Structure and Stability of a High-Coverage (1 × 1) Oxygen Phase on Ru(0001)

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The formation of chemisorbed O phases on Ru(0001) by exposure to O_2 at low pressures is apparently limited to coverages $\Theta \leq 0.5$. Using low-energy electron diffraction and density-functional theory we show that this restriction is caused by kinetic hindering and that a dense O overlayer ($\Theta = 1$) can be formed with a (1 × 1) periodicity. The structural and energetic properties of this new adsorbate phase are analyzed and discussed in view of attempts to bridge the so-called "pressure gap" in heterogeneous catalysis. It is argued that the identified system actuates the unusually high rate of oxidizing reactions at Ru surfaces under high oxygen pressure conditions. [S0031-9007(96)01370-1]

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Chemisorption studies with well-defined single crystal surfaces are propelled by the prospect to gain deeper insight into the elementary steps governing heterogeneously catalyzed reactions. Experiments of this kind are usually conducted under ultrahigh vacuum (UHV) conditions with partial pressures typically $\leq 10^{-6}$ mbar in order to apply the standard tools of surface physics and to control the state of the surface. In contrast, "real" catalytic reactions take place at much higher pressures (frequently even exceeding 1 bar); this difference is sometimes referred to as the "pressure gap."

Although there exists a number of examples for which extrapolation of data over a wide pressure range has been demonstrated to be safely justified [1], such a conclusion may by no means be generalized. The concentrations of certain surface species relevant for catalysis at high pressures may be so small under low-pressure conditions that they escape detection, either for thermodynamic (low stability and hence short surface residence time) or for kinetic reasons (low sticking coefficient). Such an example is presumably the Ru(0001) surface interacting with O_2: Dissociative chemisorption under low-pressure conditions leads to apparent saturation at a coverage $\Theta = 0.5$ (the coverage Θ being defined as the ratio of the concentration of adparticles to that of substrate atoms in the topmost layer) associated with the formation of an ordered (2 × 1) superstructure [2,3]. Since the smallest separation of O atoms in the (2 × 1)-O overlayer is only one lattice constant, also a (1 × 1)-O phase with $\Theta = 1$ in which the O atoms form the same lattice as the Ru(0001) seems to be feasible (at least from purely geometrical arguments). Indeed, from high-pressure experiments of the catalytic oxidation of carbon monoxide on Ru(0001) the formation of a high-coverage O phase was speculated [4], and recent density-functional theory (DFT) calculations suggested the existence of an ordered O adlayer with $\Theta = 1$, for which the oxygen is still well chemisorbed, but with a much weaker bond than for the other, more open phases, making the $\Theta = 1$ adlayer particularly effective for oxidizing reactions [5].

An experimental proof of this theoretical result and, in particular, an analysis of whether or not oxygen might be present below the surface Ru layer is still missing. If the formation of the high-coverage phase were indeed only kinetically obstructed, then it may be realized by high oxygen pressure or by exposure to a more strongly oxidizing molecule such as NO_2. The latter approach was first employed to reach high O coverages on Pt(111) [6,7], and more recently it was demonstrated that also for Ru(0001) a concentration of surface oxygen can be obtained reaching, or even exceeding, $\Theta = 1$ [8,9].

In the present Letter we report the confirmation of the formation of a high-coverage $\Theta = 1$ oxygen phase on Ru(0001) where, through the methods of low-energy electron diffraction (LEED) and DFT calculations, we determined the detailed atomic geometry and the associated energetics which give insight into the behavior of O on Ru(0001) in general. Using the technique of dissociative NO_2 chemisorption, we show that this phase is indeed an on-surface (1 × 1) adlayer with a negligible amount of subsurface oxygen.

The experiments were conducted in a UHV chamber (base pressure = 1×10^{-10} mbar) equipped with a display type four grid LEED optics and with standard facilities for surface cleaning and characterization. Details about the experimental setup and sample preparation can be found elsewhere [10]. The preparation of the oxygen overlayer with $\Theta = 1$ was accomplished by first exposing the Ru(0001) surface to O_2 at room temperature until saturation was reached, i.e., the (2 × 1)-O phase was formed. Subsequently, the Ru(0001)-(2 × 1)-O surface was exposed for 15 min to NO_2 at a pressure of 5×10^{-7} mbar. The sample temperature was chosen now to be 600 K so that during decomposition of NO_2 into adsorbed O and NO (the dissociative sticking coefficient of NO_2 is about 1), only O remained on the surface while NO was instantly released into the gas phase, thus enriching the oxygen content at the surface; note that NO desorption from Ru(0001) is completed at about 500 K [11]. Concomitant LEED measurements indicated at first a sharpening of

the (2×2) pattern followed by a gradual transformation into a bright (1×1) pattern with low background intensity, consistent with the formation of a (1×1)-O phase. This (1×1)-O structure remained stable even upon further NO_2 exposure so that no additional oxygen accumulated at the surface, because either the sticking coefficient dropped or the excess oxygen atoms disappear into the subsurface region. Subsequently recorded thermal desorption spectra of O, in combination with the structural analysis (described below), give compelling evidence that additional O atoms are indeed formed which dissolve into the bulk of the sample, leaving the oxygen concentration in the (1×1)-O overlayer constant. A similar behavior was also observed by Weinberg [8]. LEED intensity measurements were performed at normal incidence of the primary beam at a sample temperature of 100 K. A computer-controlled video camera was used to record integrated spot intensities of five integral-order beams (energy range 50 to 620 eV) from the fluorescence screen. LEED curves were calculated using the program code of Moritz [12] and compared with the experimental LEED curves by applying an automated least-squares optimization scheme [13], based either on the reliability (R) factors R_{DE} [14] or R_P [15].

For the DFT calculations we employed the generalized gradient approximation (GGA) of Perdew *et al.* [16] for the exchange-correlation functional and used *ab initio,* fully separable pseudopotentials. The surface was modeled by a supercell consisting of four layers of Ru(0001) where the O atoms were adsorbed on one side of this slab [17,18]. We relaxed the positions of the O atoms and of the Ru atoms in the top two layers, keeping the lower two Ru layers fixed at the bulk values. Details of the calculations, as well as a discussion of the clean Ru surface and more open O adlayers, can be found in Ref. [5].

In the LEED analysis, the O-Ru layer spacing and the first two Ru-Ru layer spacings of the Ru(0001)-(1×1)-O surface were simultaneously refined, starting the automated search from different adsorption sites of oxygen, namely the fcc, hcp, on-top, and bridge sites. The resulting optimum R factors for the quoted adsorption sites are compiled in Table I from which it becomes evident that the hcp position is clearly favored. In addition to these standard configurations, we tested a (1×1) structure placing O in both the fcc and hcp positions with variable concentrations. The mixing of adsorption sites with

TABLE I. Optimum R factors for different structural models of Ru(0001)-(1×1)-O.

O-adsorption site	R_P	R_{DE}
On top	0.68	0.47
Bridge	0.60	0.39
fcc	0.59	0.49
hcp	0.23	0.21
No oxygen	0.55	0.37

variable concentrations was simulated within the framework of the averaged-t-matrix approximation [19]. The multiple scattering between neighboring O atoms in fcc and hcp sites could alternatively be switched off. The best agreement with the experiment was in all cases achieved by the adsorption of O atoms exclusively in hcp sites. Even a small concentration $(\Theta = 0.1)$ of O atoms in fcc sites deteriorated the theory-experiment agreement appreciably, as indicated by an increase of the R factors by 0.05. The next issue we addressed carefully was as to whether the results are sensitive to the presence of subsurface oxygen. For this purpose we put, in addition to the O-(1×1) overlayer, O atoms with variable concentrations into the octahedral sites between the first two Ru layers and optimized their concentration and the structural parameters. The optimization scheme always ended with a structure in which O adsorbs again solely in hcp sites on the surface. On the basis of these simulations we can therefore safely rule out any O concentration exceeding 0.1 monolayer (ML) between the top two Ru layers. Thermal desorption spectra (TDS) of oxygen, on the other hand, indicate that there is much more oxygen than $\Theta = 1$ present in this system. Obviously, these O atoms prefer to dissolve into the bulk rather than to form a subsurface phase between the first two Ru layers.

The optimum atomic geometry of the Ru(0001)-(1×1)-O phase, as provided by the LEED analysis, is displayed in Fig. 1. The intensity spectra for this best-fit geometry are shown in Fig. 2; the corresponding R factors are $R_{DE} = 0.21$ and $R_P = 0.23$. The Ru-O bond length of 2.00 ± 0.03 Å is similar to the data reported previously for the (2×2)-O $(\Theta = 0.25)$ and the (2×1)-O $(\Theta = 0.5)$ structures which are 2.03 and 2.02 Å, respectively [20]. A remarkable feature of the (1×1)-O phase is the substantial expansion of the topmost Ru layer spacing (2.22 Å) by 3.7%. This expansion is comparable to that derived for the O/Zr(0001) system (3.1%) where 1 ML of oxygen is reported to be evenly distributed in octahedral sites between the first and second, and second and third Zr layers [21].

The experimentally derived structural data agree nicely with the results of total-energy calculations performed
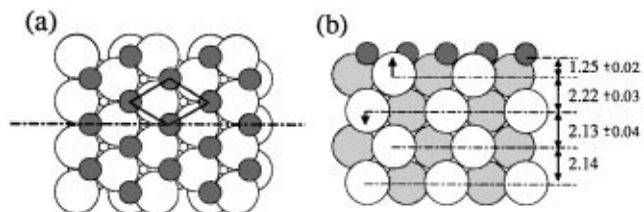

FIG. 1. Top view (a) and side view (b) of the atomic geometry of (1×1)-O/Ru(0001) with O sitting in the hcp-hollow site. The arrows indicate the direction of the displacements of the substrate atoms with respect to the bulk terminated positions. The distances are those determined by LEED and are given in Å.
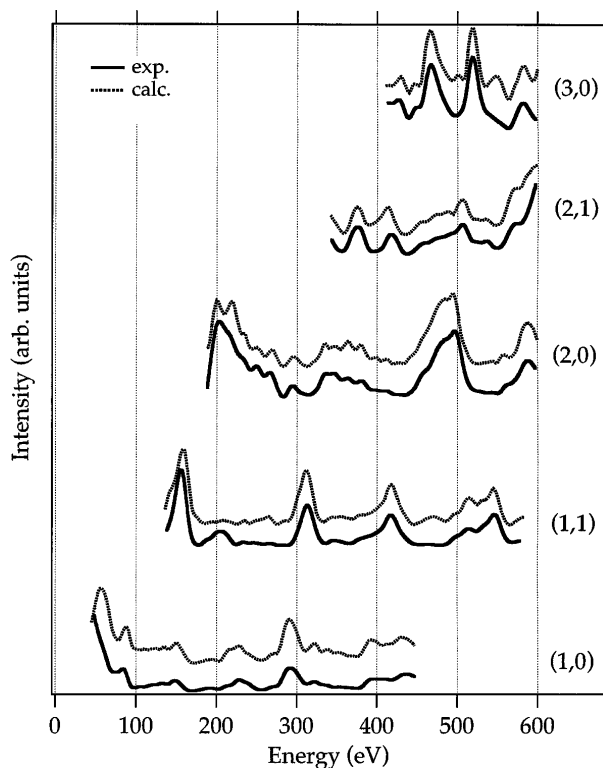
FIG. 2. Comparison between experimental and calculated LEED curves for the best-fit geometry of the (1×1)-O phase on Ru(0001). The overall R factors are $R_{DE} = 0.21$ and $R_P = 0.23$.

for varying O coverages, namely the (2×2)-O, (2×1)-O, and (1×1)-O structures. For all these phases, the energetically most favorable adsorption site was found to be the hcp site. In Table II, the structural parameters for the (1×1)-O system provided by DFT-GGA and LEED are compared; the agreement convincingly demonstrates the power and reliability of the DFT-GGA calculations. It is important to notice that the large expansion of the top Ru interlayer spacing is not due to subsurface oxygen. It results from the binding of the surface Ru atoms with on-surface oxygen which empties bonding Ru-Ru d states, weakening the attraction between the top and second substrate layers. In Fig. 3, the calculated binding energies for an oxygen atom in these three oxygen phases are compiled for the cases where the O atoms reside in hcp and fcc positions. It can be seen that with increasing O coverage the binding energy becomes smaller which reflects a repulsive interaction between the adsorbates and is stronger for oxygen in the hcp than in the fcc site. Using these results for a simulation of thermal desorption spectra [22] we obtain good agreement with experimental data [2] corresponding to the coverage range $\Theta \leq 0.5$. For oxygen in the hcp site at $\Theta = 1$, the energy required to remove one oxygen atom, i.e., the energy to create an oxygen vacancy in the adlayer is quite small, namely, 1.2 eV. This result was estimated

TABLE II. Structural parameters of the (1×1)-O phase on Ru(0001) as obtained by DFT-GGA calculations (see text and Ref. [4]) and the LEED analysis.

Parameter	DFT-GGA	LEED
Ru-O layer spacing (Å)	1.26	1.25 ± 0.02
Ru-O bond length (Å)	2.03	2.00 ± 0.03
Change of first Ru interlayer spacing (%)	+2.7	$+3.7 \pm 1.4$
Change of second Ru interlayer spacing (%)	−0.9	-0.5 ± 1.8

from calculations with a (2×2) surface cell [23]. The artificial vacancy-vacancy interaction is negligible for our concerns, i.e., less than ± 0.15 eV, as tested by larger surface cells. Comparing the binding energies per atom of the two $\Theta = 1$ layers, we find that the energy difference is only 0.06 eV. Because the $\Theta = 1$ layer forms subsequently after the completion of the lower coverage phases for which the hcp site is by several tenths of an eV more favorable, it has been argued [5] that, despite the small energy difference, the $\Theta = 1$ phase might be a rather perfect hcp-site adlayer. Nevertheless, it is obvious that an independent, experimental structure analysis of this system was mandatory. The very good agreement between the structural parameters obtained by DFT-GGA and LEED, discussed above, provides the required confirmation.

The above results imply that the saturation O coverage $\Theta \sim 0.5$, which is reached after exposing a Ru(0001) surface to O_2 at low pressure, is only apparent and in fact limited by the kinetics of dissociative adsorption. Since the rate of impingement increases in proportion to the partial pressure, catalysis under high-pressure conditions with an excess of O_2 in the feed becomes rather likely to involve surface phases with O coverages approaching $\Theta = 1$. Given the fact that the metal-oxygen bond strength is rather weak at the full coverage (see Fig. 3), it is expected to improve the reactivity for reactions of the type $O_{ad} + X \rightarrow OX$. The present
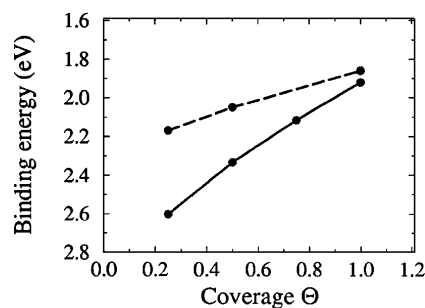

FIG. 3. Binding energy of O on Ru(0001) at various coverages, with respect to $\frac{1}{2} O_2$ molecule. Adlayers are assumed with fcc-hollow adsorption sites (dashed line) and with hcp-hollow sites (continuous line).

system hence represents, in our opinion, an example for which extrapolation of the kinetics of a catalytic reaction across the pressure gap may be questionable, as also suggested by the quoted work on CO oxidation [4].

Extrapolation of the data of Fig. 3 to even higher coverages suggests that adsorption of oxygen even beyond $\Theta = 1$ might still be exothermic. DFT-GGA calculations at coverages $\Theta = 1.25$ indicate, however, that further incorporation of O chemisorbed on the surface into the (1×1)-O structure is unstable. On the other hand, the occupation of the subsurface octahedral adsorption site, just below the first Ru layer, is still exothermic; it is, however, appreciably less favorable than on-surface sites for coverages $\Theta \leq 1$. Interestingly, for even deeper positions, the binding energy of these additional O atoms is similar. Furthermore, the diffusion energy barriers for oxygen penetrating through the first and second Ru layers are found to be such that the barrier for passing through the second layer is significantly smaller than that of the first, O-covered Ru layer. As a consequence, the theoretical results suggest that subsurface oxygen will dissolve into the bulk on entropy grounds. From these calculations (and also from our TDS experiments) the existence of a close-packed O overlayer with $\Theta = 3$ on Ru(0001) as proposed by Malik and Hrbek [9] can clearly be ruled out. Hence, an impinging NO$_2$ molecule gets either reflected by the (1×1)-O surface or dissociation takes place and the oxygen atom is incorporated into the subsurface region from where it proceeds into the bulk.

In summary, from a combined investigation using DFT-GGA and LEED we confirmed the existence of a high-coverage ($\Theta = 1$) phase of oxygen on Ru(0001) and provide a detailed identification of the geometry. Furthermore, we provided evidence that atomic oxygen may enter Ru bulk once all the on-surface hcp sites are occupied, but not staying between the first and second substrate layer. This unusually high-coverage oxygen structure on Ru(0001) is likely to enhance the rate of oxidation reactions (e.g., of carbon monoxide) and other surface reactions involving adsorbed oxygen. It also immediately raises the questions of the possible existence of other high-coverage adsorbate structures likewise achievable by bypassing the pressure gap.

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[23] The energy requred to create an O vacancy, E_f^{vac}, is obtained as $E_f^{\text{vac}} = E_{\text{tot}}^{(2\times2)-3\text{O}} + E_{\text{tot}}^{\frac{1}{2}\text{O}_2} - E_{\text{tot}}^{(2\times2)-4\text{O}}$, where $E_{\text{tot}}^{(2\times2)-3\text{O}}$, $E_{\text{tot}}^{(2\times2)-4\text{O}}$, and $E_{\text{tot}}^{\frac{1}{2}\text{O}_2}$ are the total energies at temperature $T = 0$ K for the (2×2) structures with three and four oxygen atoms in the surface unit cell, and for $\frac{1}{2}$O$_2$ in the gas phase, where for the O$_2$ dimer we have included the spin-polarization energy of 0.91 eV.