

Physical and chemical properties of high density atomic oxygen overlayers under ultrahigh vacuum conditions: (1×1) -O/Rh(111)

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In this paper, we elaborate on our previous communication of high coverages of oxygen on Rh(111) [J. Chem. Phys. **110**, 2757 (1999)]. When dosing with O₂, half of a monolayer of O is adsorbed. Higher coverages can be achieved when exposing the surface to O atoms. As the quantity of adsorbed O increases from a half to a full monolayer, the overlayer structure undergoes several distinct phase changes. At a full monolayer, the (1×1) -O structure is stable at surface temperatures less than ~ 400 K. Continued dosing with O atoms results in the rapid migration of O into the bulk. We also report on the chemical reactivity of this densely oxygen-covered surface with CO, H₂, and propene. © 2000 American Institute of Physics. [S0021-9606(00)70404-1]

I. INTRODUCTION

Knowledge of the interaction of O with metal surfaces is critical for understanding corrosion and catalytic oxidation. Working under ultrahigh-vacuum (UHV) conditions allows for the preparation of well-characterized surfaces, and affords the use of many tools to investigate any surface processes. However, this involves working at gas fluxes much smaller than would exist under the real-world conditions of high pressure where these reactions normally occur. This often causes kinetically slow or improbable reactions, which may have significant effects when the reactant pressure is several Torr or greater and the impingement rate is high, to occur too slowly to be easily observed under UHV conditions, where the pressure at the surface is typically less than 1×10^{-6} Torr. A possible example of this has been suggested by studies of CO oxidation on Ru(0001).¹⁻³ Under UHV conditions, the O coverage is less than 1.0 ML (monolayer), and the oxidation proceeds by a Langmuir-Hinshelwood (L-H) mechanism. Ru exhibits the lowest activity of the transition metals studied. However, at pressures of several Torr and under oxidizing conditions, the rate of CO₂ production on Ru at 500 K becomes higher than for other transition metal surfaces. It has been proposed that a full monolayer of O adsorbs on Ru(0001) at these pressures, and that the reaction then may proceed by an efficient Eley-Rideal (E-R) mechanism.¹⁻³ If this were the case, then the rate-limiting step might be the dissociation of molecular oxygen on the surface. To study such high-coverage reactions under UHV conditions, it should be possible to circumvent the problem of low fluxes by using *atomic* O to overcome the rate-limiting O₂ dissociation step, and adsorb the higher coverage necessary for the E-R reaction.

Much is already known about the interaction of O with rhodium.⁴ Under UHV conditions, dosing a Rh(111) surface with O₂ leads to a saturation coverage of $\Theta_{\text{O}}=0.5$ ML (ML≡monolayer is $1.6 \times 10^{15}/\text{cm}^2$).⁵⁻⁸ In a previous paper, we outlined how we prepared a (1×1) -O/Rh(111) surface.⁹ To do this, we used a radio-frequency nozzle beam source to

produce O atoms. The narrow widths of the He diffraction features indicate that the O atoms are well-ordered. Using temperature programmed desorption (TPD) measurements, where the temperature of the crystal is ramped while monitoring any reaction products evolved, it was shown that there is twice as much O deposited on the Rh for the (1×1) pattern as for the $\Theta_{\text{O}}=0.5$ ML (2×2) structure. Recent theoretical investigations have concluded that 1 ML of adsorbed O should be stable.^{10,11} Walter *et al.*¹⁰ concluded that there is a kinetic constraint to growing a full monolayer with O₂ dosing because, once the coverage reaches 0.5 ML, the sites where O₂ dissociation is energetically favorable are blocked.

For surface temperatures below ~ 400 K, this overlayer is stable for many minutes. At much higher temperatures, it is evident from diffraction measurements that the O coverage begins decreasing, due to some oxygen migration into the bulk. For surface temperatures below 400 K, it is possible to add more O with continued O dosing. Most, if not all of this additional O is absorbed into the bulk. In this paper, we will present detailed experiments which examine the growth, stability, and reactivity of the high-density (1×1) oxygen overlayer on the Rh(111) surface.

There may be other methods for growing the dense overlayer than using an atom source. It has been shown that using NO₂, instead of O₂ can produce higher coverages of O under UHV conditions on several transition metal surfaces; Pt(111),¹² Pd(111),¹³ and Ru(0001).¹⁴⁻¹⁶ In the case of Pd(111), there is evidence that at least 1 ML of O is adsorbed, but it is not clear how well this overlayer is ordered. Using a stepped Ru(0001) crystal, Parrott *et al.*¹⁷ were able to grow 1 ML of adsorbed O after long exposure of the crystal to 10^{-5} Torr of O₂ at a surface temperature $T_s = 300$ K. For Ru(0001), a (1×1) phase with $\Theta_{\text{O}}=1.0$ ML has recently been produced under UHV conditions at $T_s = 600$ K.¹⁶ In this paper, we will discuss our attempts to use NO₂ to grow a monolayer of O on the Rh(111) surface. Another possible route, which we briefly explore, is to use O₂ with high translational energies. If there is an activation bar-

rier for the dissociative chemisorption of O₂ on the half-coverage (2×2)-O surface, the higher translational energy could overcome the barrier and lead to a higher coverage of oxygen.

In our lab, the reaction of CO with adsorbed O has been extensively studied.^{18,19} For these experiments, the O was deposited by the decomposition of O₂, and the coverage was always less than 0.5 ML. We can now extend these studies to a much higher oxygen coverage regime made possible by the efficient deposition afforded by the atom beam. As already mentioned, it has been suggested that the change in the reaction kinetics for the oxidation of CO on Ru(0001) under high pressures of O₂ is due to the formation of a full monolayer of adsorbed O.¹⁻³ Stampf and Scheffler²⁰ have calculated that a (1×1)-O/Ru(0001) overlayer should be stable, and it has recently been observed under UHV conditions.¹⁶ Stampf and Scheffler also theoretically investigated the oxidation of CO on the (1×1)-O/Ru(0001) surface.^{21,22} Their conclusion was that there could be some direct E-R reaction of incoming CO molecules, but only for those having energies well in excess of 1 eV, and with a reaction rate much lower than that experimentally observed. They speculate that the initial E-R reaction creates some vacancies in the overlayer, and these can be more readily occupied by CO than an O atom from O₂ decomposition. These CO molecules then react with neighboring O atoms via a L-H mechanism, accounting for most of the CO₂ produced.

The behavior of Rh is different than that of Ru. Under the high pressure, oxidizing conditions at which the Ru shows a much enhanced rate of CO₂ production, the rate of reaction on Rh(111) is reduced.¹ However, with the atom beam, we can grow a full monolayer of oxygen under UHV conditions and at low temperatures, where the (1×1)-O/Rh(111) surface is stable. This temperature is below that where the surface temperature dependent L-H reaction rate is fast, but a direct process should be relatively insensitive to the surface temperature. This situation suggests a regime for examining possible E-R behavior on Rh.

II. EXPERIMENT

These experiments were performed in a three-molecular-beam scattering machine which has been described in detail elsewhere.^{19,23} We have also previously described the formation of (1×1)-O/Rh(111) using a beam of atomic oxygen.⁹ Accordingly, only procedures specific to this paper will be described.

For investigating the reaction of high energy CO with the O overlayer, a 1% mixture of ¹³CO in H₂ was used. It was possible to achieve a mean kinetic energy of 1180 meV when expanded through a nozzle heated to 725 K. At this temperature, disproportionation was just becoming evident, as shown by the CO₂ signal when measuring the beam directly. H₂ was chosen as the carrier gas rather than inert He because of the much higher energies achievable. Though H₂ dissociatively adsorbs on the Rh(111) surface, and also reacts with low coverages of O at elevated surface temperatures, there was little interference with the experiments reported here. More details will be given with the results.

III. RESULTS

A. Surface structures at 0.5 and 1.0 ML coverage

Figures 1 and 2 show He diffraction scans taken along two principal symmetry directions of the surface at $T_s = 325$ K. For the scans taken after O₂ exposure, the surface was prepared by dosing for 20 min at $T_s = 325$ K, and then briefly cooling to 200 K. When dosing with O, the surface was at $T_s = 325$ K when first exposed to the beam, and the dosing was continued while the surface was cooled to $T_s = 200$ K. Starting at the higher temperature prevents H adsorption, and continuing as the surface cools minimizes the amount of O absorption. For $\Theta_O = 0.5$ ML, the surface is covered by (2×1) domains with their axes oriented along different symmetry directions, giving a (2×2) diffraction pattern. Thus, there are half-order peaks, indicated by the arrows. For the $\langle 11\bar{2} \rangle$ direction, Fig. 1, depositing twice as much O clearly results in the disappearance of the half-order peaks. The angular positions of the diffraction features are consistent with a commensurate overlayer (Rh-Rh distance of 2.69 Å). For the $\langle 10\bar{1} \rangle$ direction, Fig. 2, the half-order peaks are still present after O atom dosing, but are greatly attenuated. This apparently small residual corrugation is consistent with a slight adsorbate-induced buckling of the Rh(111) surface, a common occurrence for close-packed metal surfaces.²⁴ (There is no evidence of this in the electronic structure calculations of Ganduglia-Pirovano and Scheffler.¹¹) The diffraction peaks also have distinct satellite peaks in this direction. The position of the principle peaks indicates a commensurate overlayer, and the position of the satellite peaks near specular are consistent with a superlattice structure with a repeat distance of ~ 40 Å. The near disappearance of the half-order diffraction features in both principle symmetry directions with the presence of twice as much O, as measured using TPD, is consistent with the growth of 1 ML after dosing with atomic O.

The narrow diffraction peaks indicate a well-ordered overlayer. By comparing the width of the specular reflection with that of the instrument function, it is possible to estimate the size of ordered domains, or coherence length, of adsorbed O.²⁵ The result for several incident angles gives a coherence length of between 100 and 200 Å. This is consistent with the fact that the Rh crystal is miscut by $\sim 1^\circ$, roughly along this azimuth, and that the surface has terraces that are ~ 130 Å.

B. Adsorbed oxygen ordering at coverages between 0.5 and 1.0 ML

We also investigated the surface structure as a function of Θ_O for coverages greater than 0.5 ML when dosing with the O atom beam at $T_s = 325$ K. With continued dosing, the half-order diffraction peaks present at $\Theta_O = 0.5$ ML decrease in size. However, they grew in again at $\Theta_O = 0.7 \pm 0.05$ ML. We took diffraction spectra at O coverages where the half-order intensity exhibited extrema. The results are shown in Figs. 3 and 4. As expected, there is a (2×2) pattern at $\Theta_O = 0.5$ ML and a (1×1) at $\Theta_O = 1.0$ ML. For intermediate coverages, the narrow diffraction peaks that are present indi-

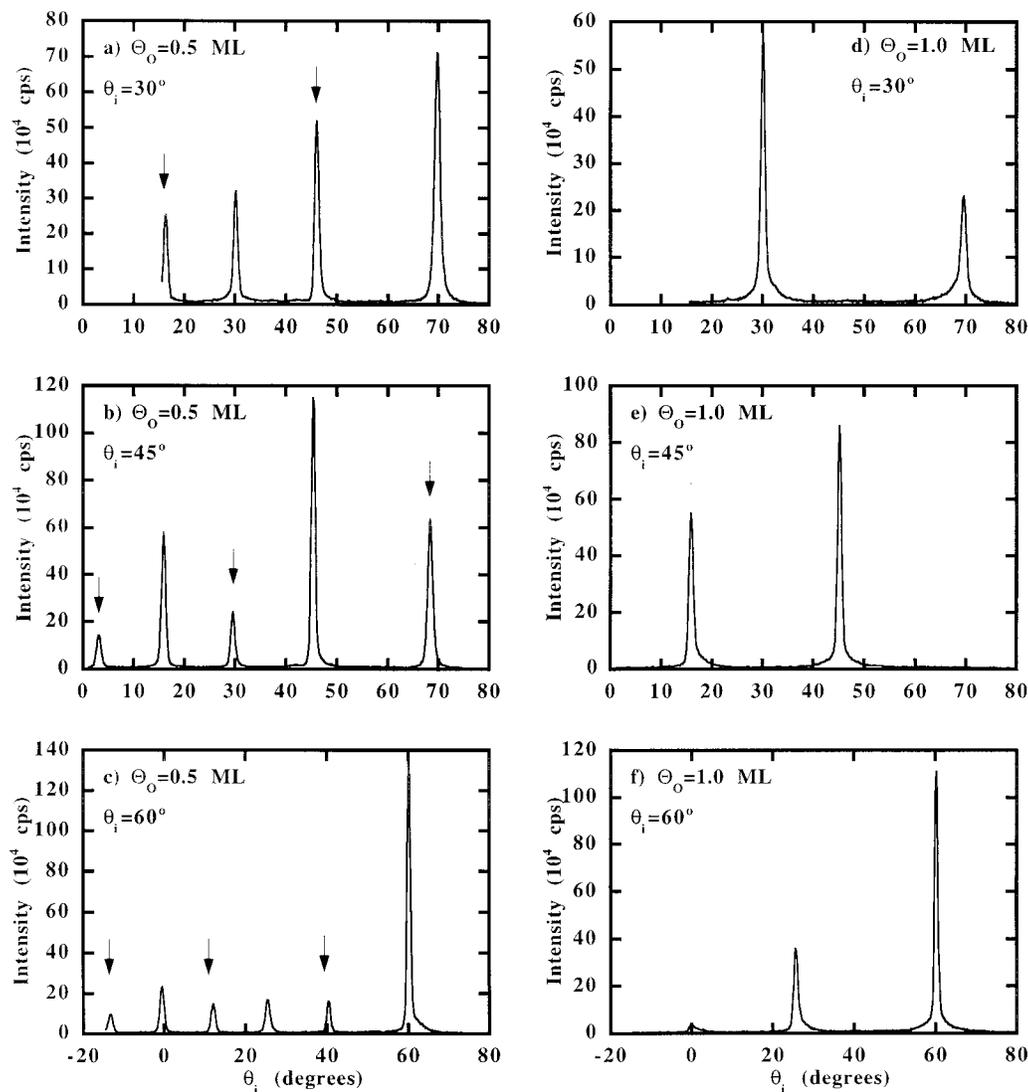


FIG. 1. He diffraction spectra taken along the $\langle 11\bar{2} \rangle$ azimuth and at three different incident angles; $E_i = 20$ meV and $T_s = 325$ K. (a), (b), and (c) are for $\Theta_0 = 0.5$ ML, deposited by O_2 dosing. Arrows indicate the positions of the half-order peaks. (d), (e), and (f) are for $\Theta_0 = 1$ ML, deposited by O atom dosing.

cate a well-ordered surface. The diffraction scans indicate the growth of different ordered structures for coverages between 0.5 and 1.0 ML. These phase changes are not kinetically limited by the dosing rate, as the same results are seen at different O atom fluxes. For the experiments shown here, the O atom flux was sufficient to reach a coverage of $\Theta_0 = 0.7 \pm 0.05$ ML in less than 7 min. By reducing the oxygen backing pressure, we also dosed at a much slower rate, and it took 28 min to reach $\Theta_0 = 0.7 \pm 0.05$ ML; the intensities of the half-order peaks showed the same progression.

C. Stability of the (1×1) -O/R1(111) overlayer

To investigate the stability of the (1×1) -O overlayer as a function of T_s , we grew 1.0 ML overlayers at 325 K. These were heated to various temperatures for 5 min and then cooled back to 325 K and the diffraction spectrum taken and compared with the spectrum taken before heating. The normalized results are plotted in Fig. 5 for the specular and 1st-order diffraction peaks. When the surface was heated to 525 K, half-order peaks are quite evident in the spectrum,

even when the time at this temperature is less than 30 s. By 400 K, there is a definite attenuation of the diffraction peaks after 5 min. Between 400 K and 425 K, small half-order peaks become clear after the 5 min time period. Oxygen does not desorb at these temperatures, implicating migration into the bulk of the Rh crystal.

D. Oxygen absorption

The saturation coverage of O when dosing with O_2 is 0.5 ML. Further O can be absorbed, but only slowly at $T_s = 325$ K. This has been measured for temperatures between 400 K and 600 K using a room temperature supersonic beam with a flux of 60 ML/min.²⁶ These results were extrapolated to produce the solid line in Fig. 6. As mentioned in the first paper,⁹ we were unable to measure any additional O uptake at $T_s = 325$ K with as much as 80 min of continued O_2 exposure after completion of 0.5 ML. That elevated temperatures are needed to adsorb O while the crystal is exposed to O_2 is consistent with the work of Wider *et al.*²⁷ At $T_s = 325$ K, O does not absorb from the (1×1) overlayer, unless there is

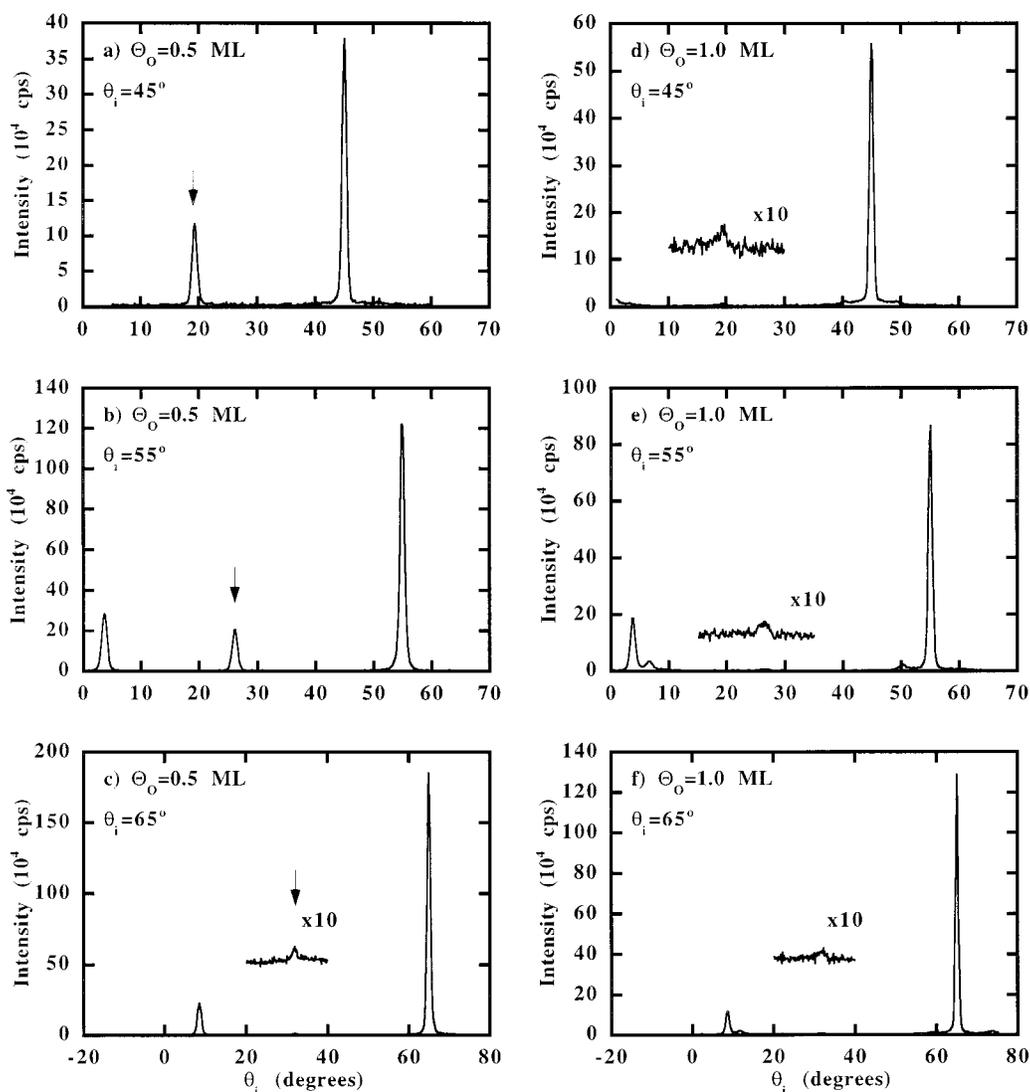


FIG. 2. He diffraction spectra taken along the $\langle 10\bar{1} \rangle$ azimuth and at three different incident angles; $E_i = 20.1$ meV and $T_s = 325$ K. (a), (b), and (c) are for $\Theta_0 = 0.5$ ML, deposited by O_2 dosing. Arrows indicate the positions of the half-order peaks. (d), (e), and (f) are for $\Theta_0 = 1$ ML, deposited by O atom dosing.

continued exposure of the surface to O atoms. The rate of absorption is dependent both on the surface temperature and the O atom flux. The results for three different fluxes are shown in Fig. 6. The surface was first dosed with O atoms at $T_s = 325$ K to produce a monolayer coverage. The surface was then exposed for an additional period of time at the indicated surface temperature. The amount of O in the TPD spectra greater than 1.0 ML was then assigned to the absorbed state.

We also have evidence that the absorption rate is not constant; after about 0.5 ML has been absorbed, the absorption rate starts to decrease. This is similar to what Peterlinz *et al.*²⁶ saw when using NO_2 dosing; we did not continue the dosing to see if it reached some asymptotic value.

E. Investigations of alternate procedures to produce high-density O overlayers

1. NO_2

It has been recently shown that NO_2 can be used to grow a monolayer of O on Ru(0001).¹⁶ This was done at 600 K, a

much higher surface temperature than the (1×1) stability regime for Rh(111). Using a neat, room temperature NO_2 beam, we did manage to grow a structure that had a (1×1) diffraction pattern and showed the equivalent of ~ 1 ML of O_2 in the TPD spectrum after exposure of the 400 K surface for ~ 10 min. The result is shown in Fig. 7, compared with a monolayer grown at $T_s = 325$ K with the O atom beam. Since O from the (1×1) overlayer still does not migrate into the bulk at a rapid rate when $T_s = 400$ K, the exact time is not critical; unlike with the O atom beam, the NO_2 beam does not load up the bulk very fast at this temperature. Presumably, the NO_2 does not dissociate as well on an oxygen-covered surface as on the bare Rh(111). With $T_s = 325$ K or lower, we were unable to deposit a monolayer of O with NO_2 even after much longer exposures.

2. O_2 beams with high translational energies

With a room temperature O_2 beam ($\langle E \rangle \approx 90$ meV) we can only achieve $\Theta_0 = 0.5$ ML on the Rh(111) surface. We also dosed the surface using an oxygen beam with higher

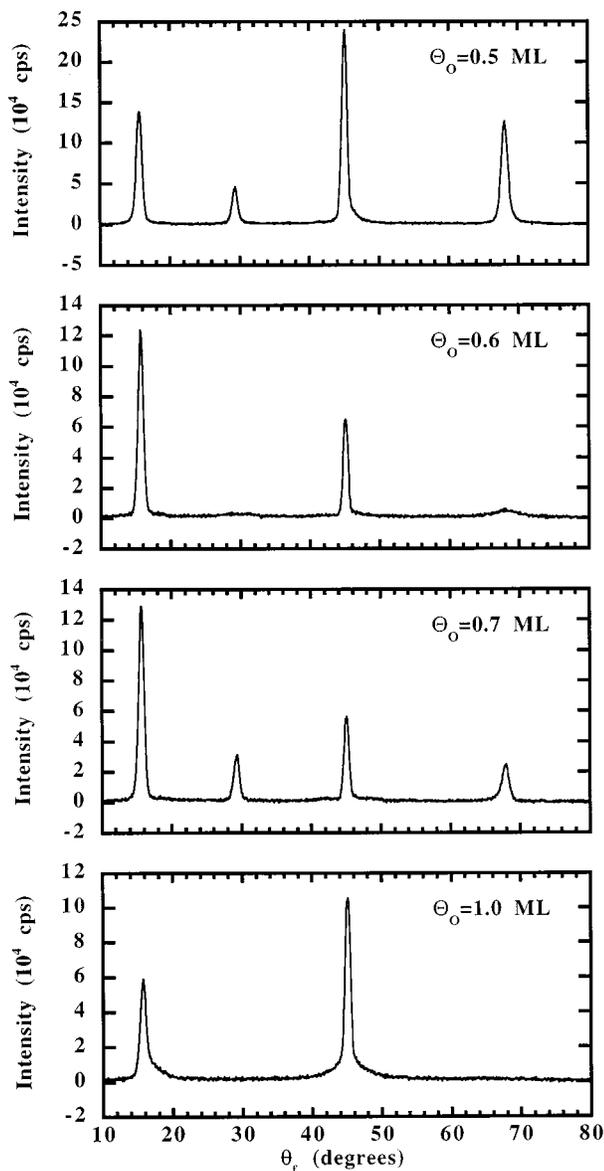


FIG. 3. He diffraction spectra taken along the $\langle 11\bar{2} \rangle$ azimuth, $E_i = 19.5$ meV, $\theta_i = 45^\circ$, and $T_s = 325$ K, after progressively longer exposures to the O atom beam at $T_s = 325$ K.

translational energy. This was done by making a mixture of 1% O_2 in He, and expanding at high pressure through a nozzle heated to 723 K. The mean energy of the O_2 molecules in this beam was 530 meV. We dosed the surface at $T_s = 250$ K and 300 K, and at incident angles of $\theta_i = 30^\circ$, 45° , and 60° . Assuming 2nd-order Langmuir adsorption kinetics²⁸ and an initial sticking coefficient of 0.5,²⁹ the initial increase in coverage was roughly consistent with the estimated O flux, but in no case did we achieve oxygen coverages greater than 0.5 ML.

F. Chemical reactivity of (1×1) -O/Rh(111)

1. CO oxidation

To begin our investigation of the reaction of CO with a monolayer of O, we used a neat beam of normal abundance $CO(^{12}C^{16}O)$, $\langle E \rangle \approx 90$ meV. The experiments were started by growing a (1×1) -O overlayer, dosing long enough that

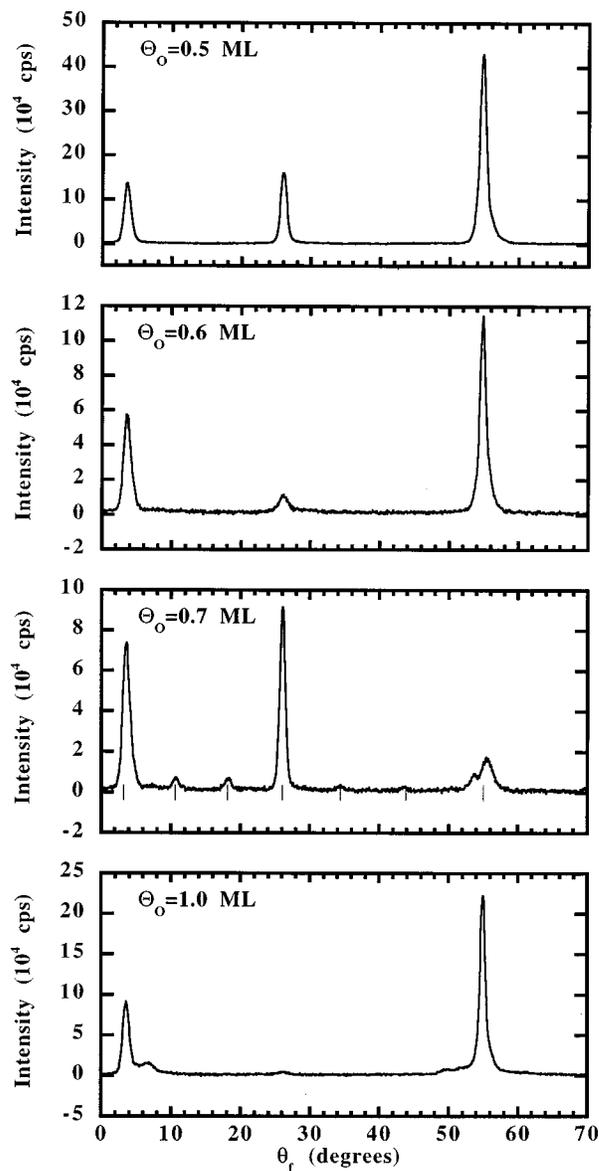


FIG. 4. He diffraction spectra taken along the $\langle 01\bar{1} \rangle$ azimuth, $E_i = 19.6$ meV, $\theta_i = 55^\circ$, and $T_s = 325$ K, after progressively longer exposures to the O atom beam at $T_s = 325$ K. The tick marks below the spectrum where $\Theta_o = 0.7$ ML are the expected positions of 1/6-order diffraction peaks.

there was a fraction of a monolayer of absorbed O. Then, while still dosing with O atoms, the surface was also exposed to the mechanically-chopped CO beam. The total waveform of any scattered or product molecules could then be collected. For $T_s \leq 400$ K, we were unable to detect any CO_2 product (a high mass 44 background in our detector makes detecting small quantities difficult). However, some reaction must have occurred because postexposure TPD spectra showed that very little O was left. The extent of the O depletion in any period of time was dependent on two factors; the relative fluxes of the CO and O atoms, and the surface temperature, with the lower temperatures resulting in the least O depletion. At $T_s = 325$ K and with a relatively intense CO beam, we used He diffraction to investigate the surface ordering. The (1×1) pattern of the well-ordered O overlayer

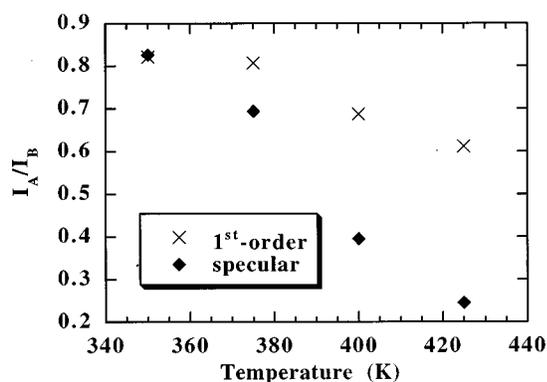


FIG. 5. Comparison of the specular and 1st-order diffraction features for the Rh(111) surface initially covered with 1.0 ML of adsorbed O, and then heated to the indicated temperature. I_B is the intensity of the feature at $T_s = 325$ K, immediately after growing the overlayer with the O atom beam. I_A is the intensity of the feature at $T_s = 325$ K, after heating the surface to the indicated temperature for 5 min. Spectra were taken along the $\langle 11\bar{2} \rangle$ azimuth, $\theta_i = 45^\circ$, and $E_i = 19.7$ meV.

quickly disappeared once the surface was exposed to CO, with a weaker but still narrow specular feature remaining. When the CO beam was stopped and exposure to the O atom beam continued, the diffraction pattern at least partially recovered, though with small half-order features.

The conclusion is that the (1×1) -O is reactive with CO, presumably slowly producing CO_2 , which we are unable to measure above the detector background. It is important to note that this was a room temperature beam with an average translational energy of $\langle E \rangle \approx 90$ meV, without molecules having translational energies close to 1 eV, which is what Stampfl and Scheffler^{21,22} predict is necessary for the reaction on the densely oxygen-covered Ru. We were unable to maintain the oxygen coverage under our experimental conditions. One possibility was that the flux of CO was too great relative to the rather weak O beam. We tried using a room temperature beam of 20% CO in He. This gives a faster, and more dilute, beam of CO. The principle findings were essentially the same; no detected CO_2 product, but an O depletion

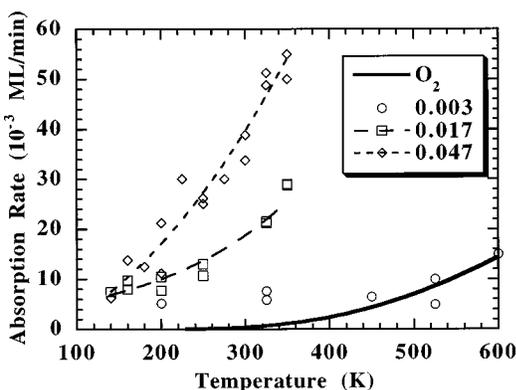


FIG. 6. The measured uptake rate of O for a surface with an initial monolayer coverage, as a function of surface temperature and O atom flux. Experimental data is shown with symbols, and are labeled with the O flux in ML/s. The solid line is for the adsorption of O using O_2 dosing, extrapolated from the results of Peterlinz (Ref. 26).

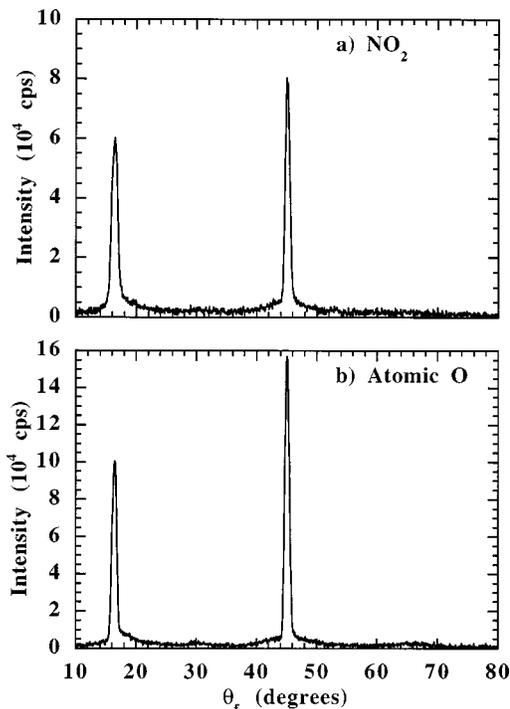


FIG. 7. He diffraction spectra taken along the $\langle 11\bar{2} \rangle$ azimuth, $E_i = 20.4$ meV, $\theta_i = 45^\circ$, and $T_s = 200$ K. The spectrum shown in (a) was taken after exposure of the surface to an NO_2 beam at $T_s = 400$ K. The spectrum shown in (b) was taken after growing a monolayer with the O atom beam at $T_s = 325$ K.

rate directly related to both the relative O atom and CO flux, and the surface temperature. Another problem is that CO sticks to clean Rh(111) at the surface temperature where the (1×1) -O overlayer is stable. It is possible that as oxygen is consumed, the vacated site is occupied by a CO molecule which blocks the adsorption of further oxygen.

Though we were unable to adjust conditions to do the continuous dosing experiments originally envisaged, it was still possible to investigate the role of CO translational energy. We can measure the initial rate of reaction by measuring the quantity of adsorbed oxygen after a short exposure to CO molecules of varying translational energies. We were also interested in detecting any small amount of reaction product. Because of the significant detector background at masses 28 and 44, we used ^{13}CO seeded with H_2 . At the surface temperatures of our experiments, the H_2 does not interfere with CO oxidation; water formation was not observed, nor was there any decrease in the quantity of adsorbed oxygen after exposure to the H_2 .

The results for CO exposure are qualitatively summarized in Fig. 8, which shows postreaction TPD spectra for O_2 , CO, and CO_2 for two different beam energies, 590 and 1180 meV, and surface temperatures, 200 and 325 K. In each case, the surface was dosed with O at $T_s = 325$ K until 1.1 ML had been deposited. The surface temperature was then changed to that indicated, and the surface exposed for a further 30 min to the O and CO/H_2 beams. There was some centerline enrichment of the heavier gas so the beams were $\sim 3\%$ – 4% CO. The flux of CO at the crystal was ~ 0.02 ML/s for the room temperature beam and ~ 0.01 ML/s for

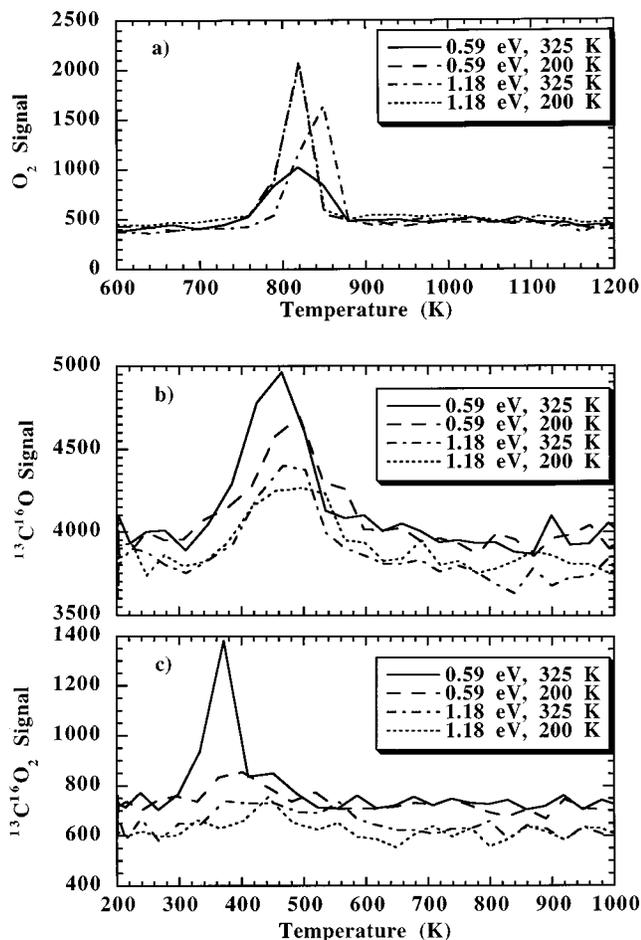


FIG. 8. Postreaction TPD spectra for O₂ (a), CO (b), and CO₂ (c) taken after exposing the (1×1)-O overlayer simultaneously to O-atoms and ¹³C¹⁶O for 30 min. Curves are labeled by the mean translational energy of the incident CO, and the surface temperature at which the exposure took place.

the higher energy beam. The O atom flux was ~0.05 ML/s.

When the relative fluxes are factored in, the apparent reaction rate is the same for both translational energies at $T_s=325$ K. The most O is left on the surface when $T_s=200$ K with the results for the two beam energies being indistinguishable. For both surface temperatures some adsorbed CO is observed, but only the 325 K surface exposed to the room temperature beam evolved much CO₂ while the surface temperature was ramped. In no case did we observe any CO₂ product while the surfaces were exposed to the CO beam.

A crude estimate of the upper bound for the reaction probability under the most reactive conditions was estimated using experiments as outlined before, where the quantity of O₂ in the TPD spectra taken after exposure of the sample to O atoms with and without CO exposure was compared. Assuming that the difference is due solely to the O+CO reaction, the probability for CO reacting with a preadsorbed overlayer of (1×1) oxygen is on the order of 2%. We also did an experiment at $T_s=400$ K with 1180 meV CO. The only difference between this experiment and those shown in Fig. 8 was that there was no CO₂ in the postreaction TPD.

These results argue against a direct (E-R) reaction and more for a L-H reaction between coadsorbed reactants. The

reactivity at both translational energies increases with surface temperature; the rate of an E-R reaction should be rather insensitive to the surface temperature. There is no evidence of a kinetic barrier; the reaction rate is roughly similar for the two very different translational energies. As mentioned earlier, even a CO beam with an average kinetic energy of 90 meV reacted readily. For surface temperatures below 400 K, some CO can stick to the Rh(111) surface.^{30,31} That we see clear evidence for adsorbed CO at the surface temperatures studied is confirmation of the previously mentioned surmise that CO was blocking sites for oxygen adsorption, thus preventing us from doing continuous dosing experiments. On the clean Rh(111) surface, CO₂ does not stick except at cryogenic temperatures. Its presence in the postreaction TPD spectra at 350–400 K is likely due to its formation while the surface temperature is ramped. One explanation for the presence of CO and CO₂ peaks in the TPD spectra is that small islands of CO are created within the O overlayer; the CO₂ is produced at the edges, where CO and O are in close proximity, and the CO evolves from the center of these islands. We have also seen that the O₂ TPD spectra are altered after reaction, so there is possibly some further change in the O overlayer. The question we cannot yet answer is how the initial CO is deposited. One possibility is that some CO is trapped in a shallow adsorption well on top of the O overlayer, from which it could then react. However, one would expect that this mechanism would favor an increased reaction rate at lower surface temperatures. Another possibility is that the initial CO could be adsorbed at defects in the overlayer. Of course, there is also the explanation mentioned in the Introduction, where the initial holes in the O overlayer are created by high translational energy ($E > 1$ eV) CO molecules via an E-R mechanism. Our results are that there is not an appreciable barrier, and the initial reaction is very sensitive to surface temperature, indicative of a L-H mechanism. Once some of the O in the overlayer is removed, CO can be adsorbed and block the further adsorption of O. Since CO bonds carbon end down, it would not be surprising that it would be unreactive with incoming O atoms.

2. H₂ oxidation

For the reaction with H₂, O was adsorbed on the surface at $T_s=325$ K, and then the sample was rapidly heated to 575 K, where the rate of water formation is rapid. When $\Theta_O < 0.5$ ML, exposure of the surface to H₂ leads to the immediate evolution of H₂O, as observed in the mass spectrometer. At $\Theta_O=0.5$ ML, the water evolution is not as rapid; there is an induction period wherein the rate of H₂O production builds to a peak, before rapidly falling off as the O is depleted. When $\Theta_O > 0.5$ ML, this induction period becomes progressively longer, and there is less signal at the position of the maximum desorption rate. When $\Theta_O \approx 1$ ML, the H₂O evolution is so slow that it is difficult to see the signal above the background in the mass spectrometer. This behavior is reasonable in all cases if the reaction proceeds by a L-H mechanism, where the first step is the dissociative adsorption of H₂, and the dissociative sticking coefficient is much higher on the bare Rh surface than on an O overlayer. For

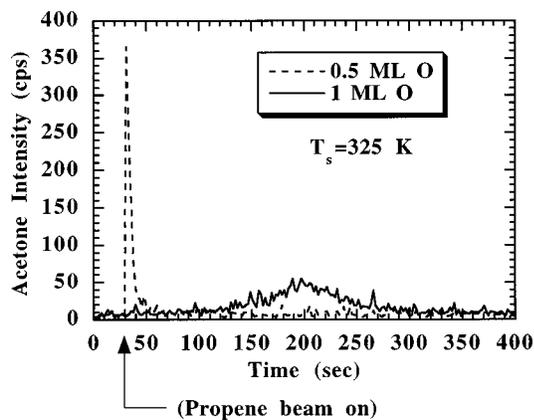


FIG. 9. Comparison of the evolution of the acetone signal produced after the exposure of the surface with $\Theta_{\text{O}}=0.5$ and 1.0 ML to propene. The arrow indicates the time that propene exposure was begun.

low coverages of O, there are many bare sites on the Rh surface for the H_2 to dissociatively adsorb before reacting. As the quantity of adsorbed O increases, the number of empty Rh sites decreases, and the reactivity is low, but builds as the number of empty Rh sites increases. When the O coverage is high, there is still some reactivity. At this surface temperature, the absorption rate for adsorbed O is becoming appreciable, and this can also open up surface sites.

3. Partial oxidation of propene

When a Rh(111) surface has 0.5 ML of adsorbed O, the surface produces acetone from propene.⁵ These temperature programmed reaction experiments were done by heating the coadsorbed reactants, starting from a low surface temperature. The experiments shown in Fig. 9 were done in a different manner, by first adsorbing the O, and then exposing the 325 K surface to a propene beam. When $\Theta_{\text{O}}=0.5$ ML, acetone is promptly evolved. When $\Theta_{\text{O}}=1.0$ ML, there is a long induction period, though from the area under the curve, approximately twice as much acetone is made. From the model of Xu and Friend,⁵ the reaction requires that the methylene carbon of the propene be bonded to the Rh, while the 2-carbon reacts with the O. The very gradually occurring increase in the reaction rate for $\Theta_{\text{O}}=1$ ML could be due to the initially very low concentration of exposed surface Rh sites, which rapidly increase as the reaction proceeds.

IV. DISCUSSION AND CONCLUSIONS

In this paper, we have investigated the growth and stability of the (1×1) -O/Rh(111) overlayer. When using O_2 to dose, only a (2×2) structure, with $\Theta_{\text{O}}=0.5$ ML, can be produced. At $T_s=325$ K, O atom dosing rapidly produces the 0.5 ML structure. With further O deposition, the overlayer goes through at least two phase changes, until the (1×1) structure is reached at $\Theta_{\text{O}}=1.0$ ML. This overlayer is stable for surface temperatures below ~ 400 K. Continued dosing with O atoms results in further uptake by migration into the bulk. This absorption is dependent on the surface temperature and the continued exposure of the surface to O atoms.

The diffraction measurements do not show any evidence of a compressed phase, where the surface coverage of O is greater than 1.0 ML. However, since the absorption is dependent on continued dosing, a reasonable supposition is that extra O atoms are transiently incorporated into the (1×1) overlayer, thus changing the energetics to favor the migration of O into the bulk. Theoretical calculations of Ganduglia-Pirovano and Scheffler¹¹ predict that O will be readily incorporated into the bulk only when the (1×1) -O overlayer is essentially complete.

We also found that it was possible to grow the (1×1) overlayer with NO_2 but, unlike O atom exposure, only at an elevated surface temperature. The growth is not as fast as when using O atoms, and leads to a much lower rate of subsurface O deposition. This is probably due a requirement that NO_2 decomposition take place on the Rh surface, and that all of the sites are effectively blocked as the O coverage reaches 1.0 ML. We did not succeed in growing a dense oxygen overlayer using high translational energy O_2 molecules.

At surface temperatures where it is stable, the (1×1) -O/Rh(111) surface is not inert to CO. The reaction takes place much more rapidly at higher surface temperatures, indicative of primarily a L-H reaction between adsorbed reactants, rather than the direct E-R mechanism. Using CO beams of varying translational energy, we also found no evidence of a kinetic barrier to the reaction. It would be interesting to perform these experiments with Ru, on which the (1×1) -O overlayer is apparently stable at much higher surface temperatures. If experiments could be done at temperatures where CO does not coadsorb, it would be possible to definitively measure both the kinetics and reaction dynamics CO_2 production.

The densely oxygen covered surface modifies the rates at which other surface reactions take place. When exposed to H_2 , low coverages of oxygen readily produce water, but on the densely oxygen-covered surface, there is no apparent reaction. This is likely due to the necessity of having bare Rh sites for the dissociative chemisorption of the H_2 . When a half monolayer of adsorbed oxygen is exposed to a propene beam, there is nearly instantaneous production of acetone. A full monolayer of oxygen also produces acetone, but only after a long induction period. Again, for the maximum reaction rate, some bare Rh sites are apparently necessary.

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