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Coadsorption of Oxygen and Hydrogen on Ru(001): Blocking and Electronic Effects of Preadsorbed Oxygen

J. Hrbek

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973
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The coadsorption of oxygen and hydrogen on Ru(001) at 80 K has been studied by thermal desorption, work function measurement, low-energy electron diffraction, and Auger spectroscopy. Oxygen adsorbed in an ordered p(2 × 2) layer induces formation of new weak adsorption sites within each unit cell and simultaneously blocks the adsorption of hydrogen in the sites typical of a clean surface. Hydrogen adsorbs dissociatively with a high sticking probability in the modified sites, and the adsorption is accompanied by a small but complex work function change. We propose that weakly bound hydrogen occupies both surface and subsurface threefold sites. With oxygen coverage increasing above 0.25, the new adsorption sites are progressively blocked and on a surface saturated by a p(1 × 2) oxygen layer the adsorption of hydrogen is completely inhibited. The coadsorption phenomena are dependent upon the sequence of adsorption in preparing the coadsorbed layer and on the ordering of the preadsorbed layer. We also find that the hydrogen overlayer suppresses completely the oxygen adsorption.

Introduction

Interest in the modification of metal surface properties derives mainly from the commercial applications of promoted catalysts. The key question in these studies is how the surface additive affects the catalytic behavior of metal. There are two categories of the effects, namely, the electronic or ligand one and blocking (steric) or ensemble one.[1] The long-range electronic effect is caused by chemical interaction of surface additive with the valence electrons of the metal and can modify the electronic structure on the far sites by through-metal interactions.[2-4] Local interactions limited to metal adatoms adjacent to the adsorption site of additive can be viewed as steric in nature.

On copper-modified Ru(001) both effects were suggested to operate simultaneously, as deduced from the probing of modified surfaces by hydrogen chemisorption.[5] Recent experiments on the same Cu/Ru(001) system support the idea of geometrical blocking only.[6] CO adsorption on the potassium-modified Ru-(001) surface is greatly affected by the electronic through-metal interaction.[7]

Ruthenium is a well-known catalyst for a variety of processes, many of which were studied on its basal plane (001) employing surface science techniques. In one respect the Ru(001) surface shows remarkable difference from the other group VIII (8–10)[42] transition metals. Its activity for CO oxidation is a few orders of magnitude lower, and the lack of activity may be related to the greater stability of chemisorbed oxygen.[8,9] Coadsorbed hydrogen and oxygen produce no H_2O; only desorption of hydrogen and oxygen is observed.[34,35] Because of this difference, the interactions of coadsorbed oxygen with other species are of interest, and we report here a first detailed study of the oxygen–hydrogen coadsorption on the Ru(001) surface.

Hydrogen adsorption has been studied extensively on the clean Ru(001) surface.[5,10-16] Thermal desorption and work function

data revealed that hydrogen atoms adsorb in two states with small positive and negative dipole moments, with different sticking behavior and coverage-dependent kinetic parameters for desorption. In a vibrational study Barteau et al.[13] concluded that H on Ru(001) occupies both types of threefold hollow sites, e.g., hcp and fcc. The penetration of hydrogen into subsurface sites on Ru(001) was reported recently,[16] while work function data[15] strongly support the occupation hcp and fcc above the surface.[15] Thermal desorption is known to have rather low accuracy when used for absolute coverage determination without any reference point. As hydrogen does not induce extra spots in low energy electron diffraction (LEED) and no other method yielding such a point is available, a dependable decision regarding surface stoichiometry is not possible. Shimizu et al.[5] based their estimate of a H:Ru = 1:1 ratio on thermal desorption, while Feulner and Menzel[15] in a recent paper suggested a 2:1 ratio as a more probable stoichiometry, using thermal desorption, work function, and vibrational data.

Our knowledge of oxygen adsorption is more definitive.[8,17-20] The oxygen adatoms with large positive dipole moment are adsorbed in the threefold sites. For coverages below 0.25 the adatoms are ordered in islands with a p(2 × 2) structure, whereas for θ_O > 0.25 a p(1 × 2) overlayer is formed. The break in work function change indicates that the dipole moment per adsorbed oxygen atom changes abruptly at θ_O = 0.25. Activation energy for desorption estimated from the thermal desorption data is 95 kcal/mol at a low coverage limit and there is experimental evidence for oxygen penetration into the bulk for temperatures higher than 1150 K.

There is only limited information available on the coadsorbed oxygen–hydrogen on Ru(001). White et al.[9] studied the reaction of preadsorbed oxygen with low-pressure (10^{-7} Torr) hydrogen at elevated temperatures (500–800 K) and reported three different regions of the reaction rate (measured as an oxygen loss by AES):

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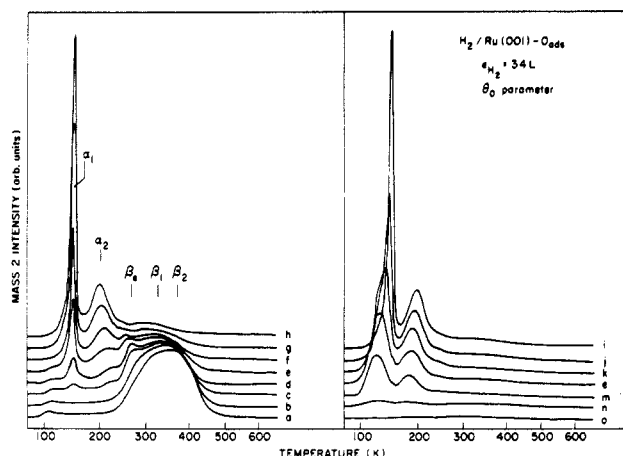(20) Surnev, L.; Rangelov, G.; Bliznakov, G. *Surf. Sci.* **1985**, *159*, 299.

Figure 1. Thermal desorption spectra of the saturated amount of hydrogen adsorbed on Ru(001) modified by an annealed oxygen overlayer. Oxygen coverages θ_O are referred to the number density of ruthenium atoms in the Ru(001) surface: (a) 0.0; (b) 0.02; (c) 0.045; (d) 0.065; (e) 0.090; (f) 0.115; (g) 0.14; (h) 0.16; (i) 0.19; (j) 0.23; (k) 0.28; (l) 0.33; (m) 0.40; (n) 0.46; (o) 0.54. Exposure of 34 L of H_2 saturates all modified surfaces but a clean one, which has $\theta_H{}^r = 0.95$.

Figure 2. Variation of the relative H_2 saturation coverage vs. the relative coverage of preadsorbed O_2.

an induction period of minimal reaction rate, where the dissociative adsorption of hydrogen is very slow due to a lack of adsorption site on oxygen saturated surface; a rapid reaction with active oxygen adsorbed in (1×2) domains; a slow reaction of hydrogen with an inactive form of oxygen adsorbed in (2×2) domains. All three regions are approximately first order in hydrogen pressure, and the size distribution and degree of ordering of (1×2) domains have a strong effect on the rate in the second region. Under ultrahigh-vacuum conditions no H_2O is seen in thermal desorption spectra from coadsorbed H and O and a similar result was obtained for the reaction of adsorbed oxygen with a low-pressure ($\sim 10^{-8}$ Torr) gas-phase H_2.[34] The effect of coadsorbed oxygen on thermal desorption spectra of hydrogen was noticed recently[15,35] but not explored in detail. The dissociative nature of weakly bound hydrogen was discussed briefly together with a possible impact of oxygen "impurity" on the hydrogen chemisorption method used to define the absolute number of active metal sites on the supported ruthenium catalyst.[21]

In this work we investigate the effect of coadsorbed oxygen on the hydrogen chemisorption for various coverages of oxygen. We find that oxygen adatoms adsorbed in the ordered $p(2 \times 2)$ domains simultaneously block hydrogen adsorption sites and form new sites for weakly bound hydrogen. Hydrogen is dissociatively chemisorbed and occupies both surface and subsurface hollow sites within the oxygen islands. The chemisorption of hydrogen is inhibited completely on oxygen-saturated surfaces. Surprisingly, preadsorbed hydrogen blocks the adsorption of oxygen even at half-saturation.

Experimental Section

A Ru(001) sample was mounted in a μ-metal ultrahigh-vacuum chamber ($p < 2 \times 10^{-10}$ Torr) equipped with a shielded quadrupole mass spectrometer for thermal desorption spectroscopy (TDS), a Kelvin probe for work function measurements, low-energy electron diffraction (LEED) optics, and a hemispherical analyzer for electron spectroscopy. The crystal was cleaned by a combination of oxygen adsorption/desorption cycles and sputtering.[22]
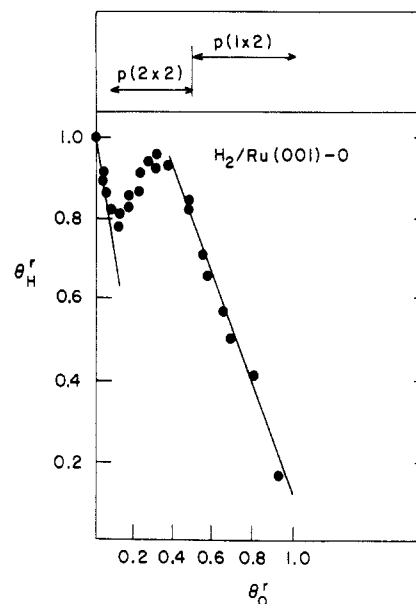
The crystal was exposed to oxygen and hydrogen by back-filling the ultrahigh-vacuum chamber through leak valves, and exposures quoted in the text were measured with a Bayard–Alpert ionization gauge corrected for relative ionization cross section. Oxygen coverage was measured by monitoring the work function changes of the ruthenium surface at 80 K and cross-calibrated by the O/Ru Auger ratio with value 0.1 for $\theta_O = 0.5$ at 300 K. Due to the low mobility of oxygen adatoms at 80 K we used the following procedure to ensure the reproducibility of the results. Oxygen was adsorbed on the surface cooled to 80 K and then was annealed to 700 K. A well-ordered island of oxygen was formed as deduced from a (2×2) LEED pattern which was visible for $\theta_O \geq 0.05$. The saturation coverages of hydrogen were estimated from a series of TD spectra for each θ_O.

Results

Desorption Data. Figure 1 shows changes in the desorption spectra from saturated hydrogen layers as the coverage of oxygen is increased. Broad desorption maximum of clean Ru(001) is composed of two unresolved hydrogen desorption states β_1 and β_2 in agreement with work of others.[5,15,16] The first noticeable change induced by preadsorbed oxygen is the β_e shoulder at 250 K and diminishing $\beta_{1,2}$ states. The 250 K feature is most prominent at $\theta_O = 0.065$ and disappears together with the β states at $\theta_O = 0.25$.

For oxygen coverages above 0.045 two new desorption maxima appear simultaneously: the α_1 state at 156 K, whose position is independent of oxygen coverage in the low-θ_O region and which is unusually narrow; the α_2 state which is coverage dependent in the whole range of coverages. Both α states grow in intensity only up to $\theta_O = 0.20$. a further increase in oxygen coverage brings about the changes of shapes and positions of the α states. As a low-temperature shoulder grows in on the onset of the α_1 state the narrow maximum falls in intensity and shifts to lower temperature. The intensity of the α states decreases with further increase of oxygen coverage and at saturation the adsorption of

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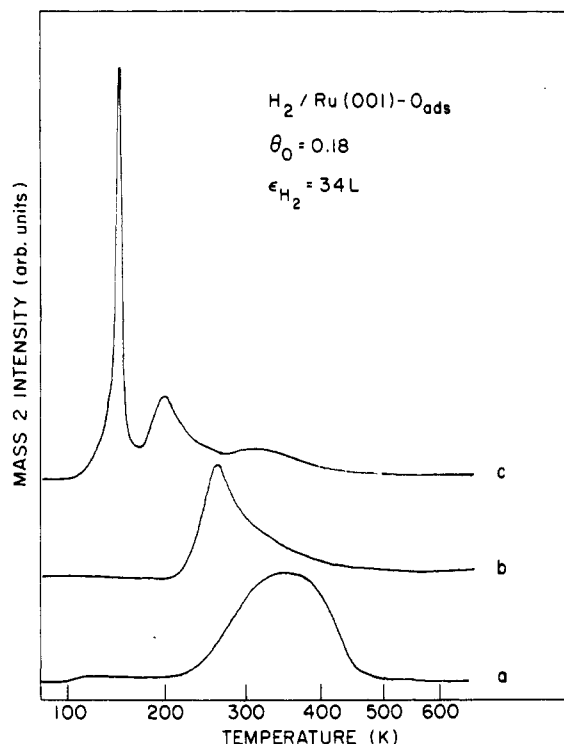
Figure 3. Comparison of hydrogen desorption from a clean Ru(001) surface (a) and Ru(001) surfaces modified by disordered (b) and ordered (c) overlayer of oxygen. $\theta_O = 0.18$ for both ordered and disordered spectra.
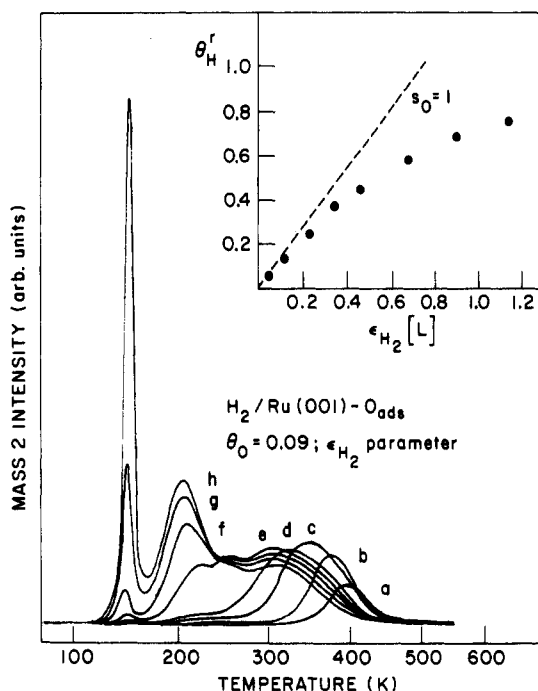

Figure 4. Thermal desorption spectra of hydrogen adsorbed on Ru(001) modified by an ordered oxygen layer with $\theta_O = 0.09$ as a function of increasing H_2 exposure (L): (a) 0.05; (b) 0.11; (c) 0.15; (d) 0.23; (e) 0.34; (f) 0.45; (g) 0.68; (h) 1.14. The insert shows the hydrogen uptake as a function of exposure.
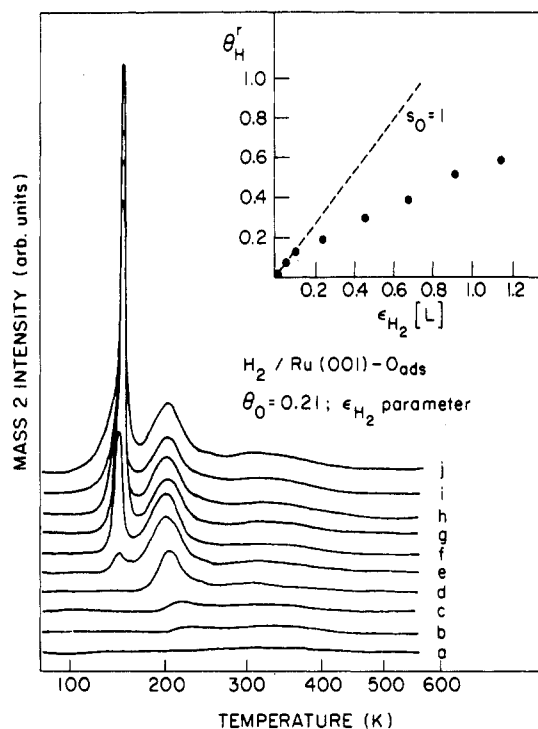

Figure 5. Same as Figure 4 except $\theta_O = 0.21$ and the following hydrogen exposures (L): (a) 0.01; (b) 0.05; (c) 0.11; (d) 0.23; (e) 0.45; (f) 0.68; (g) 0.91; (h) 1.14; (i) 2.3; (j) 34.

hydrogen is completely blocked.

The saturation coverage of hydrogen on oxygen-modified surfaces normalized to the saturation hydrogen coverage on the bare Ru(001) is plotted as a function of relative oxygen coverage θ_O^r in Figure 2. One can distinguish three regions in the plot: the low-θ_O^r region, where the θ_H^r is dominated by the decreasing intensity of the β states and scales down linearly; the intermediate region, where the saturated coverage of hydrogen increases close to the value of a bare Ru(001) surface mainly due to the fast-growing α states; the high-θ_O^r region with a linear fall of θ_H^r which is caused by the blocking of the α states.

The hydrogen coverage is strongly dependent on the degree of ordering of the oxygen overlayer. At 80 K oxygen adsorbs dissociatively[19] but does not form ordered layers due to limited mobility. Temperatures higher than 250 K are needed to anneal the disordered layer, and annealing to at least 700 K, where the order–disorder transition takes place, is necessary to ensure perfectly ordered overlayers. Hydrogen adsorption allows the degree of ordering to be probed, as demonstrated in Figure 3, where we compare desorption spectra from hydrogen-saturated layers on three different surfaces. The disordered oxygen layer with $\theta_O = 0.18$ has a half-capacity for hydrogen adsorption as compared with the ordered one having the same θ_O. The highly asymmetrical desorption curve has its maximum at 250 K, the temperature of the β_e state. Notice also the absence of any low-temperature α states.

The sticking coefficient of hydrogen on a clean surface is strongly coverage dependent: its initial vallue $s_0 = 0.6$ at low θ_H falls to 0.05 as θ_H increases.[5,15] The sticking behavior on an oxygen-modified surface is different, as can be seen in Figures 4 and 5. At $\theta_O = 0.09$ the fast-filling β_2 and β_1 states are shifted to low temperature as compared to the clean surface and their position is coverage dependent. The behavior of the β_e state is difficult to characterize due to its overlap with the β_1 and α_2 states. The α_2 state fills rapidly and shifts to lower temperature only slightly with increasing coverage. The fast-growing α_1 state has few unusual features: its fwhm is only 6 K (see also Figure 8), a value too small even for the desorption peak at 150 K; the position of maximum shifts to higher temperature by 5 K; 3 L of H_2 is an exposure high enough to saturate the state. The

desorption kinetics that can result in such a behavior will be discussed later.

The initial sticking coefficient of hydrogen was estimated from the plot of the normalized hydrogen coverage vs. hydrogen exposure for both oxygen coverages to be unity. Such a high value of s_0 means that the whole surface is effectively trapping and dissociating the hydrogen molecules. Hydrogen adatoms are highly mobile at 80 K and can fill the energetically most favorable sites, i.e., the adsorption sits on a bare metal surface.

Data presented in Figure 4 were collected in an experimental run, where the original oxygen overlayer was used throughout the
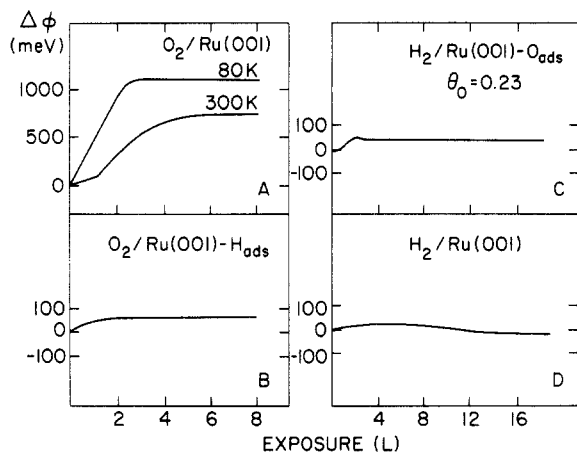
Figure 6. Work function changes vs. exposure of O_2 (left panel) and H_2 (right panel) to a clean or modified Ru(001). Ruthenium was precovered by an ordered oxygen layer (upper right panel) or saturated with hydrogen (lower left panel).
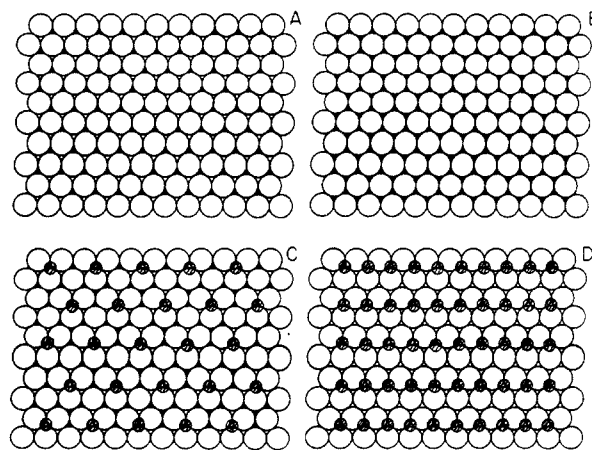

Figure 7. Real space structure of hydrogen and oxygen adsorbed on a Ru(001) surface: (A) hydrogen (filled threefold sites) coverage $\theta_H = 1$; (B) saturated hydrogen overlayer $\theta_H = 2$; (C) the p(2 × 2) structure of oxygen with $\theta_O = 0.25$ and with hydrogen adsorbed in unobstructed hollow sites; (D) a single domain of the p(1 × 2) structure of oxygen inhibits completely the H_2 adsorption.

entire experiment shown. After each hydrogen desorption the crystal was cooled and exposed to hydrogen. The set of desorption curves clearly shows the increase of oxygen coverage (compare curve h in Figure 4 with curve e of Figure 1). Additional measurements of oxygen coverage by AES confirmed the increase of θ_O from 0.09 to about 0.18. Because we can with confidence exclude the oxygen adsorption from the gas phase as the background pressure is better than 2×10^{-10} Torr and there are no traces of oxygen in hydrogen, the only possible source of oxygen must be the bulk of the ruthenium crystal itself. It is known that at elevated temperatures oxygen dissolves readily in ruthenium,[20] and it is possible that the adsorbed hydrogen may cause the surface segregation of dissolved oxygen.

Hydrogen preadsorption suppresses oxygen chemisorption to a great extent. We established that oxygen will adsorb on a Ru(001) surface precovered with hydrogen only if the $\theta_H{}^r < 0.5$ and the desorption spectrum of hydrogen is similar to the one in Figure 3b. The desorption spectrum of oxygen is not changed as compared to a clean surface. Once a half-saturation coverage is reached no adsorbed oxygen is found on the surface, and the surface fully saturated with hydrogen behaves identically.

LEED and Work Function Data. In an agreement with previous work[15] no hydrogen-induced extra spots were seen with LEED on a clean surface. Similarly, no extra spots were observed after adsorption of oxygen at 80 K. A "(2 × 2)" pattern seen for annealed oxygen layers did not change during or after adsorption of hydrogen, thus excluding the possibility of adsorbate-induced surface reconstruction. When the order of adsorption was reversed, no oxygen-induced extra spots were seen by LEED, in agreement with TDS data.

Work function changes are displayed in Figure 6. Hydrogen adsorption on a clean surface leads to small $\Delta\phi$, as expected from comparable electronegativities of H and Ru and discussed by Ertl[5] and Menzel.[15] Oxygen adsorption, on the other hand, causes a large $\Delta\phi$ of 750 meV at 300 K and 1130 meV at 80 K. In contrast to the room temperature data the $\Delta\phi$ increases linearly with oxygen exposure at 80 K over a wide range of exposures and can therefore be used to monitor oxygen coverage.

A transient change of $\Delta\phi$ on an oxygen-modified surface ($\theta_O = 0.23$) is followed by a rapid 50-meV increase of $\Delta\phi$ and a small decrease to a saturation value of 35 meV, which is reached after exposure to only 3 L of H_2. In accord with previously discussed TDS and LEED data, adsorption of oxygen on a hydrogen-saturated surface brings about only a small positive change of $\Delta\phi$.

Discussion

The dramatic effect of oxygen preadsorption on the coadsorbed hydrogen on the Ru(001) surface does not have an analogue among the transition metals studied so far. As mentioned above, no H_2O was observed among desorption products from the coadsorbed layer. Several studies of H_2O on Ru(001) have been

performed recently, including adsorption of water on oxygen-modified Ru(001).[36,37] Only water TDS peaks were observed and no evidence was obtained for water decomposition.

The formation of H_2O from coadsorbed O and H is known to cause a large decrease in the work function,[32] which was not observed on Ru(001). Binding energy of the O 1s core level of adsorbed oxygen is not shifted after the coadsorption of hydrogen Ru(001).[34] Large shifts of the O 1s binding energy were, however, reported for the transformation of oxygen to adsorbed water[38] and on the formation of adsorbed OH groups.[39] On the basis of the negative results of three surface techniques (TDS, $\Delta\phi$, and XPS), we can exclude with confidence the possibility of H_2O and OH formation.

Blocking and Electronic Effects. Thermal desorption data presented in Figures 1, 4, and 5 convincingly demonstrate the geometrical blocking and the electronic effects of preadsorbed oxygen on the coadsorbed hydrogen. The saturated amount of adsorbed hydrogen falls linearly in the coverage region up to $\theta_O{}^r = 0.2$, as seen in Figure 2. The x intercept of the line is less than 0.5, thus showing that one-quarter of an oxygen monolayer would be sufficient to inhibit the H_2 adsorption if the geometrical blocking was the only manifested effect by preadsorbed oxygen.

The models of real space structures of hydrogen and oxygen layers adsorbed on a Ru(001) are shown in Figure 7, with oxygen adatoms drawn to scale with their covalent radius, the smallest size expected for the atom. The drawing depicts, however, the lower limit of the oxygen radius because a large increase in the work function indicates charge transfer from the metal to oxygen adatom. Adsorbed oxygen, occupying, e.g., one hcp threefold site, crowds three fcc neighboring ones and renders all four useless for hydrogen adsorption as shown in Figure 7c. The estimate of site exclusion will depend on the H:Ru stoichiometry, which is not known, and on the knowledge of adsorption sites for O and H adsorption.

In the same low-θ_O region the $\beta_{1,2}$ states shift to lower temperature and a new β_e state grows in. Its intensity scales up with increasing θ_O and at $\theta_O = 0.07$ reaches maximum. We propose that the origin of the β_e state is the adsorption site next to the edge atoms of the oxygen island. At low θ_O a higher intensity of the β_e state reflects the fact that there are many relatively small (2 × 2) islands. As θ_O increases, additional oxygen adatoms are with high probability attached to the already existing islands and the ratio of oxygen atoms on the edges of islands to the total number of oxygen adatoms gets smaller. We can see in Figure

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1 the β_e state falling in intensity above $\theta_O = 0.07$, and its disappearance coincides with the completion of a p(2 × 2) oxygen layer at $\theta_O = 0.25$.

Independent support for the β_e-state assignment comes from experiments with the disordered oxygen layer (Figure 3). Upon adsorption at 80 K the oxygen adatoms are distributed in threefold sites at random forming the disordered layer with some fraction of adatoms in adjacent sites. Such a disordered layer has most of its adatoms in the edges and therefore the β_e dominates the spectrum as seen in Figure 3b. Adsorption of hydrogen in the edge site can therefore provide information on the degree of ordering in the oxygen overlayer and when combined with LEED data[23] possibly on the size distribution of oxygen islands.

As θ_O increases above 0.1, two new low-temperature states of weakly bound hydrogen appear in the desorption spectra (Figure 1, curves d–i), and the total amount of adsorbed hydrogen increases. One can see that the loss of hydrogen in all β states is more than compensated by the faster growth of the α states. The net effect is an increase of the total amount of hydrogen in the intermediate region of the $\theta_H{}^r$ vs. $\theta_O{}^r$ plot (Figure 2). As the formation of the α states coincides with the formation and growth of an ordered (2 × 2) oxygen island, we conclude that new adsorption sites have to be formed within each unit cell of the p(2 × 2). Hydrogen desorption from a disordered oxygen overlayer which presumably has no (2 × 2) islands does not show any low-temperature α states, in agreement with the proposed model.

Just below the saturation of a p(2 × 2) layer the hydrogen capacity of the modified surface is within experimental error the same one as of a clean surface. Such an unusual result warrants further discussion. There are eight threefold sites in each unit cell of the p(2 × 2). As pointed out above one site is occupied by the oxygen adatom and the three nearest-neighbor sites are obstructed. Assuming hydrogen saturation coverage on a clean surface $\theta_H{}^s = 1$,[5] one has two ways to arrange the O and H adatoms in the remaining hollows. The competition of adatoms for the same type of site (e.g., hcp) leads to the hydrogen coverage of 0.75, and in case of different sites for O and H adatoms the coverage is 0.25. Recently proposed in ref 15, $\theta_H{}^s = 2$ leads to unity hydrogen coverage in the presence of the p(2 × 2)–O structure. In either case the estimated hydrogen coverages on the oxygen-modified surface are smaller than the observed one. Thus to account for the unchanged hydrogen capacity of the modified surface the adsorption sites within each unit cell of the p(2 × 2) have to be doubly occupied. A model with $\theta_H{}^s = 2$ agrees reasonably well with the experiment, while for the assumption of $\theta_H{}^s = 1$ the discrepancy of experimental results and model prediction is outside the ±10% margin, an estimated precision of relative coverage determination. Since the molecular adsorption of hydrogen in the α states was excluded,[21] we suggest that the hydrogen adatoms rests in the surface threefold sites as well as in subsurface sites. This conclusions finds additional support in the desorption kinetics of the α_1 state as discussed later.

Once the p(2 × 2) layer is saturated, additional adatoms of oxygen will adsorb in the remaining empty threefold sites to form three domains of a p(1 × 2) structure rotated 120°. This oxygen inhibits hydrogen adsorption and besides the geometrical blocking an electronic modification takes place. Changes in the shapes and a further weakening of the α states demonstrate the destabilization effect of a p(1 × 2) domain on the hydrogen adsorbed in a p(2 × 2) layer. Once we reach the saturation of a p(1 × 2) layer no hydrogen will adsorb on the surface, regardless of the fact that there is still one uncrowded threefold site within each unit cell of the p(1 × 2) available (Figure 7d). These sites are ineffective not only for dissociation of hydrogen molecules but also for the adsorption of an atomic hydrogen as we have shown in an additional experiment with the atomic hydrogen.[34]

As discussed in the previous paragraphs, the geometrical blocking is caused by individual oxygen adatoms. On the other hand, only a particular 2D arrangement of oxygen adatoms will form new weak adsorption sites due to the cooperative electronic effect of the p(2 × 2)–O structure. This effect should be distinguished from a regular one, which is additive and causes the
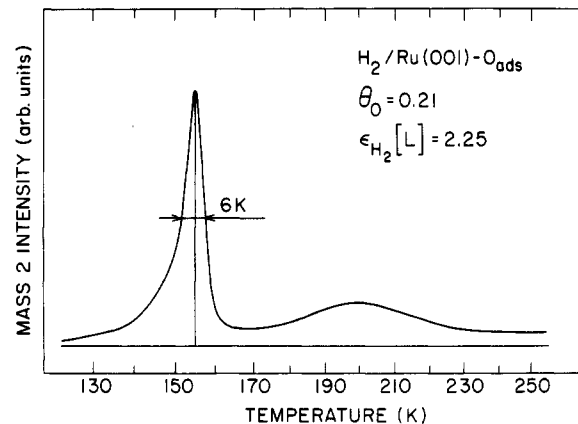

Figure 8. Thermal desorption spectrum of the α states. Notice the width and the asymmetrical shape of the α_1 peak.

formation of the β_e states or changes in the α states for $\theta_O > 0.25$.

A ruthenium surface saturated with hydrogen does not adsorb oxygen at all, as seen in desorption spectra, LEED, and $\Delta\phi$. One would expect that hydrogen will be easily displaced by the more strongly bound oxygen. There are, however, no threefold sites available on the hydrogen-saturated surface if we assume $\theta_H{}^s = 2$ (see Figure 7b). Surprisingly, half the hydrogen monolayer with hydrogen adatoms adsorbed mainly in hcp hollow sites[15] blocks also oxygen adsorption completely. Two possible explanations are that oxygen molecules need at least two adjacent hollows for dissociation or that both hydrogen and oxygen are competing for the same hcp threefold sites, i.e., the site over a second-layer Ru atom. There are, however, no experimental data to support either explanation and the actual adsorption site of oxygen (hcp vs. fcc) is unknown.[19]

Nature of the α States. We have shown recently that weakly bound hydrogen in the α states is not adsorbed molecularly since both α states undergo rapid hydrogen–deuterium exchange.[21] The shape and coverage shift of the α_2 peak are consistent with second-order kinetics, and the estimate of activation energy of desorption from the slope of the ln $(T_m{}^2 n_m)$ vs. $T_m{}^{-1}$ plot gives 15.8 kcal/mol and $\nu(2) = 10^2$ cm^2 s^{-1}. The behavior of the α_1 peak is totally different, as documented in Figure 8, which displays the close up of the α states. The α_1 peak is highly asymmetric, unusually sharp with a half-width of 6 K, and its maximum shifts to higher temperatures with increasing coverage only slightly (by 5 K).

The leading edge of the α_1 peak obeys the logarithmic law, and a plot of ln R (relative desorption rate) vs. T^{-1} gives a straight line from which we estimate the activation energy of desorption to be 5.1 kcal/mol. Attempts to fit the desorption data with a fractional ($0 < n < 1$) order kinetics failed and the application of Redhead and Edwards equations[27,28] gave physically unreasonable values for the α_1 state.

There are several processes that may lead to the observed kinetics: desorption from the condensed molecular layer,[26] desorption from the surface/subsurface states,[29,30] desorption from the multiple surface phases in equilibrium,[40,41] and surface explosion.[24,25] The autocatalytic mechanisms[25] can be ruled out as no self-accelerating surface reaction was observed in auxiliary isothermal experiments.[34] Saturation behavior and H–D exchange do not support desorption from the condensed layer. Lack of structural data on H/Ru–O adsorption systems prevents the application of multiple surface phases model, which was recently used for deuterium adsorption on Ni(110).[41]

(40) Nagai, K.; Shibanuma, T.; Hashimoto, M. *Surf. Sci.* **1984**, *145*, L459.
(41) Norton, P. R.; Bindner, P. E. *Surf. Sci.* **1986**, *169*, L259.
(42) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Zero-order desorption kinetics of the α_1 state supports the above proposed model of surface/subsurface desorption. As long as the desorption takes place from the doubly occupied hollow sites, hydrogen desorbs into the α_1 state without experiencing the deep potential well of the still occupied chemisorption sites and the desorption process is governed by zero-order kinetics. Hydrogen desorbing from the surface is immediately replaced by atoms from the subsurface sites. The low temperature at which the exponential increase of desorption rate occurs and the saturation behavior of the α states rule out any diffusion-controlled steps. Once all subsurface hydrogen moved to the surface, the desorption from the singly occupied site will need an additional activation energy and hydrogen will desorbed at a higher temperature, i.e., in the α_2 state.

A normal kinetic isotope effect deduced from the difference of adsorption rate of H_2 and D_2 provides additional support for the model of surface/subsurface adsorption sites. The α states are filled faster by hydrogen than by deuterium, while in hydrogen/deuterium bulk diffusion the activation energy for diffusion is lower for D than for H atoms. A similar "inverse isotope effect" was observed recently in the desorption of H_2 and D_2 from a clean Ru(001) surface.[16] Isotope effects can be used to distinguish between surface/subsurface and bulk processes as suggested by Behm.[29,30]

Although work function changes were not studied in greater detail, the data presented here are consistent with the results of other techniques used. As on a clean Ru(001) surface, hydrogen adsorption on oxygen-modified Ru ($\theta_O = 0.23$) leads to small work function changes so the possibility of H_2O or OH group formation can be ruled out. The species with negative outward moment adsorb first and are responsible for a 50-meV increase in the work function. Because the initial sticking coefficient is close to unity, we can estimate the initial dipole moment of -0.01 D. The species with a positive-outward moment are responsible for the decreasing part of the work function curve and the dipole moment is comparably small. Fairly small dipole moments of the adsorption complexes suggest a covalent character of H–Ru for both clean and modified Ru surfaces.

Comparisons with Other Systems. Sulfur preadsorbed on Ru(001) acts as a site-blocking additive.[11] For $\theta_s < 0.25$ the hydrogen adsorption falls linearly with increasing θ_s and no hydrogen will adsorb on a Ru(001)–(2 × 2)–S surface. The study was carried out at adsorption temperatures of 250 K and no new adsorption states were reported. A low-temperature study may be a useful extension of the experiments, considering the similarities of the surface chemistry of oxygen and sulfur.

Preadsorbed carbon monoxide blocks hydrogen adsorption on Ru(001),[31] and there is also evidence for strong long-range CO–H repulsive interaction and segregation of H and CO on the surface. Although weak hydrogen states were observed for CO–H coadsorbed on Rh(100) and Ni(100), the closed-packed face of Ru(001) is less active in the destabilization of coadsorbed hydrogen and carbon monoxide.

It has been established that the most reactive metals for the $H_2 + O_2$ reaction exhibit the lowest heat of adsorption of oxygen.[32] This fact prevents study of the interaction of coadsorbed species on many metals, e.g., Pt, Pd, Ir, and Ni. Thiel et al.[33] published a detailed study of O_2 and H_2 coadsorption on Rh(111), where the reaction probability for water formation is fairly small. Adsorbed oxygen blocks extensively sites for hydrogen chemisorption and disordered oxygen overlayer is most effective for surface blocking. A similar effect is seen in the present study,

where $\theta_O = 0.18$ will decrease the hydrogen chemisorption capacity to half of a clean surface value, while an ordered oxygen layer with identical coverage will, within experimental error, adsorb the same amount of hydrogen as a clean surface. The saturation amount of hydrogen on Rh(111) decreases linearly with increasing oxygen coverage, suggesting that site exclusion by oxygen occurs in low-temperature coadsorption. The desorption spectrum of hydrogen is very sensitive to the effects of annealing the oxygen overlayer, reflecting both ordering of oxygen and its penetration into the bulk. Hydrogen preadsorption has little effect on subsequent oxygen adsorption: although a layer of hydrogen suppresses the formation of ordered oxygen superstructure, the total oxygen coverage is reduced only by approximately 20%. The interactional effects are not due to the reaction of H and O since the yield of H_2O is very small compared to the mutual effects of the coadsorbed adatoms on each other.

As we have pointed out in the foregoing paragraphs, the coadsorption behavior of H and O on Ru is quite unique. We find, surprisingly, a close analogy with the desorption of hydrogen from the more open face of Pd(110):[29,30] as on an oxygen-modified ruthenium, there are two weak adsorption states, with desorption peaks at 225 and 160 K, in addition to the β states at higher temperatures. The origin of the α states is related to the surface reconstruction occurring at hydrogen exposures above 10 L, which creates a new active surface and opens up channels for hydrogen subsurface diffusion. Though we do not see any evidence for surface reconstruction with a completion of a p(2 × 2) layer on Ru, our model of surface/subsurface adsorption sites is based on a similar assumption, i.e., accessibility of subsurface site on a modified surface.

Conclusions

We have reported in the present study a unique and complex behavior of hydrogen–oxygen coadsorption on the Ru(001) surface. Adsorbed oxygen affects coadsorbed hydrogen in three different ways: (i) by a steric effect which is caused by the physical blocking of the threefold site and the crowding of nearest-neighbor hollows; (ii) by a simple electronic effect which is responsible for the weakening of the H–Ru adsorption bond at the edges of oxygen islands and in the vicinity of individual oxygen adatoms; (iii) by a cooperative electronic effect, where a particular structure of surface modifier is required to form a new adsorption site within the modifier array itself.

We have proposed that hydrogen occupies surface/subsurface threefold sites within the p(2 × 2) oxygen layer, in agreement with the measured hydrogen chemisorption capacity and desorption kinetics of a new state. Although the saturated oxygen overlayer does not block and crowd all threefold sites, the chemisorption of hydrogen is completely suppressed at $\theta_O = 0.5$. Similarly effective blocking effects are observed for the chemisorption of oxygen on hydrogen precovered ruthenium surfaces.

Due to its unique behavior, the coadsorption system deserves additional studies. Photoemission and simulated desorption and vibrational spectra will certainly contribute to a deeper understanding of the interaction of coadsorbed adatoms and it is our hope that a theory will help to clarify the nature of these interactions.