

# CO Oxidation Reaction over Oxygen-Rich Ru(0001) Surfaces

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The formation of CO<sub>2</sub>, by exposing oxygen precovered Ru(0001) surfaces to CO, was investigated as a function of the oxygen coverage for sample temperatures up to 900 K. It turned out that the reaction probability per incident CO molecule is below  $5 \times 10^{-4}$  for O coverages up to 3 monolayers (ML); oxygen in excess of 1 ML is located in the subsurface region. The reaction probability for the (1 × 1)-1O phase is in agreement with the data derived from high-pressure experiments by Peden and Goodman [*J. Phys. Chem.* **1986**, *90*, 1360]. Even for CO molecules with a translational energy of 1.2 eV (supersonic molecular beam experiments), the reaction probability is less than  $5 \times 10^{-2}$ . This value is consistent with the activation barrier derived from DFT calculations for a reaction by direct collision from the gas phase (Eley–Rideal mechanism). Beyond an oxygen load of 3 ML, however, the reaction probability increases by 2 orders of magnitude. It is suggested that this enhancement is due to a further destabilization of the surface oxygen by the onset of oxide formation.

## I. Introduction

The catalytic oxidation of carbon monoxide at platinum-group metal surfaces is probably the most extensively studied reaction under ultrahigh vacuum (UHV) as well as under real reaction conditions qualifying it to be a prototypical system. There is general agreement that the reaction proceeds via the so-called Langmuir–Hinshelwood mechanism (LH), which requires chemisorption of both reactants prior to their recombination.<sup>1</sup> Many of these studies indicated that results obtained under UHV conditions such as the reaction rate can readily be transferred to the high-pressure regime. Therefore, elementary steps of the reaction mechanism identified under UHV conditions were considered to be equally important under real reaction conditions.

One prominent example for which this simple correspondence apparently failed is the CO oxidation reaction over a Ru(0001) surface. It is well documented that Ru is the least active platinum-group metal in CO oxidation under UHV conditions,<sup>2</sup> while the reaction rate under high-pressure and oxidizing conditions turned out to be exceptionally high.<sup>3</sup> Since in both studies a Ru(0001) single crystal was used, this apparent discrepancy was considered to underline the importance of the so-called “pressure gap”. In contrast to ruthenium, other platinum-group metals, such as Pt, Rh, and Pd, are most active under conditions where the CO coverage is about as high as the O coverage. Since the high reaction rate over Ru(0001) was achieved under conditions where the oxygen coverages were high and the CO coverage negligibly small, two conclusions were drawn:<sup>4</sup> First, the high O coverage phase (about 1 monolayer) may be responsible for this “pressure gap” since under normal UHV conditions it is not easy to produce such high oxygen coverages on Ru(0001) for kinetic reasons.<sup>5</sup> Under UHV conditions oxygen exposure leads only to the formation of (2 × 2)-O and (2 × 1)-O overlayers on Ru(0001). Below we will see that oxygen exposures of several millions of

langmuirs are able to produce a (1 × 1)-O overlayer and varying concentrations of subsurface oxygen; in the following the pure (1 × 1)-O adlayer without subsurface oxygen is referred to as (1 × 1)-1O, while (1 × 1)-xO defines a surface with (1 × 1) symmetry which contains *x* monolayers (ML) of oxygen (1 ML of oxygen on top and (*x* − 1) ML in the subsurface region). Second, the CO oxidation reaction may proceed via the so-called Eley–Rideal mechanism (ER); i.e., only one of the reactants (O) is chemisorbed, while the other species (CO) reacts by direct collision from the gas phase.

Recently, it has been shown<sup>6,7</sup> that the high-coverage (1 × 1)-O phases can also be produced under UHV conditions simply by exposing the surface to NO<sub>2</sub> instead of O<sub>2</sub>. At 600 K, NO<sub>2</sub> dissociates into O<sub>ad</sub> and NO<sub>ad</sub>, and NO desorbs immediately into the gas phase. As a consequence, the Ru(0001) surface becomes enriched with adsorbed oxygen, and oxygen loads equivalent to several monolayers (ML) are easily prepared in this way. Oxygen in excess of 1 ML is located in the subsurface region. The energetics and the atomic geometry of the novel (1 × 1)-1O overlayer phase were carefully analyzed by employing both density functional theory (DFT) calculations and quantitative LEED.<sup>7</sup> It turned out that the adsorbed oxygen atoms are less strongly bound by 0.8 eV in comparison with the low-coverage (2 × 2)-O phase. Since the activation barrier for CO oxidation is considered to be related to the strength of the metal–O bond,<sup>8</sup> the oxygen species in this high-coverage phase might be considered as the active species for CO oxidation reaction under oxidizing conditions; this O species would therefore bridge the above-mentioned “pressure gap”. To elucidate the mechanism leading to this high reaction rate over Ru(0001), further detailed DFT calculations for the (1 × 1)-1O precovered Ru(0001) surface were carried out.<sup>9</sup> The main conclusions drawn by this investigation were that the ER mechanism cannot account for the observed high CO oxidation reaction rate, and a lower bound for the activation barrier of about 1.1 eV was derived. The experimentally found high turnover rates for the CO oxidation reaction<sup>3</sup> were attributed to

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CO chemisorption in an imperfect ( $1 \times 1$ )-IO overlayer and further reaction to  $\text{CO}_2$ , thus favoring the LH mechanism.

In this contribution we report on CO reaction experiments over oxygen precovered Ru(0001) surfaces with varying O coverages up to and beyond 1 ML. It will be shown that the probability for CO oxidation is negligibly small for all cases with O coverages up to 1 ML. We do, however, find high reaction rates if the O content of the surface region exceeds about 3 ML. By this effect the apparent existence of a "pressure gap" under steady-state reaction conditions can be rationalized.

## II. Experimental Details

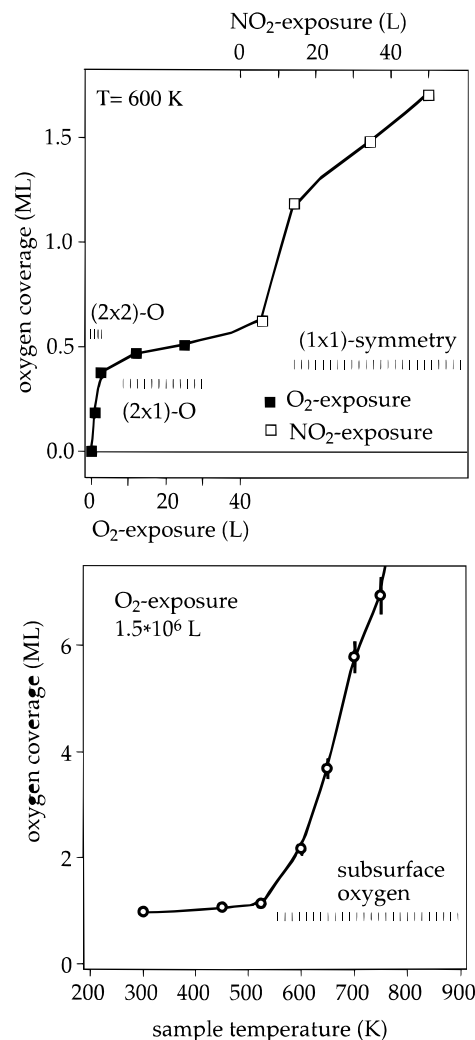
The experiments were conducted in a newly designed UHV chamber which houses standard facilities for surface characterization and preparation such as ultraviolet photoelectron spectroscopy (UPS), quadrupole mass spectrometry (QMS), and low-energy electron diffraction (LEED). The base pressure was better than  $1 \times 10^{-10}$  mbar. The UHV chamber is connected to a two-stage molecular beam source which is able to produce a CO molecular beam with well-defined translational energy and momentum. Utilizing a seeded beam technique and heating the nozzle to about 950 K, we could vary the kinetic energy of the impinging CO molecules up to 1.2 eV, maintaining a CO flux which corresponds to an effective pressure within the CO beam of  $1.3 \times 10^{-9}$  mbar.

Preparation of the Ru(0001) sample was performed by repeated cycles of  $\text{Ar}^+$  ion sputtering ( $5 \mu\text{A}/2 \text{ kV}/2 \times 10^{-5}$  mbar of Ar) and baking the sample at 1100 K in an oxygen back-pressure of  $10^{-7}$  mbar for 10 min. Final annealing of the sample to 1600 K removes the residual oxygen on the surface. With LEED the sample showed a bright ( $1 \times 1$ ) pattern with low background intensity.

The ( $1 \times 1$ )-O phases were prepared in a two-step procedure. First, the sample was exposed to 30 langmuirs of  $\text{O}_2$  (Messer Griesheim, purity 99.998%), resulting in a ( $2 \times 1$ )-O phase on Ru(0001). Next, this overlayer was exposed to 15 langmuirs of  $\text{NO}_2$  (Messer Griesheim, purity 98%, main contaminants  $\text{HNO}_3$  with volume concentration  $\leq 1.5\%$  and  $\text{H}_2\text{O}$  with volume concentration  $\leq 0.5\%$ ) which transforms the ( $2 \times 1$ )-O into a ( $2 \times 2$ )- $3\text{O}^{10}$  and eventually into a ( $1 \times 1$ )-IO overlayer structure. Even higher  $\text{NO}_2$  doses lead to the formation of subsurface oxygen, keeping the ( $1 \times 1$ )-O overlayer on the surface. The coverage was determined by the integral thermal desorption  $\text{O}_2$  signal which is calibrated against the ideal O coverage of the ( $2 \times 1$ )-O (assumed to be 0.5 ML). To accommodate even more oxygen at the surface, one has to expose the Ru(0001)-(2  $\times$  1)-O surface to still higher doses of  $\text{NO}_2$ . The various oxygen coverages achieved in this way at 600 K are summarized in Figure 1a.

Alternatively, one can produce the high O concentration phases by dosing several  $10^6$  of langmuirs of molecular oxygen. The actual uptake of oxygen on Ru(0001) depends then critically on the sample temperature as indicated in Figure 1b. The observed critical temperature of about 600 K might indicate the onset of subsurface penetration and surface oxide formation, as beyond this temperature substantially higher O coverages are achievable. To introduce such high  $\text{O}_2$  doses into the UHV system, the chamber was backfilled with  $10^{-2}$  mbar of oxygen. A very efficient pumping system, in particular a large-area liquid nitrogen cooled sublimation pump, ensures the base pressure of  $1 \times 10^{-10}$  mbar to be restored within 15 min.

The CO oxidation reaction rate (by postdosing CO) for most of these precovered O phases on Ru(0001) is extremely low; i.e., the probability for an impinging CO molecule to form  $\text{CO}_2$  is in the range of  $10^{-4}$ – $10^{-6}$  and therefore hardly to be detected



**Figure 1.** (a) Amount of oxygen taken up by the Ru(0001) when first exposed to molecular oxygen and subsequently to  $\text{NO}_2$ . The sample temperature was kept at 600 K. The coverage given in ML is calibrated by assuming that the coverage at  $\text{O}_2$  saturation is 0.5 ML. (b) Amount of oxygen taken up by the Ru(0001) when exposed to  $1.5 \times 10^6$  langmuirs of molecular oxygen at various sample temperatures. At about 600 K the oxygen uptake increases steeply due to oxygen penetration (activated process) into the subsurface region.

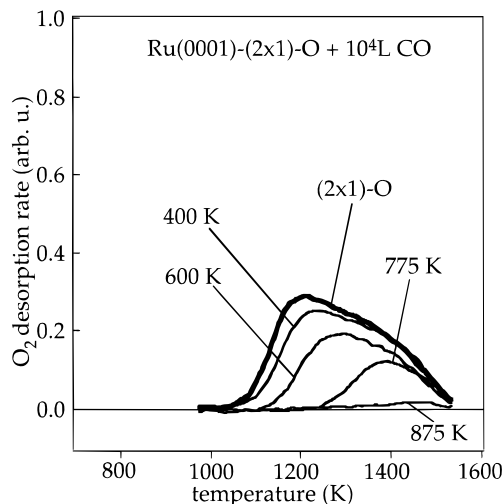
on-line by a mass spectrometer (QMS). Hence, we used an integral method to determine the mean CO/ $\text{CO}_2$  conversion probability. For this purpose, we postexposed the O precovered Ru(0001) (at a fixed sample temperature) to various amounts of CO (Messer Griesheim, purity 99.997%,  $\text{H}_2$  concentration  $< 1$  ppm) and afterward determined the oxygen coverage left at the surface by a thermal desorption experiment. Assuming that only the process of CO oxidation depletes the oxygen content at the Ru(0001) surface, the amount of removed oxygen at the surface gives a direct measure of the mean probability for CO to form  $\text{CO}_2$ . To be sure that predominantly the impinging CO molecules and not other gas molecules remove oxygen from the surface under our experimental conditions, we alternatively exposed  $\text{H}_2$ , the main constituent of the background pressure, instead of CO. We did not observe any measurable oxygen depletion on introducing 100 langmuirs of  $\text{H}_2$  into the chamber and keeping the sample temperature at 600 K, as long as the oxygen content exceeds 1 ML at Ru(0001). Therefore, hydrogen, which might also be introduced during CO dosing, does not play a role in the O abstraction process.

### III. Results

**3.1. Molecular Beam Experiments.** A thermal CO molecular beam providing an effective partial pressure within the beam of about  $10^{-7}$  mbar was scattered at the  $(1 \times 1)$ -1O precovered Ru(0001) surface, keeping the sample at well-defined temperatures, and the  $\text{CO}_2$  molecules coming off the surface were monitored by a QMS. For sample temperatures between 200 and 750 K, the measured  $\text{CO}_2$  signal was, however, not affected by the presence of the CO beam. To improve the signal-to-noise ratio, we also employed the lock-in technique by chopping the CO beam with a frequency of 167 Hz. But also here no  $\text{CO}_2$  signal resulting from reaction at the surface was detectable. Finally, we increased the nozzle temperature to enhance the translational and vibrational energy of the impinging CO molecules, giving the same negative result. The CO molecules reflected from the surface can readily be measured so that the signal-to-noise ratio was estimated to be  $5 \times 10^{-4}$ . Since the sensitivity of our mass spectrometer for CO and  $\text{CO}_2$  is very similar, we are able to infer from this negative result an upper bound for the CO/ $\text{CO}_2$  conversion rate of  $5 \times 10^{-4}$ . This result can now be compared with the reaction probability as found under high-pressure conditions by Peden et al.<sup>3</sup> Assuming that the CO gas temperature is 300 K (partial CO pressure 16 Torr) and that all CO molecules striking the surface have the same probability<sup>11</sup> to be converted into  $\text{CO}_2$ , a turnover frequency of 50  $\text{CO}_2$  molecules/s and  $(1 \times 1)$  unit cell area corresponds to a CO/ $\text{CO}_2$  conversion probability of  $2.3 \times 10^{-5}$ . This is still about 1 order of magnitude smaller than the achieved sensitivity of our molecular beam experiment. At this point, it is worth mentioning that a Cs precovered surface is much more active so that CO oxidation could readily be observed in molecular beam experiments.

Recent DFT calculations found that the activation barrier for an impinging CO molecule to form  $\text{CO}_2$  over a  $(1 \times 1)$ -1O precovered Ru(0001) surface (via an ER mechanism) is in the range 1.1–1.6 eV, depending on the orientation of the CO axis relative to the surface normal (ranging from  $0^\circ$  to  $49^\circ$ ).<sup>9</sup> These activation barriers were determined by assuming that the CO molecules approach directly above the adsorbed oxygen atoms so that the phase space explored by the DFT calculation was quite small. Motivated by this theoretical study, we performed another molecular beam experiment using the seeded beam technique in order to determine the activation barrier inherent in that CO oxidation process. Using a gas mixture of 99% He and 1% CO and heating the nozzle to 950 K increased the kinetic energy of the CO molecules in the beam to 1.2 eV. The sample temperature was varied between 500 and 800 K. Even under these conditions, no  $\text{CO}_2$  formation was detected. From the measured intensity of CO molecules reflected from the surface, the CO/ $\text{CO}_2$  conversion rate can be estimated to be lower than  $5.0 \times 10^{-2}$ , which corresponds to an (over the whole phase space) averaged activation barrier of  $\geq 1.4$  eV. This value is consistent with the activation barrier derived from the DFT calculations (recall that the phase space explored by the DFT calculations was rather small).<sup>9</sup>

**3.2. Integral Reaction Rates Monitored by the Residual O Coverage.** Figure 2 shows oxygen desorption spectra that were taken after a  $(2 \times 1)$ -O precovered Ru(0001) surface had been exposed to  $10^4$  langmuirs of CO at various sample temperatures as specified in the figure. (For each sample temperature the  $(2 \times 1)$ -O phase was again prepared.) From these experiments it is seen that with increasing sample temperature the oxygen coverage left on the surface decreases or, in other words, the mean probability for  $\text{CO}_2$  formation increases. The reaction probability at 600 K is  $6 \times 10^{-5}$ . CO

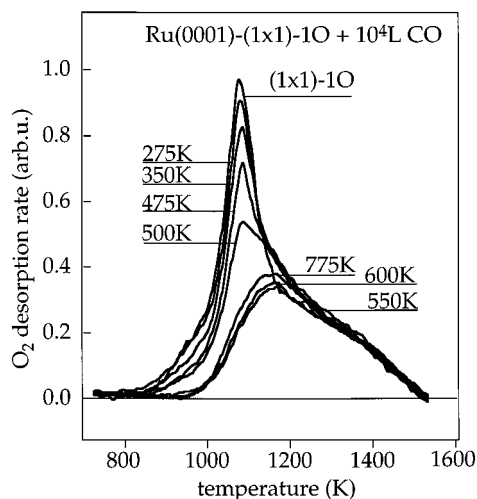


**Figure 2.**  $\text{O}_2$  thermal desorption spectra taken after a  $(2 \times 1)$ -O precovered Ru(0001) surface was exposed to  $10^4$  langmuirs of CO, keeping the sample at various temperatures as specified in the figure. The reference TD spectrum is that of the untreated  $(2 \times 1)$ -O phase.

oxidation sets in at about 400 K. Exposing the Ru(0001)– $(2 \times 1)$ -O surface to CO at lower temperatures does not affect the oxygen coverage at all. The reason is that for sample temperatures as low as 200 K CO molecules just adsorb at the surface, and on performing the thermal desorption experiments, CO comes off the surface below 400 K before forming  $\text{CO}_2$ .<sup>12</sup> Obviously, the activation energy for  $\text{CO}_2$  formation is too high to be overcome at 400 K. Around room temperatures oxygen atoms become mobile enough to arrange themselves into a honeycomb structure in the presence of coadsorbed CO molecules, leading to an ordered  $(2 \times 2)$ – $(2\text{O} + 1\text{CO})$  overlayer structure.<sup>13</sup> It is an intriguing feature of this mixed overlayer structure that O atoms occupy both fcc (face-centered-cubic) and hcp (hexagonal-close-packed) sites in order to open on-top sites for CO to chemisorb on; note that the difference in the binding energy for fcc and hcp sites is about 0.3 eV in the  $(2 \times 1)$ -O phase.<sup>14</sup> The oxygen site change stabilizes CO in this coadsorbate phase up to about 400 K. This temperature is high enough to surmount the activation barrier for CO oxidation during the TD experiment, but the probability for this process is quite small.<sup>11</sup>

Beyond 500 K, CO is only temporarily adsorbed on the surface during which the CO oxidation reaction must take place. Depending on the sample temperature, the impinging CO molecules accommodate only for a short time at the surface while they can react with oxygen to form  $\text{CO}_2$ . Hence, with increasing sample temperature two competing effects are simultaneously operative at the surface. On one hand, the mean residence time of CO on the oxygen precovered surface is shortened with increasing sample temperature. This reduces the probability for CO oxidation in an Arrhenius-like way. On the other hand, the activation barrier can be overcome more easily with increasing sample temperature; the CO/ $\text{CO}_2$  conversion rate increases now in an Arrhenius fashion. Inspection of Figure 2 indicates that for  $\theta_{\text{O}} \leq 0.5$  the net reaction rate increases with temperature, suggesting that the activation energy for the process  $\text{O}_{\text{ad}} + \text{CO}_{\text{ad}} \rightarrow \text{CO}_2$  exceeds that for CO desorption.

Analogous experiments were also conducted with the  $(1 \times 1)$ -1O precovered Ru(0001) surface (cf. Figure 3). In this case, the situation might be less involved than for the  $(2 \times 1)$ -O case, as structural rearrangements of oxygen in the  $(1 \times 1)$  phase are not expected to occur at the beginning, while, on the other hand, the CO coverage will be very low for sample temperatures above

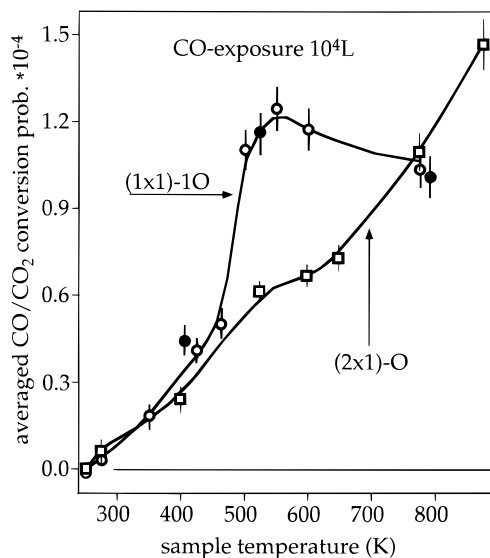


**Figure 3.**  $\text{O}_2$  thermal desorption spectra taken after a  $(1 \times 1)\text{-O}$  precovered Ru(0001) surface was exposed to  $10^4$  langmuirs of CO, keeping the sample at various temperatures as indicated in the figure.

275 K, as evidenced by recent infrared absorption spectroscopy (IRAS) measurements.<sup>15</sup> Yet, CO molecules can adsorb on this surface when vacancies are created into the  $(1 \times 1)\text{-O}$  network. With rising sample temperature, again the number of oxygen atoms removed from the surface by impinging CO molecules is increased (cf. Figure 3). At about 550 K, the oxygen removal levels off, leaving 0.6 ML of oxygen at the surface. At a first glance, it seems that the measurements in Figure 3 for reaction temperatures above 550 K conflict with the measurements shown in Figure 2 since there, even at O coverages of 0.5, impinging CO molecules are able to abstract oxygen atoms from the surface. However, it might be that at temperatures above 500 K and  $\theta_{\text{O}} > 0.5$  the mean residence time of CO becomes crucial; i.e., with increasing sample temperature the time interval for a CO molecule on the surface to form  $\text{CO}_2$  is too short. CO titration experiments at 550 K and with larger CO exposures indicate that more oxygen can be readily removed from the  $(1 \times 1)\text{-O}$  precovered Ru(0001) surface.

In Figure 4 the integral reaction rates, i.e., the averaged CO/ $\text{CO}_2$  conversion probabilities, are compared for the  $(2 \times 1)\text{-O}$  and  $(1 \times 1)\text{-O}$  precovered Ru(0001) surfaces. It should be noted that the applied CO exposures in these experiments are quite large so that the reaction probability turns out to be systematically underestimated for higher reaction temperatures due to an averaging over a considerable O-coverage range. Therefore, the interpretation of the observed decrease of conversion probability for the  $(1 \times 1)\text{-O}$  phase is not straightforward although its effect is reproducible. It might be that this decrease is related to the short mean residence time of CO at higher temperatures.

Since both the metal–O bond strength and the sticking probability for CO are notably different in both phases,<sup>4</sup> it is quite surprising that at low sample temperatures from 260 to 450 K the reaction probabilities for the  $(2 \times 1)\text{-O}$  and  $(1 \times 1)\text{-O}$  phases are almost identical. This may point toward a mechanism that is associated with defects at the surface, such as steps, which are independent of the actual oxygen coverage. The CO oxidation reaction starts then predominantly from steps; the importance of steps for the reaction rate of water on Ru(0001) was recently discussed.<sup>16</sup> If this simple interpretation holds, the  $(2 \times 1)\text{-O}$  phase on an ideal Ru(0001) surface might be considered as being almost inactive, and the  $(1 \times 1)\text{-O}$  phase is substantially more active above 500 K than the  $(2 \times 1)\text{-O}$  phase. For the  $(2 \times 1)\text{-O}$  phase on the real Ru(0001) surface,

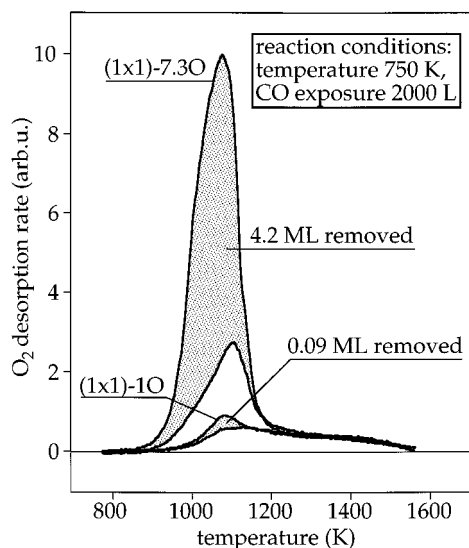


**Figure 4.** Integral CO reaction rates in terms of the averaged CO/ $\text{CO}_2$  conversion probabilities are shown for the  $(2 \times 1)\text{-O}$  phase in comparison with the  $(1 \times 1)\text{-O}$  precovered Ru(0001) surfaces as function of the sample temperature at which the CO oxidation reaction takes place. Both surfaces were exposed to  $10^4$  langmuirs of CO. Solid and open symbols indicate measurements taken at different days. Circular symbols correspond to conversion probabilities of the  $(1 \times 1)\text{-O}$  phase, while rectangular symbols indicate conversion probabilities of the  $(2 \times 1)\text{-O}$  phase.

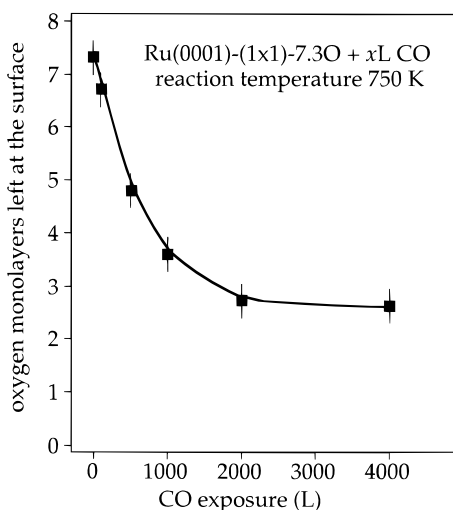
the initial probability for an impinging CO molecule to form  $\text{CO}_2$  can be estimated to be less than  $6 \times 10^{-5}$  for  $T \leq 500$  K.

As already pointed out in section II, very high O loadings can also be prepared by just exposing the Ru(0001) surface to several  $10^6$  langmuirs of  $\text{O}_2$ . This kind of preparation bears the appealing advantage of being closer to conditions where CO is catalytically oxidized by oxygen (rather than by  $\text{NO}_2$ ). Figure 1b indicates that an exposure of  $1.5 \times 10^6$  langmuirs of  $\text{O}_2$  at a sample temperature of 750 K is sufficient to accumulate an amount of oxygen that is equivalent to about 7 ML where most of the oxygen must be located in the subsurface region. Exposing the thus prepared surface to  $2 \times 10^3$  langmuirs of CO—keeping the temperature at 750 K—depletes the overall oxygen concentration via  $\text{CO}_2$  formation at Ru(0001) to about 3 ML (cf. Figure 5). To get an estimate of how efficient this process is, varying CO exposures were applied at a fixed sample temperature (750 K), and the number of O atoms removed from the initial coverage of 7.3 ML were determined by subsequent  $\text{O}_2$  TDS (cf. Figure 6). The initial conversion rate turns out to be of the order of  $10^{-2}$ . At an exposure of  $2 \times 10^3$  langmuirs of CO, the number of abstracted O atoms from the surface levels off, leaving about 3 ML of oxygen at the surface. This might point toward a critical oxygen coverage of 3 ML, below which the CO oxidation reaction rate slows down rapidly.

To study the activity of the Ru(0001)– $(1 \times 1)\text{-7.3O}$  phase in comparison to the  $(1 \times 1)\text{-O}$  phase, we measured the CO/ $\text{CO}_2$  conversion rate depending on the sample temperature (Figure 7); note that the  $(1 \times 1)\text{-O}$  phase was exposed to  $10^4$  langmuirs of CO, while the  $(1 \times 1)\text{-7.3O}$  phase was exposed to  $10^3$  langmuirs of CO. Since we are dealing always with a  $(1 \times 1)\text{-O}$  overlayer on top of the Ru(0001) sample for O coverages beyond 1 ML, the initial conversion rate is directly related to the turnover frequency as defined by Boudart.<sup>17</sup> Clearly, the high concentration O phase is by 2 orders of magnitude more active than the  $(1 \times 1)\text{-O}$  phase. While the CO/ $\text{CO}_2$  conversion probability on the  $(1 \times 1)\text{-O}$  phase remains always below  $2 \times 10^{-4}$ , it is about  $10^{-3}$  for the high concentration phase at low temperatures and jumps to about



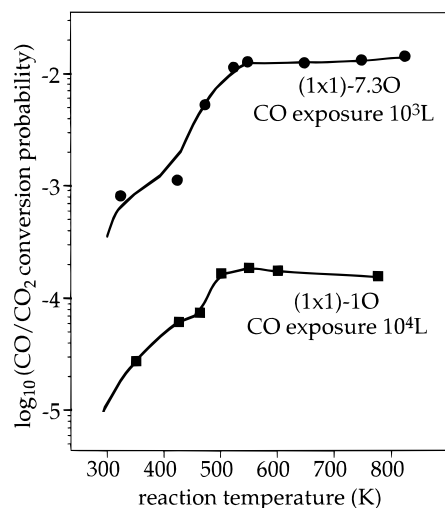
**Figure 5.**  $O_2$  thermal desorption spectra of a  $(1 \times 1)$ -7.3O precovered Ru(0001) surface before and after exposing to  $2 \times 10^3$  langmuirs of CO; the sample temperature was kept at 750 K during CO exposure. About 4.4 ML of oxygen is removed by CO oxidation. The same experiment was carried out with a  $(1 \times 1)$ -1O precovered Ru(0001) surface. Here only 0.09 ML of oxygen was removed by CO oxidation. The  $(1 \times 1)$ -7.3O phase was prepared by exposing the Ru(0001) surface to  $1.5 \times 10^6$  langmuirs of  $O_2$  at a sample temperature of 750 K. The  $(1 \times 1)$ -1O phase was prepared by exposing the Ru(0001) surface to  $1.5 \times 10^6$  langmuirs of  $O_2$  at a sample temperature of 500 K.



**Figure 6.** At a fixed sample temperature of 750 K, a Ru(0001)-(1  $\times$  1)-7.3O surface was exposed to various doses of CO, and the amount of oxygen in ML left on the surface was recorded. The initial CO/ $CO_2$  conversion rate is of the order of  $10^{-2}$ . The  $(1 \times 1)$ -7.3O phase was prepared by exposing the Ru(0001) surface to  $1.5 \times 10^6$  langmuirs of  $O_2$  at a sample temperature of 750 K.

$10^{-2}$  when the sample temperature exceeds 500 K. Above 550 K, the conversion probability levels off. The threshold temperature of 500 K is presumably not related to the activation barrier for the surface reaction, but more likely corresponds the onset of forth and back-migration of oxygen between the surface and the subsurface region. It should be noted that the small CO/ $CO_2$  conversion probability on the  $(1 \times 1)$ -1O phase of  $\leq 10^{-4}$  agrees quite well with a turnover frequency of 50  $CO_2$  molecules/s and  $(1 \times 1)$  unit cell area, i.e., a CO/ $CO_2$  conversion probability of  $2.3 \times 10^{-5}$ , as found by Peden and Goodman.<sup>3,11</sup>

To estimate the number of static defects in the 1–30 ML oxygen phases on Ru(0001), we exposed 20 langmuirs of CO to the sample at 160 K. Subsequent CO TDS measurements have, however, shown that CO does virtually not chemisorb on



**Figure 7.** CO/ $CO_2$  conversion rate is shown as a function of the reaction temperature. At a given sample temperature, the Ru(0001)-(1  $\times$  1)-7.3O surface was exposed to  $10^3$  langmuirs of CO, while the Ru(0001)-(1  $\times$  1)-7.3O surface was exposed to  $10^4$  langmuirs of CO.

the surface; the upper bound of adsorbed CO is about 0.05 ML, which is consistent with a previous estimation.<sup>18</sup> Complementary measurements have indicated that substantial amounts of CO can be accommodated at the Ru(0001)-(1  $\times$  1)-xO ( $x \geq 1$ ) surface only for temperatures  $\leq 55$  K.

#### IV. Discussion

From the present experiments two conclusions can be drawn immediately. First, the  $(1 \times 1)$ -1O phase on Ru(0001) is not exceptionally active in CO oxidation. Second, a high reaction rate requires the accumulation of an appreciable amount of O atoms below the surface. However, the  $(1 \times 1)$ -1O phase and the presence of subsurface oxygen are closely related. The oxygen penetration takes place only after the  $(1 \times 1)$ -1O overlayer structure has been completed and for sample temperatures above 600 K (cf. Figure 1b), which is consistent with previous high-resolution electron-energy loss spectroscopy (HREELS) and LEED measurements.<sup>6,7,19</sup> Recent DFT calculations have shown that the occupation of octahedral sites below the first and deeper Ru layers is exothermic by about 1 eV (with respect to free molecular oxygen).<sup>7</sup> This energy is substantially lower than for surface oxygen in the  $(1 \times 1)$ -1O phase (1.9 eV) so that oxygen atoms are taken up first on the surface. The completion of the  $(1 \times 1)$ -1O overlayer is accompanied by a substantial expansion of the topmost Ru layer spacing which was argued to actuate the oxygen incorporation into the subsurface or into the bulk region.<sup>7</sup>

We have demonstrated that  $CO_2$  formation by reaction of the oxygen from the  $(1 \times 1)$ -1O overlayer by postadsorbed CO is not very efficient (cf. Figure 7). Even a situation of more than 1 ML of oxygen and less than 3 ML (from TDS) is not very beneficial for the oxidation reaction of CO. The conversion probability of an incident CO molecule is still below  $10^{-4}$ . For the impinging CO molecules it seems that the  $(1 \times 1)$ -1O adlayer is not sufficiently altered by the presence of  $< 2$  ML of subsurface oxygen. However, if the total oxygen concentration exceeds 3 ML, the CO/ $CO_2$  conversion probability increases steeply to  $10^{-2}$ . This enhanced activity in CO oxidation might be related to the onset of oxide formation, which requires a minimum amount of 2 ML subsurface oxygen.

One may speculate that the surplus oxygen (2 ML), which is driven into the subsurface region, does not like to stay too close to the topmost layer since the interaction with overlayer oxygen

is repulsive. On the other hand, subsurface oxygen also does not like to penetrate too far into the bulk region because there the energetic situation is less favorable than close to the surface where substrate atoms can more easily be displaced. This defines the so-called selvedge region,<sup>20</sup> which is several monolayers thick with properties intermediate between surface and bulk and which is able to take up a finite amount of oxygen. From the observed critical O coverage of 3 ML one could guess that this subsurface region consists of the outermost 4–5 Ru layers with a “dead” or “oxygen-free” layer just below the topmost Ru layer. When adding even more oxygen atoms to the 3 ML oxygen phase, either oxygen atoms can be embedded between the topmost two Ru layers experiencing then, however, the repulsion from the  $(1 \times 1)$  overlayer O atoms, or these atoms are used to continue the growth of the subsurface oxygen region toward the bulk. From the enhanced activity in CO oxidation, it is reasonable to assume that part of those oxygen atoms are built between the top two Ru layers, assuming, of course, that the strength of the O–metal bond is predominantly responsible for the activation barrier of the CO oxidation reaction. Assuming the interaction between oxygen atoms just below the topmost Ru layer and overlayer oxygen atoms is repulsive, the on-surface O atoms should get markedly destabilized, with the consequence that the activation energy for CO oxidation drops down, consistent with an enhanced CO/CO<sub>2</sub> conversion rate.

With progressing oxygen deposition, more and more oxygen is accumulated in the subsurface region, which serves as a reservoir of weakly bound atomic oxygen. X-ray photoelectron spectroscopy (XPS) measurements of the O 1s and the Ru 3d core levels for O coverages up to 40 ML at Ru(0001) do not provide any evidence for oxide formation.<sup>21</sup> Oxide formation was only observed for oxygen loadings exceeding 50 ML.<sup>22</sup> Therefore, the subsurface oxygen in the experiments discussed here might be regarded as a bulk-chemisorbed species, i.e., as the onset of oxide formation. It is not very likely that the subsurface oxygen species itself is the catalytically relevant species, but rather the (through subsurface oxygen) destabilized on-surface oxygen will undergo the actual reaction with CO.

Under steady-state reaction conditions over Ru(0001) ( $p_{\text{O}_2} = 8$  Torr,  $p_{\text{CO}} = 16$  Torr, and sample temperature = 500 K),<sup>3,4</sup> oxygen adsorption results in the formation of a  $(1 \times 1)$ -1O overlayer. Substantial concentrations of subsurface oxygen were not observed under these reaction conditions<sup>3</sup> as postreaction AES measurements always indicated a 1 ML O coverage. This is consistent with the temperature-dependent oxygen uptake (cf. Figure 1b) where oxygen penetration starts only beyond 550 K and almost no subsurface oxygen is produced at 500 K. The small CO/CO<sub>2</sub> conversion probability for the  $(1 \times 1)$ -1O phase of  $\leq 10^{-4}$  agrees nicely with the optimum turnover frequency of 50 CO<sub>2</sub> molecules/s and  $(1 \times 1)$  unit cell area (for  $p_{\text{CO}} = 16$  Torr), i.e., a CO/CO<sub>2</sub> conversion probability of  $2.3 \times 10^{-5}$ , under steady-state reaction conditions.<sup>3,11</sup> This demonstrates that there exists no “pressure gap” if identical situations (here, reaction of the  $(1 \times 1)$ -1O phase) are considered. Clearly, the surface conditions for which the optimum reaction rate was found by Peden and Goodman<sup>3</sup> are different from those ( $>3$  ML oxygen case) leading to the high CO/CO<sub>2</sub> conversion probabilities of  $10^{-2}$ . One might expect to find much higher turnover frequencies when the partial pressure of CO is kept at 16 Torr, but the oxygen partial pressure is increased to 200 Torr for instance (sample temperature  $>550$  K) so that oxygen loadings of  $>3$  ML can be maintained even under steady-state reaction conditions.

Peden and Goodman<sup>3</sup> have also shown that the CO oxidation reaction rate drops by about 1 order of magnitude when going

to less oxidizing conditions for which postreaction AES measurements indicated an O coverage of 0.5. By contrast, for temperatures above 450 K our measurements indicated that the CO/CO<sub>2</sub> conversion probability over the  $(1 \times 1)$ -1O phase is only twice as large as over the  $(2 \times 1)$ -O phase (cf. Figure 4). However, as already discussed in section III.2, the conversion probabilities of both phases may be equally affected by the presence of steps. Subtracting this contribution from both conversion probabilities could readily account for the 1 order of magnitude larger CO oxidation reaction rate of the  $(1 \times 1)$ -1O phase.

A very peculiar property of Ru(0001) among the densely packed platinum metal surfaces is the existence of a  $(1 \times 1)$ -1O overlayer phase. On the (111) surface of Pd, Rh, and Pt the  $(1 \times 1)$ -O overlayer phase is not stable, and the oxygen atoms are incorporated into the subsurface region after the on-surface coverage exceeds 0.5–0.6 ML.<sup>23,24</sup> This effect might be associated with the very strong Ru–O bonding which distinguishes Ru from Rh, Pd, and Pt and which makes oxygen in the  $(1 \times 1)$ -1O overlayer energetically more favorable than subsurface oxygen. DFT calculations show for example that the O–Rh and O–Ru binding energies differ by about 0.9 eV on the close-packed surfaces.<sup>25</sup>

To learn more about the outstanding activity of the oxygen-rich Ru(0001) surface in CO oxidation, we shall concentrate on the question why Rh(111) under oxidizing and high-pressure conditions is a very poor catalyst, while under UHV conditions Rh(111) is much more active than Ru(0001). Extensive exposure of Rh(111) to oxygen leads to oxygen incorporation which can also be removed by heating to 900–1000 K.<sup>26d</sup> It might be that in the case of Rh(111) the near-surface region turns into an oxide which is less active in CO oxidation. Oxide formation of Rh(111) has already been considered by several authors to poison the CO oxidation reaction.<sup>26</sup> The LEED pattern shows a coincidence lattice with  $(9 \times 9)$  symmetry which indicates substantial rearrangements of the Rh(111) lattice. At Ru(0001), on the other hand, extensive oxygen exposures do not oxidize the surface<sup>21,22</sup> but rather lead to an accumulation of oxygen in the subsurface region. For high O exposures as used here the Ru(0001) surface always exhibited a  $(1 \times 1)$  LEED pattern.

Another interesting question concerns the microscopic process that actually converts CO into CO<sub>2</sub>. A typical LH mechanism is only conceivable if the  $(1 \times 1)$ -O overlayer contains numerous vacancies into which CO molecules can adsorb and eventually react with oxygen. The number of static defects in the  $(1 \times 1)$ -xO phases is quite small, and substantial CO uptake is observed only for temperatures below 55 K. However, at higher sample temperatures (at which the CO oxidation reaction takes place, say about 600 K), these vacancies might be automatically generated on entropic grounds via migration of oxygen atoms between the surface and the subsurface region.

As mentioned in the Introduction, the ER mechanism was also discussed in the context of the high CO oxidation rates over Ru(0001) under high-pressure and oxidizing conditions,<sup>4</sup> although the ER mechanism has so far been identified only in quite artificial cases, such as the reaction of atomic H with deuterium and chlorine precovered metal surfaces.<sup>27</sup> There are two arguments (weakly) in favor of an ER mechanism, although, certainly, additional experiments are required to identify this reaction mechanism unequivocally. First, the ER mechanism would not require the adsorption of CO onto the surface and would therefore not need the introduction of vacancies into the  $(1 \times 1)$ -O overlayer. Second, since it is likely that subsurface oxygen further destabilizes the on-surface oxygen, the ER

activation barrier for CO oxidation could be even lower than in the case of the pure (1 × 1)-O overlayer. To substantiate this argument, further molecular beam experiments and DFT calculations are mandatory.

## V. Summary

CO reaction experiments over oxygen precovered Ru(0001) surfaces with varying O coverages up to 20 ML show that the CO/CO<sub>2</sub> conversion rate is below 10<sup>-4</sup> for O coverages up to 3 ML. Even with a seeded CO beam (translational energy of more than 1.2 eV) the probability for an incident CO molecule to become oxidized at the surface (sample temperature ≤ 800 K) is smaller than 5 × 10<sup>-2</sup> so that the activation barrier averaged over the whole phase space is higher than about 1.4 eV. The most intriguing and novel aspect revealed by our measurements is the exceptionally high CO/CO<sub>2</sub> conversion probability for oxygen loadings beyond 3 ML. The presence of subsurface oxygen at Ru(0001) destabilizes the on-surface oxygen and in this way increases the probability for CO to form CO<sub>2</sub> by about 2 orders of magnitude.

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