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ON THE STEPPED RHODIUM (755) AND (331) SURFACES

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Abstract

The chemisorption of H_2 , O_2 , CO , CO_2 , NO , C_2H_2 , C_2H_4 and C has been studied on the clean stepped $Rh(755)$ and (331) surfaces. Low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) were used to determine the size and orientation of the unit cells, desorption temperatures and decomposition characteristics for each adsorbate. All of the molecules studied readily chemisorbed on both stepped surfaces and several ordered surface structures were observed. The LEED patterns seen on the (755) surface were due to the formation of surface structures on the (111) terraces, while on the (331) surface the step periodicity played an important role in the determination of the unit cells of the observed structures. When heated in O_2 or C_2H_4 the (331) surface was more stable than the (755) surface which readily formed (111) and (100) facets. In the CO and CO_2 TDS spectra a peak due to dissociated CO was observed on both surfaces. NO adsorption was dissociative at low exposures and associative at high exposures. C_2H_4 and C_2H_2 had similar adsorption and desorption properties and it is likely that the same adsorbed species was formed by both molecules.

Introduction

The chemisorption properties of rhodium surfaces have not been well documented until recently (1 - 5) despite rhodium's importance as a versatile industrial catalyst. Rhodium is capable of reducing nitrogen oxides, inserting CO molecules into hydrocarbons and producing methane and other hydrocarbons from CO and H₂. Rhodium differs from platinum in that it can readily break C-O bonds in addition to H-H, C-H and C-C bonds.

Most of the previous chemisorption studies on rhodium single crystals have been carried out on the low index faces. Marbrow and Lambert (2,3) have studied O₂, CO and NO adsorption on Rh(110). Grant and Haas (4) reported briefly on the adsorption of CO, CO₂ and O₂ on Rh(111). We have reported earlier on the chemisorption properties of H₂, O₂, CO, CO₂, NO, C₂H₄, C₂H₂ and carbon on the Rh(111) and (100) surfaces (1). The lack of chemisorption data on rhodium stepped surfaces has prompted us to investigate the Rh(755) and (331) surfaces to see what effect the presence of steps has on the chemisorption properties of these small molecules. Oxygen adsorption on Rh(210) has been reported in an early paper by Tucker (15).

In this paper we report the results of a systematic survey of the chemisorption properties of several small molecules (H₂, O₂, CO, CO₂, NO, C₂H₄, C₂H₂ and C) on the clean Rh(755) and (331) crystal faces. Low-energy electron diffraction (LEED) was used to determine the surface structures that form at exposures of 1-10³ Langmuirs (1 Langmuir = 1L = 10⁻⁶ torr seconds) in the pressure range of 10⁻⁸-10⁻⁵ torr and

surface temperatures of 0-800°C. Auger electron spectroscopy (AES) was used to monitor the surface composition. Thermal desorption spectroscopy (TDS) was used to obtain information about the binding of the adsorbates on the rhodium surfaces.

Step effects were more evident on the highly stepped (331) surface (40% step density) compared to the (755) surface (17% step density).

The LEED patterns observed on the (755) surface were determined by the (111) terraces, while on the (331) surface the step periodicity controlled the type of LEED patterns that were formed. Only two types of step effects were detected on the Rh(775) surface, enlarged adsorbate diffraction spots due to a decrease in long range order and the dissociation^{of} adsorbed CO at step sites. Step effects in the chemisorption properties of CO, CO₂, NO, O₂, C₂H₄ and C₂H₂^{were} detected on the Rh(331) surface. The stability of the two stepped surfaces in the presence of O₂ and C₂H₄ at high temperatures were very different, with the (331) surface more stable.

The chemisorption properties of the stepped rhodium surfaces has been compared with the low index rhodium surfaces and stepped platinum and iridium surfaces. The effect of the steps on the chemisorption properties on these three metals varied for each adsorbate. Dissociated CO was only detected on the rhodium stepped surfaces.

Experimental

The experiments were carried out in a Varian ion pumped UHV system which has LEED, retarding field AES and TDS capabilities. Samples 1mm thick were cut from a 6 mm diameter rhodium single crystal rod of >99.99% purity by spark erosion after orienting the rod to within $\pm 1^\circ$ of the desired crystal face. The crystals were then mechanically polished with the final polishing done on a syntron containing^a slurry of $0.05\mu \text{ Al}_2\text{O}_3$ in H_2O .

The crystals were connected to 1/4 inch square Cu bar supports by thick 0.007 inch Ta foil, with crystals attached to the Ta foil by spot welds. The samples were mounted such that the Ta foil masked off the back side of the crystals. The heating leads outside the vacuum chamber were LN_2 cooled so adsorptions could be carried out at temperatures between 0 and 25°C . The crystals were heated resistively and the crystal temperature was monitored by a chromel-alumel thermocouple spot welded to the back side of the crystal.

The crystals were cleaned by cycles of argon ion bombardment and annealing. Sulfur, boron and carbon were the major impurities detected when the crystals were first put in the vacuum chamber. The carbon was removed by annealing the crystal at 1000°C in vacuum. The sulfur was

removed by ion bombardment (2000 eV, 5×10^{-5} torr Ar, 25°C). Boron, which is a major bulk impurity (17 ppm), segregated to the (755) surface and required many cycles of ion bombardment (500 eV, 5×10^{-5} torr Ar, 25°C) and annealing at 800°C to deplete it from the near surface region. On the (331) surface boron segregation was not a major problem and it ceased segregating to the surface after a few cycles of ion bombardment and annealing.

Each gas was adsorbed at pressures between 1×10^{-8} and 1×10^{-5} torr and at temperatures between 0 and 800°C . Surface structures were observed both with increasing exposure and after the gas was pumped away. TDS spectra were taken by plotting the output of a particular mass number from the quadrupole mass spectrometer (UTI model 100C) versus temperature while the crystal temperature was being increased linearly. A scan of the entire temperature range between 0 and 1000°C was made for each adsorbate except for oxygen where the range was extended to 1300°C . Blank TDS experiments were performed by replacing the Rh crystals with Ta foil to insure that desorption peaks in the rhodium TDS spectra were from the Rh crystals and not the Ta supports.

Results and Discussion

1. Clean Surfaces

LEED patterns and real space representations for the clean Rh(755) and (331) surfaces are shown in Figure 1. These patterns exhibit the (1x1) symmetry characteristic of an unreconstructed clean surface. The AES spectrum of the clean rhodium surfaces is shown in Figure 2.

The (755) surface is at an angle of 9.5° from the (111) surface and using Somorjai's notation (7), can be labeled as $\text{Rh(S)}-[6(111)\times(100)]$. This notation is more descriptive of the surface structure since the surface is actually made up of a series of six atom wide (111) terraces separated by one atom high (100) steps. Therefore the LEED pattern can be thought of as a set of hexagonal spots due to the (111) terraces in which all spots are split by the step periodicity. The terrace width can be calculated from the splitting observed in the LEED pattern. Since the LEED patterns observed on the (755) surface can be easily indexed as diffraction spots from structures on the (111) terrace which have been split by the step periodicity the $\text{Rh(S)}-[6(111)\times(100)]$ notation will be used for the remainder of this paper.

The (331) surface corresponds to a $\text{Rh(S)}-[3(111)\times(111)]$ surface in Somorjai's notation, but since the LEED patterns produced on this surface could be most easily indexed using the (331) unit cell vectors we will use the (331) notation in the rest of the paper. The unit cell of the (331) surface is oblique as can be seen from Figure 1b,

2. Surface Structures, Thermal Desorption and Ordering Characteristics Of Adsorbates on the Rh(S)-[6(111)x(100)] and (311) Surfaces

The surface structures which were observed in our investigations on the two Rh stepped surfaces are summarized in Table 1. Also included in Table 1 are the structures reported for the same adsorbates on the Rh(111) surface. In Table 2 the surface structures we observed on the Rh(S)-[6(111)x(100)] surface are compared with surface structures reported for the Pt(S)-[6(111)x(100)] and Ir(S)-[6(111)x(100)] surfaces.

2a. Hydrogen

The chemisorption properties of hydrogen on the two rhodium stepped surfaces were very similar to those found for hydrogen on Rh(111). Exposing either stepped surface to hydrogen did not noticeably alter their clean (1x1) LEED patterns. Hydrogen was adsorbed as indicated by the TDS spectra shown in Figure 3. The spectra from both surfaces were identical so that only the results from the (311) surface are shown in Figure 3. The hydrogen desorption peak is slightly asymmetric, tailing on the high temperature side. The desorption temperature decreases as the exposure is increased indicating second order desorption kinetics.

The LEED and TDS results for hydrogen adsorption on the various rhodium crystal faces were similar to results reported on the Ir(S)-[6(111)x(100)]⁸ and Ir(111)⁸ surfaces. The only difference was that the high temperature tailing was more pronounced on the Ir(S)-[6(111)x(100)] surface, indicating more strongly bound hydrogen at the step sites. Comparison of the TDS results from the Pt(S)-[6(111)x(100)]⁹, Pt(S)-[6(111)x(111)]⁹ and Pt(S)-[3(111)x(100)]¹⁰ surfaces to the Pt(111) surface^{9,11} shows the presence of an

additional peak on the stepped surfaces due to more strongly bound hydrogen at the step sites. This additional peak is also detectable on a Pt(111) surface which has been roughened by ion bombardment,¹¹ From these observations it can be concluded that for hydrogen adsorption platinum surfaces show the most pronounced step effects, rhodium surfaces show no step effects and iridium surfaces are in between these two metals.

2b. Oxygen

The oxygen chemisorption properties were markedly different on the two rhodium stepped surfaces. The only step effect detected on Rh(S)-[6(111)x(100)] was enlarged diffraction spots while on Rh(331) more pronounced step effects were seen by both LEED and TDS.

Several ordered oxygen LEED patterns were observed on the Rh stepped surfaces. Exposing the clean Rh(S)-[6(111)x(100)] surface to 1 L of oxygen at 25°C produced the LEED pattern in Figure 4b corresponding to a (2x2) surface structure on the (111) terraces. This chemisorbed oxygen structure was very reactive and disappeared in a few seconds when heated to 50°C in 5×10^{-7} torr of H₂. Upon heating the [6(111)x(100)] surface in oxygen (1×10^{-7} torr, 800°C) two new faceted surfaces were seen. First the splitting of the substrate and overlayer doublets decreased by one half as shown in Figure 4c. This surface converted back to the clean Rh(S)-[6(111)x(100)] surface when heated for 30 seconds in vacuum at 900°C. Further high temperature oxygen treatment followed by a short anneal in H₂ (2 min., 5×10^{-7} torr H₂ at 500°C) produced the LEED pattern in Figure 4d where the substrate doublets are streaked and overlayer spots are not split. The oxygen species present in this structure was not easily removed and required high temperature anneals (900°C) in hydrogen to regenerate the

clean $[6(111) \times (100)]$ surface. The oxygen AES signal increases as the LEED pattern changes from 4a to 4d.

Exposure of the clean Rh(331) surface to 1L of oxygen at 25°C results in half order streaks forming in the LEED pattern (Figure 5b). Heating the crystal at 800°C for one minute in 1×10^{-7} torr of oxygen results in spots appearing in the streaks (Figure 5c). This diffraction pattern is from a surface structure indexed in matrix notation ¹² as $a \begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$. Further heating in oxygen (1×10^{-6} torr, 800°C for 5 min.) results in the spots moving away from the half order positions (Figure 5d). Prolonged high temperature oxygen treatment results in the fully developed diffraction pattern in Figure 5e. The diffraction pattern in Figures 5d and 5e are from a $\begin{pmatrix} 1 & 2 \\ 7 & -1 \end{pmatrix}$ surface structure. The Rh(331) surface was stable in oxygen pressures up to 1×10^{-5} torr and crystal temperatures up to 1000°C. A heavily faceted surface was produced by heating the (331) crystal at 800°C for 15 minutes in ~1 torr of oxygen. Immediately after this treatment the LEED pattern had a very high background intensity with almost no discernable spots, but flashing the crystal to 900°C in vacuum revealed the faceted surface in Figure 5g. Removing oxygen from the surface region by annealing the crystal at 1000°C in vacuum resulted in the faceted surface reverting into a clean (331) surface. During this conversion a $\begin{pmatrix} \frac{1}{2} & 1 \\ -2 & 0 \end{pmatrix}$ oxygen structure corresponding to the LEED pattern in Figure 5f was observed. The oxygen AES signal increases upon going from the LEED pattern in Figure 5a to the LEED pattern in Figure 5g. The real space unit cells of the oxygen structures on Rh(331) are shown in Figure 6.

The TDS spectra for oxygen adsorbed on the two clean stepped Rh surfaces are shown in Figure 7. Oxygen desorption appears to follow second order desorption kinetics on both surfaces. From Figure 7 two differences

between the stepped Rh surfaces are apparent. At exposures below 5L oxygen desorption occurs 100°C higher on the (331) surface. At exposures of 5 and 10L the oxygen desorption peak is 100°C broader on the (331) surface. The first two or three times oxygen is adsorbed at 25°C on a clean Rh surface and the crystal flashed to 1000°C, no desorption peaks (O_2 , CO, CO_2 , etc.) are detected by TDS. After the flashing no oxygen AES signal is detected, implying the oxygen has diffused into the bulk. Following two to three oxygen adsorptions oxygen was detected desorbing from the surface. Oxygen desorption was not seen if carbon was present in the near surface region, but instead a CO desorption peak was detected at ~600°C.

The LEED patterns in Figure 4 are from (2x2) structures on the (111) terraces, with the changes in spot splitting due to the changing step periodicity of the metal substrate. In Figure 4b the surface is still the $[6(111) \times (100)]$, but in Figure 4c the substrate has faceted to a $[12(111) \times 2(100)]$ surface. The half order spots in Figure 4d are due to a (2x2) structure on large (111) facets and substrate doublets are streaked due to oxygen free areas of the crystal returning to the $[6(111) \times (100)]$ configuration. (2x2) surface structures have been seen for oxygen adsorption on Ir(S)- $[6(111) \times (100)]$ ¹³, Pt(S)- $[9(111) \times (100)]$ ¹⁴ and Rh(111)¹. Half order streaks indicating one dimensional order have been observed for oxygen on Pt(S)- $[6(111) \times (100)]$.^{15,16}

Step effects were seen with LEED for oxygen adsorption on Rh(331). The half order streaks in Figure 5b resulting from oxygen adsorption at room temperature correspond to a 2(1d) surface structure. The 2(1d) label denotes an ordered one dimensional array parallel to the step edge having a repeat distance of two rhodium atoms. Two dimensionally ordered surface structures appear only after the (331) surface is annealed in O_2 . Correlations among

the Rh(331) oxygen structures and the Rh(111)-(2x2) oxygen structure are evident from Figure 6. The 2(1d) and $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ structures have repeat distances of two rhodium atoms only along the step edge, whereas the (2x2) structure has a repeat distance of two rhodium atoms in two directions. For the case of the 2(1d) structure the steps prevent ordering in one direction and for the $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ structure the step periodicity determines the repeat distance in that direction. The $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ and $\begin{pmatrix} 1 & 2 \\ 7 & 1 \end{pmatrix}$ structures both have a periodicity of two terrace widths. This periodicity is the shortest repeat distance perpendicular to the step edge on the (331) surface. The $\begin{pmatrix} \frac{1}{2} & 1 \\ 2 & 0 \end{pmatrix}$ structure seen during the removal of oxygen from the faceted surface has a repeat distance of just one terrace width. Since the (331) surface does not possess this periodicity it is reasonable to assume the step atoms have not completely reverted from the faceted surface to their (331) positions. Further removal of oxygen does result in the reappearance of oxygen structures possessing repeat distances of two terrace widths. No ordered oxygen structures were found on Ag(331), but high exposures of O₂ (~2000L) on the Ag(331) surface was found to produce a faceted Ag(110)-(2x1)-O phase¹⁷. Third order streaks have been seen on Pt(S)-[3(111)x(100)]¹⁶, a surface which differs from the (331) only by the fact that it has (100) oriented steps.

The oxygen TDS spectra for the Rh(S)-[6(111)x(100)] surface are identical to the previous spectra published for the Rh(111) surface¹. This is in contrast to the TDS results on Ir(S)-[6(111)x(100)]¹³ and Pt(S)-[6(111)x(100)]⁹ where an additional high temperature shoulder is seen on the stepped surfaces. Two binding states are present in the TDS spectra on the Rh(331) surface, however. Apparently the high density of step atoms on the (331) surface is needed to observe a step effect on rhodium surfaces. The diffusion of oxygen into the bulk which was detected during the TDS experiments has also been observed for oxygen on Rh(110).²

The LEED and TDS results for oxygen adsorption on the Rh(S)-[6(111)x(100)] surface are essentially identical to the results found on Rh(111), indicating that the steps of this surface do not effect oxygen chemisorption. On the Rh(331) surface an additional binding state and several new LEED pattern show that a high density of step atoms is needed before a definite step effect is detected in the oxygen chemisorption properties. In this way rhodium surfaces differ from the platinum and iridium surfaces since step effects are already present on the Pt and Ir [6(111)x(100)] surfaces.

2c. Carbon Monoxide and Carbon Dioxide

Step effects were observed in the chemisorption properties of both carbon monoxide and carbon dioxide on the rhodium stepped surfaces. Dissociated CO, which was not seen on Rh(111), was detected on both rhodium stepped surfaces. The CO and CO₂ chemisorption properties were identical indicating that CO₂ dissociates to CO upon adsorption. Since CO and CO₂ behaved similarly this section will pertain mainly to CO, but any differences between the two gases will be pointed out.

Both CO and CO₂ produced an identical sequence of LEED patterns, with the only difference being that a factor of 5 higher pressure of CO₂ was required to form the patterns. On the [6(111)x(100)] surface the first CO diffraction pattern occurs at 3L and corresponds to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure on the (111) terrace. Increasing the CO exposure further caused the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern to fade and streaks to form in the diffraction pattern. Raising the CO pressure to 1×10^{-5} torr caused these streaks to coalesce into a (2x2) structure on the (111) terraces. All diffraction spots in both CO LEED patterns are split by the step periodicity. The diffraction spots formed by

the CO structures on the $[6(111) \times (100)]$ surface were not as sharp as those formed on the (111) surface.

The three LEED patterns observed for CO adsorption on the Rh(331) surface are shown in Figure 8. The LEED pattern in Figure 8a forms at a CO exposure of 3L and corresponds to a $\begin{pmatrix} 1 & 2 \\ 3 & -1 \end{pmatrix}$ surface structure. Increasing the CO exposure to 7L causes the extra diffraction spots to move to the positions shown in Figure 8b. This is the LEED pattern of a $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ surface structure. Increasing the CO pressure to 1×10^{-5} torr results in the formation of the LEED pattern shown in Figure 8c. The real space unit cells of these CO structures are shown in Figure 9.

The TDS spectra for CO and CO₂ on the Rh stepped surfaces are shown in Figure 10. The CO TDS spectra was the same on both stepped surfaces. As can be seen from Figure 10, the CO₂ desorption spectra has two peaks, whereas the CO desorption spectra only has one. Using AES in conjunction with TDS showed that after adsorbing ^{CO} on the stepped surfaces at 25°C and then flashing the crystal to 400°C so that all the CO had desorbed by TDS, a carbon AES signal was present. This carbon signal was present until 800°C at which time the carbon diffused into the bulk. By pretreating either step surface in oxygen (1×10^{-6} torr O₂ at 800°C) this surface carbon desorbed from the surface between 500 and 600°C as CO, giving a TDS spectrum essentially identical to that for CO₂ on Rh(S)- $[6(111) \times (100)]$. CO was the only gas detected desorbing during the CO and CO₂ TDS experiments. No CO₂ (mass 44) was seen, even after CO₂ adsorptions.

The $(\sqrt{3} \times \sqrt{3})R30^\circ$ and (2x2) CO surface structures observed on Rh(S)- $[6(111) \times (100)]$ have been seen on Rh (111).¹ The (2x2) structure is due to a close packed hexagonal CO overlayer with a coverage of $\theta=0.75$. The hexagonal CO overlayer results from compressing the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure by increasing the

CO exposure . The steps of the Rh(S)-[6(111)x(100)] surface do not interfere with the formation of the hexagonal CO overlayer but do limit the long range order as evident from the enlarged diffraction spots on the stepped surface.

The CO LEED patterns on Rh(331) can also be related to the Rh(111) surface. The highest coverage CO LEED pattern on Rh(331), Figure 8c, is due to a close packed hexagonal CO overlayer. This CO LEED pattern is explained by scattering from the CO overlayer, the rhodium substrate and multiple scattering from both layers as shown in the schematic in Figure 8d. Two domains are present in the LEED pattern and their real space structures are given in Figures 9c and 9d. An arrangement of CO molecules within the unit cells of the first two structures formed on Rh(331) can be proposed using the results obtained on the Rh(111) and [6(111)x(100)] surfaces.

On those two Rh surfaces the first structure formed is the $(\sqrt{3} \times \sqrt{3})R30^\circ$, a hexagonal array of CO molecules.

Placing CO molecules in a hexagonal array on the (331) surface as shown in Figure

9a the $\begin{pmatrix} 1 & 2 \\ 3 & -1 \end{pmatrix}$ structure is obtained.

The $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ CO structure is an intermediate in the transformation between the $\begin{pmatrix} 1 & 2 \\ 3 & -1 \end{pmatrix}$ and hexagonal overlayer. A reasonable transformation mechanism would be compression parallel to the steps, giving the structure shown in Figure 9b.

From this structure further compression along the steps would give one of the domains of the hexagonal overlayer (Figure 9c).

Compression perpendicular to the steps would give the other domain (Figure 9d).

Rhodium seems to be one of a few metals studied whose stepped surfaces produce ordered CO LEED patterns. No ordered CO LEED patterns have been observed for Ir(S)-[6(111)x(100)]¹³ or the (111) vicinal surfaces of Pt^{15,16}. On Pd, CO forms identical LEED patterns on both the [9(111)x(111)] and (111) surfaces¹⁸, with the extra diffraction spots more diffuse on the stepped surface. This is the

same relationship that we found between the $[6(111)\times(100)]$ and (111) Rh surfaces. Ordered (1×1) and (1×2) CO structures formed on the Pd(210) surface have been interpreted as a close packed overlayer of CO on the Pd surface¹⁸. CO adsorption on Pd (311) results in streaks occurring in the LEED pattern indicating that only one dimensional order is present in the CO overlayer.¹⁸

The large low temperature desorption peak in the CO TDS spectra is due to molecular CO bound on the (111) terraces. The position and behavior of this peak is identical to the CO desorption peak on Rh(111).¹ The molecular CO desorbs with first order kinetics but has an activation energy of desorption, E_d , which decreases with increasing coverage. This is reasonable since as the CO overlayer compresses the repulsive forces between CO molecules will increase yielding a decrease in E_d . Following Readhead¹⁹ and assuming first order desorption kinetics and a pre-exponential factor of 10^{13} sec^{-1} a value of 31 kcal/mole is calculated for E_d at a CO exposure of 5L. The high temperature desorption peak seen on the Rh stepped surfaces is due to dissociated CO. This peak was not detected in either the CO or CO₂ TDS spectra on Rh(111) but was reported for CO desorption from Rh foils⁵ and Re.^{20,21} The evidence for dissociation of CO on the Rh stepped surfaces is the presence of a carbon AES signal after all the molecular CO had desorbed and the desorption of this carbon as CO when excess surface oxygen is present. Carbon was not present on the Rh(111) surface under identical conditions indicating that C-O bond breaking occurs at the step sites. Since no major step effects were discernible by LEED for room temperature CO adsorption, it appears that CO dissociation occurs as the crystal is heated in the TDS experiments. A possible explanation why no high temperature desorption peak is detected after CO adsorption on a clean Rh stepped surface is that oxygen would rather diffuse into the bulk than recombine with carbon and

desorb as CO. In the previous section it was reported that oxygen diffuses preferentially into the bulk.

Comparing the TDS results of Rh to Pt and Ir stepped surfaces different types of step effects are seen. On Pt(111) vicinal surfaces^{9,16} there is, in addition to the desorption peak seen on Pt(111), a resolvable high temperature shoulder due to stronger binding of molecular CO at the step sites. On Ir(S)-[6(111)x(100)] this shoulder is not resolved, but there is a definite tailing on the high temperature side of the main desorption peak. On the Pt and Ir stepped surfaces no evidence for CO dissociation was seen. Thus, all three metals show step effects, but only rhodium stepped surfaces dissociate CO.

2d. Nitric Oxide

The presence of steps had a major effect on the ordering of NO. NO adsorption produced only ^{one ordered structure} on Rh(S)-[6(111)x(100)] and no ordered structures at room temperature on Rh(331). This is in contrast to Rh(111) where two ordered structures were formed by NO adsorption.¹ Exposing the Rh(S)-[6(111)x(100)] surface to NO at 25°C initially resulted in complex streaking in the LEED pattern. Further NO exposure caused the streaking to coalesce into a LEED pattern from a (2x2) structure on the (111) terraces. The extra diffraction spots were split by the step periodicity and are larger than those found on the (111) surface. NO adsorption on Rh(331) at 25°C was disordered producing only and increased background intensity in the LEED pattern. Half order streaks and the LEED pattern in Figure 11a formed as the (331) surface was flashed to 500°C then cooled to 100°C in a NO background pressure of 1×10^{-8} torr. The half order streaks formed at 500°C then transformed into a $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ structure upon cooling to 100°C. The real space unit cell of the $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ structure is shown in

Figure 11b. The half order streaks were also observed when a disordered layer of NO was flashed to 500°C in vacuum.

TDS studies detected gases desorbing at masses 28(N₂), 30(NO), 32(O₂) and 44(N₂O). The TDS spectra for N₂, NO and N₂O are shown in Figure 12. The spectra for both stepped surfaces were similar so only the [6(111)x(100)] data is shown. The N₂ spectrum has one dominant peak which occurs at 200°C. The NO spectrum exhibits a first order desorption peak at 175°C with a second peak appearing at 150°C for higher NO exposures. No NO was detected desorbing for exposures less than 1L. The 150°C desorption peak was not detected until the (2x2) structure had formed. The only difference between the TDS spectra of the two Rh stepped surfaces was that the 150°C NO desorption peak was only a very small shoulder on the (331) surface. The oxygen desorption peak from NO adsorption occurred 150°C higher than the oxygen desorption peak from oxygen adsorption. The N₂O spectrum has 2 peaks whose relative intensities change with exposure as shown in Figure 12c.

The (2x2) structure formed on the Rh(S)- [6(111)x(100)] surface is the same as the highest coverage structure formed on the Rh(111) surface.¹ The (2x2) structure has also been seen for NO on Pt(S)- [12(111)x(111)]²² and Pd(111).²³ On Pd(111) and Rh(111) the (2x2)-NO structure has been interpreted as a hexagonal overlayer of NO, similar to the CO case. NO also form a hexagonal overlayer on Ni(111).²⁴ The amount of compression and ordering in the NO overlayer is affected by the step density. On the [6(111)x(100)] surface the full (2x2) structure is still reached although the domain size is smaller than on the (111) surface. On the (331) surface complete compression and ordering could not be attained as shown by the presence of only one peak in the mass 30 TDS spectra and the existence of no ordered LEED patterns at room temperature.

The half order streaks formed from heating the NO overlayer on the (331) surface are due to adsorbed oxygen. The TDS spectra in Figure 12 show that all of the nitrogen containing species have been desorbed by 500°C, so only adsorbed oxygen is present when the streaks form. The same half order streaks were also seen for oxygen adsorbed on the clean (331) surface. The $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ surface structure is formed from the adsorbed oxygen interacting with gaseous NO. Since several different types of adsorbed species could be formed from the interaction of oxygen and NO further studies are needed to determine the identity of this adsorbed species.

The TDS spectra indicate that NO is dissociatively adsorbed at exposures less than 1L and associatively adsorbed above 1L. The desorption peaks correlate with the type of NO adsorption that is occurring. The high temperature N₂ and N₂O desorption peaks result from dissociative adsorption and reach their maximum height by 1L. As associative adsorption begins the NO and low temperature N₂ and N₂O desorption peaks appear. N₂ desorption is detected for both types adsorption, the low temperature peak from the NO dissociating as the crystal is heated and the high temperature peak from the NO dissociating upon adsorption. The NO desorption peaks appear with the onset of associative adsorption and follow first order desorption kinetics. Assuming a pre-exponential factor of 10¹³ sec⁻¹ yields values of 24.5 and 26 kcal/mole for the E_d's of the 150 and 175°C NO desorption peaks. The dissociative adsorption of NO at low exposures followed by associative adsorption at higher exposures has been observed on other surfaces. On Rh(110),² the crossover to associative adsorption is at 0.5L, while on Ni(111),²⁴ the crossover occurs at 6L. For NO adsorbed on Ru(10 $\bar{1}$ 0) at 90°C the crossover is at 5L.²⁵ Dissociative and associative NO adsorption

have been detected on Ir(111) and (100).²⁶ Only associative adsorption has been detected on Pt(S)-[12(111)x(111)]²² and Pd(111).²³ Thus these six metals can be separated into two groups. One group (Pt and Pd) where NO always adsorbs associatively and another group (Rh, Ru, Ir and Ni) where dissociative adsorption occurs at low NO exposures and associative adsorption at higher NO exposures.

2e. Ethylene and Acetylene

The ordering of ethylene and acetylene were markedly affected by the steps present on the two Rh surfaces. Adsorbing C_2H_4 and C_2H_2 at 25°C produced no ordered structures on the [6(111)x(100)] surface and a $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ structure on the (331) surface. On the [6(111)x(100)] surface two spots near the $(\sqrt{3}x\sqrt{3})R30^\circ$ position were seen, but these spots were diffuse and streaked. The diffraction spots of the $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ hydrocarbon structures were larger than the spots in the $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ structure seen during NO adsorption. The hydrocarbon LEED patterns irreversibly disordered when heated above 150°C in vacuum. By 150°C the hydrocarbons had begun decomposing with H_2 the major gas detected desorbing. The TDS spectra for H_2 desorption after adsorbing C_2H_4 on the [6(111)x(100)] surface at 25°C are shown in Figure 13. The H_2 desorption spectra from acetylene adsorption on both stepped surfaces and ethylene on the (331) surface were the same as the spectra shown in Figure 13. The amount of C_2H_4 desorbed from C_2H_4 adsorption was less than 1% of the desorbed H_2 . The C_2H_4 desorbed at 100°C. No C_2H_2 could be detected desorbing after C_2H_2 adsorption.

After all the hydrogen had desorbed (~550°C) AES showed that carbon was still present on the surface. By heating the crystal to 900°C this surface carbon dissolved into the bulk and further hydrocarbon adsorptions could be

carried out. After several cycles of hydrocarbon adsorption and heating to 900°C the near surface region became saturated with carbon and this resulted in the appearance of new surface structures. These structures will be discussed in the next section.

C₂H₄ and C₂H₂ were the only two molecules in this study that did not form ordered structures on the [6(111)x(100)] surface. These hydrocarbons formed ordered C(4x2) surface structures on Rh(111).¹ The first two spots seen on Rh(111) when the C(4x2) structure was forming were in the same location as the diffuse spots observed from C₂H₄ adsorption on the [6(111)x(100)] surface. So a C(4x2) structure was beginning to form on the terraces, but apparently never fully developed due to the presence of the steps. Poorly ordered (2x2) structures have been seen for C₂H₄ and C₂H₂ adsorption on Ir(S)-[6(111)x(100)]⁸ and C₂H₄ adsorption on Pt(S)-[6(111)x(100)]^{15,27}. The unit cell of Rh(331)-- $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ hydrocarbon structure is 75% larger than the primitive unit cell of the C(4x2) structure, indicating the step periodicity influences the arrangement of the hydrocarbons on the (331) surface.

The TDS spectra from C₂H₄ and C₂H₂ adsorption on the stepped surfaces is similar to the spectra for Rh(111) and Ir(S)-[6(111)x(100)]⁸. Due to the similar chemisorption properties of C₂H₄ and C₂H₂ it is likely that room temperature adsorption of these hydrocarbons yields the same adsorbed species.

2f. Carbon

Carbon structures on the two stepped surfaces were obtained by heating the crystal at 800°C in a C₂H₄ pressure of 5x10⁻⁷ torr for 5 to 10 minutes. The behavior of the two stepped surfaces under these conditions

were markedly different. The $[6(111)\times(100)]$ surface faceted into large domains of (111) and (100) orientation. The faceting is accompanied by an increased background intensity in the LEED pattern and the formation of a (12x12) coincident lattice structure on the (111) facets. This (12x12) coincident lattice has been seen for carbon on Rh(111) and is due to the formation of the graphite basal plane on the rhodium surface.¹

The (331) surface was stable when heated in C_2H_4 and a segmented carbon ring was formed from C_2H_4 decomposition. LEED patterns of the carbon ring are shown in Figure 14. The segmented carbon ring indicates the existence of a partially disordered graphite overlayer on the surface. The (0,0) beam of the carbon ring lies 22° away from the (331) (0,0) beam in a direction perpendicular to the step edges. The orientation difference between the (111) and (331) planes is 22° , indicating that the graphite overlayer is formed on the (111) terraces. Several carbon structures have been observed for C_2H_4 decomposition on the Pt(S)- $[6(111)\times(100)]$ surface^{27,28} while no ordered carbon structures were seen on the Ir(S)- $[6(111)\times(100)]$ surface⁸. Carbon deposition also caused the Pt(S)- $[6(111)\times(100)]$ surface to facet into large domains of (111) orientation²⁸.

Carbon was not detected desorbing from the surface, but as noted above carbon could be dissolved in the bulk by heating the crystal to $900^\circ C$. To remove large amounts of carbon the crystal had to be heated in oxygen (1×10^{-6} torr of O_2 at $900^\circ C$). This led to a regeneration of the clean stepped surfaces.

Summary

The chemisorption properties of H_2 , O_2 , CO, CO_2 , NO, C_2H_4 , C_2H_2 and carbon have been investigated on the Rh(S)- $[6(111)\times(100)]$ and (331) surfaces

by LEED, TDS and AES. All the gases readily adsorbed on the rhodium surfaces and several ordered surface structures were observed. Many of the chemisorption properties were markedly influenced by the presence of steps on the high step density (40%) Rh(331) crystal face while the effects due to steps were minimal on the low step density (17%) Rh(S)-[6(111)x(100)] surface. Thus, the influence of steps on the rhodium surface chemistry increases with step density, Rh(111)<Rh(S)-[6(111)x(100)]<Rh(331).

The most important step effect was the dissociation of adsorbed CO by both rhodium stepped surfaces. The stepped surfaces also affected the adsorbate ordering. On Rh(S)-[6(111)x(100)] long range ordering was decreased while on Rh(331) several new adsorbate unit cells were observed. Both dissociative and associative NO adsorption occurred on the rhodium surfaces, with the changeover from dissociative to associative adsorption occurring at 1L. The similar chemisorption properties of C₂H₄ and C₂H₂ indicate that the adsorption of these hydrocarbons at 25°C produce the same surface species.

Comparison of our studies on rhodium to the reported results on stepped iridium^{8,13} and platinum^{9,10,14,15,16,22,27,28} show that the chemical effects of steps during the chemisorption of small molecules increase in the order Rh<Ir<Pt. The important exception is CO, since its dissociation was only detected on the stepped rhodium surfaces. The differences detected between chemisorption on rhodium, iridium and platinum stepped surfaces is in contrast to the very similar chemisorption properties of these small molecules on the (111) crystal faces of these metals.¹

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TABLE 1.

Surface Structures of Chemisorbed Small Molecules
on the (111), [6(111)x(100)] and (331) rhodium surfaces

Gas	Rh(111) ^a	Rh(S)-[6(111)x(100)] ^b	Rh(331) ^c
H ₂	(1x1) or disordered	(1x1) or disordered	(1x1) or disordered
O ₂	(2x2)	(2x2)	2(1d) $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ $\begin{pmatrix} 1 & 2 \\ 7 & -1 \end{pmatrix}$
CO, CO ₂	($\sqrt{3} \times \sqrt{3}$)R30° split (2x2) (2x2)	($\sqrt{3} \times \sqrt{3}$)R30° (2x2)	$\begin{pmatrix} 1 & 2 \\ 5 & -1 \end{pmatrix}$ $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ "hexagonal"
NO	C(4x2) (2x2)	(2x2)	disordered
C ₂ H ₄ , C ₂ H ₂	C(4x2)	disordered	$\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$
C	(8x8) (2x2)R30° ($\sqrt{19} \times \sqrt{19}$)R23.4° (2 $\sqrt{3} \times 2\sqrt{3}$)R30° (12x12)	carbon covered Rh surface facets to (111) and (100) planes	graphite overlayer

a) From reference (1).

b) Structures indexed with respect to (111) terraces.

c) Structures indexed with respect to (331) unit cell vectors.

TABLE 2.

Surface Structures of Chemisorbed Small
Molecules on the $[6(111) \times (100)]$ Surfaces of
Rhodium, Iridium and Platinum

Gas	Rh(S) - $[6(111) \times (100)]$	Ir(S) - $[6(111) \times (100)]$	Pt(S) - $[6(111) \times (100)]$
H ₂	(1x1) or disordered	(1x1) or disordered [8]	2(1d) [15]
O ₂	(2x2)	(2x1) [13]	2(1d) [15]
CO	$(\sqrt{3} \times \sqrt{3}) R30^\circ$ (2x2)	disordered [13]	disordered [15]
CO ₂	$(\sqrt{3} \times \sqrt{3}) R30^\circ$ (2x2)		
NO	(2x2)		
C ₂ H ₄	disordered	(2x2) [8]	(2x2) [27]
C ₂ H ₂	disordered	(2x2) [8]	
C	carbon covered Rh surface facets to (111) and (100) planes	disordered [8]	$\begin{pmatrix} 3 & 2 \\ -2 & 5 \end{pmatrix}$ [27] $\begin{pmatrix} 6 & 1 \\ -1 & 7 \end{pmatrix}$ [27] $(\sqrt{19} \times \sqrt{19}) - R23.4^\circ - [28]$ $(\sqrt{13} \times \sqrt{13}) - R13.9^\circ - [28]$ $(\sqrt{39} \times \sqrt{39}) - R16.1^\circ - [28]$

Figure Captions

Figure 1. LEED patterns and real space models of the clean rhodium stepped surfaces. Cross hatched circles represent step atoms and the unit cells of the (755), (331) and step planes have been drawn in. Both surfaces have (111) terrace planes.

(a) $\text{Rh}(755) \leftrightarrow \text{Rh}(\text{S}) - [6(111) \times (100)]$, 90eV;

(b) $\text{Rh}(331) \leftrightarrow \text{Rh}(\text{S}) - [3(111) \times (111)]$, 139eV.

Figure 2. AES spectrum of the clean rhodium stepped surfaces shown in Figure 1.

Figure 3. TDS spectra obtained from adsorbing 0.01L to 1L of hydrogen at 0°C on Rh(331).

Figure 4. LEED patterns formed from oxygen adsorption on Rh(S)-[6(111)x(100)]. (a) clean Rh(S)-[6(111)x(100)] at 90eV; (b) (2x2) structure on Rh(S)-[6(111)x(100)] at 65eV; (c) (2x2) structure on Rh(S)-[12(111)x2(100)] at 56eV; (d) (2x2) structure on Rh(111) facets at 52eV.

Figure 5. LEED patterns formed from oxygen adsorption on Rh(331). (a) clean Rh(331) at 93eV; (b) 2(1d) structure at 68.5eV; (c) $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ structure at 46eV; (d) $\begin{pmatrix} 1 & 2 \\ 7 & -1 \end{pmatrix}$ structure forming at 66eV; (e) fully developed $\begin{pmatrix} 1 & 2 \\ 7 & -1 \end{pmatrix}$ structure at 53eV; (f) $\begin{pmatrix} \frac{1}{2} & 1 \\ 2 & 0 \end{pmatrix}$ structure at 43.5eV; (g) faceted surface at 33.5eV.

Figure 6. Real space unit cells of the oxygen surface structures on Rh(331). (a) $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$; (b) $\begin{pmatrix} 1 & 2 \\ 7 & -1 \end{pmatrix}$; (c) $\begin{pmatrix} \frac{1}{2} & 1 \\ 2 & 0 \end{pmatrix}$. A and B are the Rh(331) unit cell vectors.

Figure 7. TDS spectra from oxygen adsorption on (a) Rh(S)-[6(111)x(100)] and (b) Rh(331).

Figure 8. LEED patterns formed from CO adsorption on Rh(331).
 (a) $\begin{pmatrix} 1 & 2 \\ 3 & -1 \end{pmatrix}$ structure at 25.5eV; (b) $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$ structure at 82eV;
 (c) hexagonal CO overlayer at 54eV. (d) Schematic of LEED pattern (c) where ● are diffraction spots from the rhodium lattice, o are diffraction spots from the CO overlayer and ■ are the multiple diffraction spots from both the rhodium and CO lattices.

Figure 9. Real space models for the CO surface structures on Rh(331). The cross hatched circles represent CO molecules, the open circles are the rhodium atoms, A and B are the Rh(331) unit cell vectors and the arrows show the direction of compression. The CO molecule diameter is $3.2\overset{\circ}{\text{Å}}$ and the rhodium nearest neighbor distance is $2.69\overset{\circ}{\text{Å}}$. (a) $\begin{pmatrix} 1 & 2 \\ 3 & -1 \end{pmatrix}$; (b) $\begin{pmatrix} 1 & 2 \\ 2 & 0 \end{pmatrix}$; (c) one domain of hexagonal overlayer; (d) second domain of hexagonal overlayer.

Figure 10. TDS spectra from adsorption of (a) CO on Rh(331), (b) CO₂ on Rh(S)-[6(111)x(100)] and (c) CO₂ on Rh(331). The only species detected desorbing in all three cases was CO.

Figure 11. (a) LEED pattern of Rh(331)- $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ structure at 44eV.
(b) Real space unit cell of $\begin{pmatrix} -1 & 1 \\ 3 & 0 \end{pmatrix}$ structure. A and B are Rh(331) unit cell vectors.

Figure 12. TDS spectra obtained from NO adsorption on Rh(S)-[6(111)x(100)] for (a) N₂ desorption, (b) NO desorption and (c) N₂O desorption.

Figure 13. (a) Hydrogen desorption from C₂H₄ adsorption on Rh(S)-[6(111)x(100)].

Figure 14. LEED patterns of segmented carbon ring on Rh(331) at 47.5eV.

(a) Rh (755) $\leftrightarrow$ Rh (S) - [6 (111) x (100)]

(b) Rh (331) $\leftrightarrow$ Rh (S) - [3 (111) x (111)]

XBB 786-7517

Fig. 1

XBL 786-5 202

Fig.2

XBL 7811-12930

Fig.3

Oxygen LEED Patterns on Rh(S)-[6(111)x(100)]

a

b

c

d

XBB 786-7516

Fig. 4

Oxygen LEED Patterns on Rh(331)

Fig. 5

XBB 786-7518

OXYGEN SURFACE STRUCTURES ON Rh(331)

XBL 786-9266

Fig.6

XBL 7811-12932

Fig.7

CO LEED Patterns on Rh(331)

a

b

c

d

Fig. 8

CO SURFACE STRUCTURES ON Rh(331)

XBL 786-5201

Fig.9

XBL 786-5203

Fig.10

$$\text{Rh}(331) - \left| \begin{smallmatrix} -1 & 1 \\ 3 & 0 \end{smallmatrix} \right|$$

a

b

Fig. 11

NO/Rh(S) - [6(III) x (100)]

XBL 786-5207

Fig.12

XBL 7811-12931

Fig.13

Carbon rings on Rh(331)

-42-

XBB 786-7514

Fig. 14

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