(1 × 1)-O surface; the magnified inset reveals a hexagonal arrangement of dots corresponding to the Ru(0001) lattice where the dark spots mark the locations of the chemisorbed O atoms in the (1 × 1) overlayer (*21*). The bright spots represent Ru atoms coordinated to three O atoms. On the left side, $RuO_2(110)$ domains are visible. The magnified inset shows the internal structure of this phase (parallel rows along the [001] direction) and its rectangular unit cell. The latter is identical to that derived from the LEED pattern. Tunneling parameters are $U = -1.21$ V and 0.46 nA.

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density difference maps (Fig. 3). These plots reflect the hybridization of Ru and O upon bond formation in the solid phase. For example, the O atoms accumulate electron density and adopt the planar sp^2 hybridization (Fig. 3, left). The hybridization of the O and Ru atoms at the surface is very similar to that of related bulk atoms. Thus, these surface atoms expose a kind of dangling bond. Another prominent feature in Fig. 3 is the substantial charge transfer along the Ru–O bonds and the charge accumulation along the Ru–Ru bonds.

The as-grown RuO_2(110) surface has a complete array of bridging oxygens that are formed along the [001] direction, the direction of the rows seen in STM (Fig. 1). The plane formed by the bridging O atoms is located 1.15 Å above the topmost plane of Ru atoms, leading to an Ru–O bond length of 1.93 Å. These values are significantly larger than those determined for TiO_2(110) (*12*). It is important to note that all structural parameters of RuO_2(110) derived from LEED and DFT agree with each other within 0.03 Å, which gives confidence that the approximations made in our DFT calculations are reliable (*13*). The model shown in Fig. 2A represents 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) 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_{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_2O_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 × 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 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 cus-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 ($1 \text{ L} = 1.3 \times 10^{-6}$ mbar·s). 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 energeti-

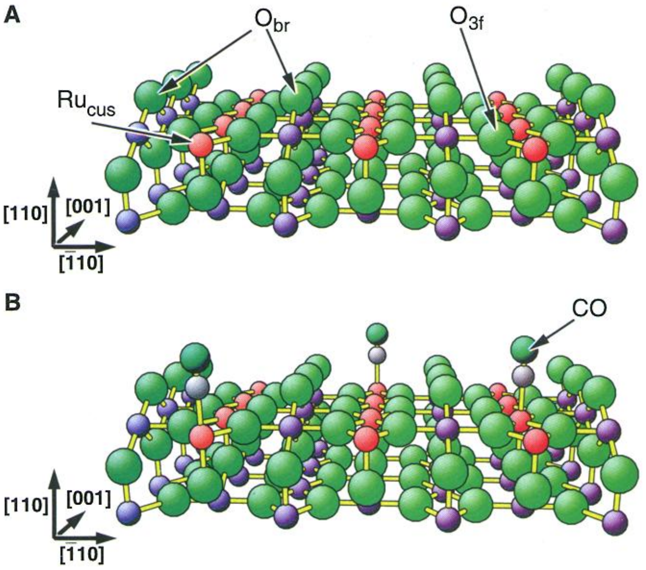

Fig. 2. (**A**) Ball-and-stick model of the bridging O–terminated RuO_2(110) surface. Large (green) balls represent O, and small (blue, red) balls represent Ru atoms of RuO_2(110). A highly active coordinatively unsaturated Ru atom (red atom, cus) as well as bridge-bonded and threefold coordinated O atoms are indicated by arrows. (**B**) Ball-and-stick model of the bridging O–terminated RuO_2(110) surface on which additional CO is adsorbed.

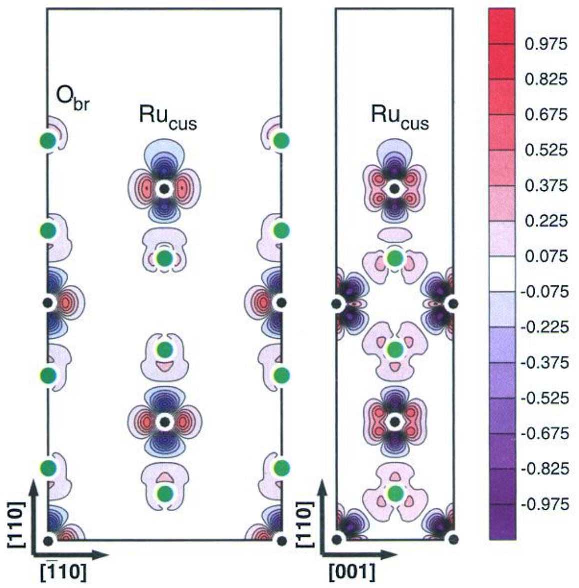

Fig. 3. Pseudovalence charge density contour plots of the RuO_2(110) surface cut through the cus-Ru atom along the [$\bar{1}$10] and the [001] directions from DFT calculations. These plots are defined as the difference between the total valence electron density as determined by DFT calculations, and a linear superposition of radially symmetric atomic charge densities (*22*). Contours of constant charge density are separated by 0.15 eV/Å^3. Electron depletion and accumulation are marked by red and blue areas, respectively.

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.

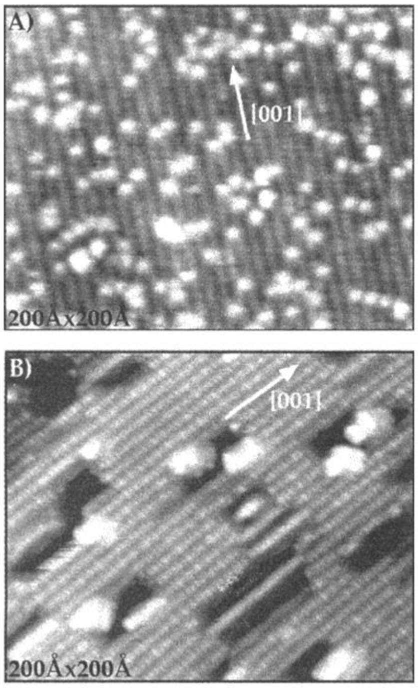

Fig. 4. (**A**) STM image (200 Å by 200 Å, $U = -1.08$ V, $I = 0.46$ nA, constant current mode) of the RuO_2(110) surface after exposure of 10-L CO. The CO molecules are imaged as bright protrusions with an apparent height of 0.5 Å. The CO molecules are sitting between the bright rows. (**B**) STM image (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

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