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The interaction of carbon monoxide and hydrogen with the (1010) face of ruthenium

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The interaction of carbon monoxide and hydrogen with the $(10\bar{1}0)$ face of ruthenium

by

Terry Lee Tomcsik

A Dissertation Submitted to the
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INTRODUCTION

A significant challenge to the scientific community for many years has been a better utilization of the energy resources available. Coal, because of its relative abundance, is receiving an increasing amount of attention as a fuel source. An integral part of the process of changing coal into usable hydrocarbons, e.g., gasoline, is the process of converting carbon monoxide and hydrogen into hydrocarbons. This conversion is greatly aided by specific catalysts.

The simplest, hydrocarbon-producing interaction of carbon monoxide and hydrogen is methanation, i.e., $CO + 3H_2 \rightarrow CH_4 + H_2O$. An understanding of methanation is vital for the maximum yield of hydrocarbons in the interaction of carbon monoxide and hydrogen over certain catalysts.

As early as 1902, Sabatier and Senderens [1] showed that methane could be formed by the hydrogenation of both carbon monoxide and carbon dioxide over nickel. In the 1920's Fischer, Tropsch, and Dilthey [2] compared the methanation properties of various metals at temperatures up to 800 ^{o}C. The decreasing order of methanation activity was Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, Ag. Thus by 1925 all of the metals now considered active for methanation of carbon oxides had been identified [3].

Ruthenium is such a good methanation catalyst it will produce methane from carbon monoxide and hydrogen at about 100 ^{o}C and a total pressure of less than 100 torr (1 torr = 1 mm of Hg) [4] . Ruthenium will also form high molecular weight paraffinic waxes at low temperatures and high pressures [5] . Even at atmospheric conditions ruthenium gives the highest average molecular weight distribution of hydrocarbons and the largest C_5^+ fraction [6] . Therefore ruthenium is an excellent methanation and hydrocarbon forming catalyst over which to study the interaction of carbon monoxide and hydrogen. It is also an excellent catalyst for studying methanation at low pressure and temperature.

Ultrahigh vacuum techniques have been used extensively in the past few decades to study catalytic processes. The principal reason for using an ultrahigh vacuum is control of surface composition, particularly impurities. In addition, the principal surface sensitive techniques for determining structure and composition of surface layers require an ultrahigh vacuum. Therefore these ultrahigh vacuum surface sensitive techniques will provide information about the interaction of carbon monoxide and hydrogen with ruthenium, since this interaction occurs at low temperatures and pressures.

My primary goal in this study was to use ultrahigh vacuum techniques to find out how carbon monoxide, hydrogen, and both together interacted with ruthenium at different temperatures and pressures and to use this and other information to infer possible mechanisms for the methanation reaction. To study the species formed on the ruthenium surface by carbon monoxide, hydrogen, and both together, I utilized low energy electron diffraction (LEED) to give information about the steady-state surface structures formed by these surface species and Auger electron spectroscopy (AES) to identify their composition. Results were obtained at reactant partial pressures in the range of 10^{-9} to 10^{-6} torr and substrate temperatures from -135 °C to 200 °C. The interaction of molecular oxygen with the surface was also examined for comparison purposes.

REVIEW OF PREVIOUS RESEARCH ON THE INTERACTION OF CARBON MONOXIDE AND HYDROGEN WITH RUTHENIUM

Introduction

The interaction of carbon monoxide and hydrogen with ruthenium is studied primarily because of interest in hydrocarbon formation from this interaction. Energy sources such as coal, residues, oil shale, and tar sands can be gasified with steam or oxygen to produce a gas containing large quantities of carbon monoxide and hydrogen. Once methane is removed from this carbon monoxide-hydrogen mixture, it is purified to remove sulfur poison and then allowed to flow over a catalyst to produce a variety of organic products. Methanation is the formation of methane from this carbon monoxide-hydrogen mixture. The Fischer-Tropsch synthesis reaction is the formation of hydrocarbons other than methane from this carbon monoxide-hydrogen mixture [7]. Of the many different carbon monoxide-hydrogen reactions that can occur, ruthenium is used primarily to form high molecular weight paraffinic waxes at low temperatures and very high pressures [8,9].

To understand long chain hydrocarbon production one must first understand methane production on ruthenium. The study of methanation over ruthenium can be divided into two categories. There are the studies that have been done in reactor systems using mostly ruthenium supported by alumina, Al_2O_3, and there have been the studies done on single crystals, field emission and field ion tips, and films of ruthenium, in ultrahigh vacuum systems. I will discuss the reactor system results first.

Reactor System Results

Pichler [5] has investigated ruthenium catalysts over a wide range of synthesis pressures. He found that hydrogen-carbon monoxide mixtures give only methane at 300 °C and atmospheric pressure. At higher pressures the reaction initiated at lower temperature, but higher molecular weight products formed with increasing pressure. This work had originally been intended as a possible route to carbohydrates, but no oxygenated products were found.

Catalytic activity remained unchanged over a period of 6 months for an experiment conducted at 100 atmospheres and 195 °C. However, traces of sulfur compounds rapidly deactivated the ruthenium catalyst.

The U.S. Bureau of Mines, in its search for catalysts capable of producing liquid and gaseous fuels, examined a ruthenium catalyst using hydrogen-carbon monoxide feedstocks [10]. A catalyst containing 0.5 weight % ruthenium on aluminum was tested over the range of 1 to 21.4 atmospheres at about 225 °C using various H_2/CO ratios. The H_2/CO ratio profoundly influenced the product distribution; low ratios invariably gave large amounts of high molecular weight products while relatively more methane formed using a higher H_2/CO ratio. Also, as Pichler [5] had found, lower pressure favored methane production.

Experimentally it was found that high carbon monoxide pressures inhibit catalyst activity. For example, the use of 1 to 1 synthesis gas (hydrogen and carbon monoxide) always caused a temporary activity loss, but activity was soon regained upon return to higher H_2/CO ratios.

In a study of the interaction of H_2 and CO on various Group VIII metals, McKee [4] has shown the unique behavior of ruthenium in the adsorption of these two gases. Carbon monoxide was much more strongly chemisorbed on platinum, rhodium, and iridium than on ruthenium, and the adsorption of hydrogen on ruthenium was enhanced by the presence of carbon monoxide. At temperatures above 100 °C, methane was produced at a total pressure of less than 100 torr over ruthenium, whereas only trace amounts were found with rhodium or iridium and none with platinum as catalysts.

Vannice [6,11] found, using a differential flow microreactor operated at steady state conditions, that alumina supported ruthenium was the most active methanation catalyst of the Group VIII metals. He also concluded from his kinetic measurements that weakening the metal-carbon monoxide bond appears to result in higher activity.

Rabo et al. [12] have used a pulse reactor system to study the reaction of carbon monoxide and hydrogen with ruthenium at 300 °C and room temperature. The ruthenium was supported on a silica gel, SiO_2. They reported that carbon monoxide dissociated at 300 °C and hydrogen produced methane readily from the dissociated carbon monoxide. At room temperature they reported that the carbon monoxide did not dissociate and hydrogen did not produce methane but was readily adsorbed by the surface.

Bell and Davydov [13] and Ekerdt et al. [14] have done reactor work involving infrared spectroscopy that is of considerable interest. They studied carbon monoxide adsorbed on a silica-supported ruthenium catalyst and inferred from infrared data that carbon monoxide bonded linearly to ruthenium. They also passed hydrogen and carbon monoxide mixtures over silica-supported ruthenium at a total pressure of 1 atmosphere and H_2/CO ratios between 2 and 20. Methane was observed as the primary product. Small concentrations of ethane were detected as well, and the selectivity towards ethane increased rapidly as the H_2/CO ratio approached 2. Infrared spectra recorded under reaction conditions showed only a single band associated with chemisorbed carbon monoxide. The position of the band shifted from 2030 to 2010 cm^{-1} as the H_2/CO ratio was increased. This trend suggested that adsorbed hydrogen atoms contribute electrons to surface ruthenium atoms, thereby enhancing the back donation of electrons to adsorbed carbon monoxide. Back donation was also observed from carbon atoms produced on the ruthenium surface through dissociation of carbon monoxide.

Studies of the kinetics of methane synthesis showed that the rate could be correlated to the ratio of H_2/CO concentrations over the catalyst. However, it was observed that the catalyst activity declined with time, the decline being most rapid for reaction mixtures in which H_2/CO was low. Reactivation of the catalyst could be achieved by heating it in hydrogen.

Bell's reactor results suggested that under reaction conditions the catalyst surface was covered almost exclusively by carbon monoxide and that hydrogen competed with carbon monoxide for the remaining vacant sites. The adsorption of hydrogen promoted a weakening of the carbon monoxide bond and may have facilitated carbon monoxide dissociation. That carbon monoxide dissociation occurred was evident from the large amounts of carbon present on the surface, and it appeared that this carbon played an active role in the synthesis of methane. Oligomerization of carbon atoms to form graphite was a competing reaction and was the most likely cause of catalyst deactivation.

Ultrahigh Vacuum System Results

The studies done in ultrahigh vacuum have been on different types of ruthenium surfaces and have used many different types of instrumental techniques.

Melmed [15,16] characterized the clean ruthenium surface using field ion microscopy [17]. Field emission microscopy [17] has been used extensively to study carbon monoxide, hydrogen, and both together adsorbed on ruthenium. In field emission microscopy work function changes indicate how the adsorbate and substrate interact. Increases and decreases in the work function indicate negative outward and positive outward dipoles perpendicular to the surface, respectively, in adsorbed molecules. An electronegative state is a negative outward dipole, while an electropositive state is a positive outward dipole [18]. If the adsorbed atoms are ionized and transfer electrons into the solid surface, the work function decreases. Conversely, the formation of adsorbed negative ions increases the work function [18].

Klein [19] did one of the first field emission studies of carbon monoxide adsorbed on ruthenium. He concluded that carbon monoxide is weakly bound to ruthenium and that surface migration of carbon monoxide on ruthenium can take place at 125 K. He also observed that carbon monoxide is desorbed at 225 K, and most of the carbon monoxide is off the surface after ruthenium is heated to 400 K. He concluded from his heating curve that two electronegative states are desorbed in the ranges 150 to 350 K and 350 to 500 K, apart from the evidence of the desorption of an electropositive state around 220 K.

Charkabortty and Grenga [20] did a field ion and field emission study of adsorption and desorption of carbon monoxide on several crystal faces of ruthenium. They reported evidence of an electropositive state on the low index $(10\bar{1}1)$ and $(10\bar{1}0)$ planes, and an electronegative state as well as physisorbed carbon monoxide on all planes, from field desorption measurements. Substrate and/or adsorbate rearrangements also occurred on all regions. While the M-CO bond energy was found to be less on ruthenium than that reported for tungsten, the ratio of the M-CO to M-M bond energy was found to be greater in the case of ruthenium.

Bouwman and Sachtler [21] determined work functions for carbon monoxide adsorbed on ruthenium films by a photoelectric technique; the work function change for a full carbon monoxide layer at 300 K they reported agreed with that found by Kraemer and Menzel [22] in their field emission study of carbon monoxide adsorbed and desorbed from ruthenium. Kraemer and Menzel [22] also found that carbon monoxide adsorbed with a high initial sticking coefficient, of the order of 0.5, on ruthenium field emitters at 300 K, and carbon monoxide increased the work function by 1.4 to 1.6 eV. Desorption of carbon monoxide began immediately above room temperature, showing that the high coverage part was reversibly bound, and was completed at about 550 K. The results suggested that an electropositive state was desorbed up to about 220 K, and a rather broad range of states desorbed between 300 K and 500 K. An estimate gave a binding energy of 28 Kcal/mole for the more strongly bound part of the layer in good agreement with isoteric and kinetic measurements on the close-packed (0001) face [23] .

Madey and Menzel [23] adsorbed carbon monoxide on ruthenium (0001) at temperatures $\geq$ 300 K. They used a combination of techniques: low energy electron diffraction (LEED)/Auger spectroscopy [24,25] , Kelvin probe contact potential changes, and flash desorption mass spectrometry [26] . They found two electronegative states for carbon monoxide desorbing at 390 K and 450 K by flash desorption. At low doses of carbon monoxide, i.e. $<$2L, the 390 K flash desorption peak did not appear. Grant and Haas [27] were the first to study carbon monoxide adsorbed on ruthenium with LEED. They observed that carbon monoxide formed a 2 X 2 LEED structure on ruthenium (0001). Madey and Menzel [23] showed that carbon monoxide adsorption is reversible at temperatures and pressures as high as 700 K and 10^{-4} torr, respectively. Madey and Menzel also came to the conclusion that work function changes due to gas adsorption on close packed planes of metal, i.e. ruthenium (0001), are frequently smaller than those determined on rougher surfaces. They also found that carbon monoxide appears to have a sticking probability of ~ 0.5 for low carbon monoxide coverage on ruthenium. This sticking probability decreased rapidly with increasing carbon monoxide coverage.

Madey and Menzel [23] also showed that the LEED beam causes carbon monoxide to change its state on ruthenium, possibly dissociating. Reed et al. [28] studied the adsorption of carbon monoxide on ruthenium ($10\bar{1}1$) and concluded the LEED beam was dissociating carbon monoxide.

The study of carbon monoxide on ruthenium has been pursued by such techniques as: x-ray photoelectron spectroscopy (XPS) [29], x-ray excited Auger spectroscopy (XAES) [30], XPS satellites [31], and ultraviolet photoemission spectroscopy (UPS) [32]. In a study of carbon monoxide adsorption on ruthenium (0001) by Fuggle et al. [32] using these techniques plus temperature programmed desorption, it was concluded that a LEED beam will dissociate carbon monoxide adsorbed on ruthenium (0001) at room temperature and pressures below 10^{-5} torr. They also state that at room temperature carbon monoxide adsorbs molecularly onto ruthenium (0001) surfaces in an adsorption layer similar to the molecular carbon monoxide states found on other metals. Thermal desorption spectroscopy is the same thing as temperature programmed desorption and flash desorption mass spectrometry.

Ku et al. [33] studied the adsorption of carbon monoxide on ruthenium $(10\bar{1}0)$. They found that carbon monoxide desorbs at ~ 130 °C and ~ 240 °C by thermal desorption spectroscopy. They calculated the desorption energies to be 24.4 Kcal/mole and 30.1 Kcal/mole, respectively, which are in good agreement with previous results.

Kraemer and Menzel [34] studied hydrogen adsorption on ruthenium using field emission microscopy. They found that hydrogen adsorbs on ruthenium field emitters with a high initial sticking coefficient of about 0.5 at both 100 K and 300 K. Hydrogen adsorption increased the work function 0.65 eV at 100 K and 0.4 eV at 300 K, indicating formation of fairly strong negative outward dipoles. Thermal desorption of the layer was complete at about 360 K. Adsorption energies were found to drop from 24 Kcal/mole at 0.25 to about 15 Kcal/mole for 0.9 of the room temperature coverage. The binding energy for the layer produced below 250 K was much lower, 7-12 Kcal/mole.

A conversion seemed to take place in the layer produced at 100 K when heating it above 260 K. It appeared possible that the layer was essentially molecular at low temperatures and atomic at higher temperatures. Both states are electronegative however. The electronegative state would tend to indicate atomic hydrogen.

Goodman et al. [35] also found that hydrogen desorbed at 300 K with an energy of 17.5 Kcal/mole by temperature programmed desorption from ruthenium (11$\bar{2}$0). They also determined, from isotopic mixing experiments of hydrogen and deuterium with temperature programmed desorption, that hydrogen was in the atomic state when it desorbs at 300 K after being adsorbed at 300 K. They also found that hydrogen desorption from ruthenium (11$\bar{2}$0) following adsorption at 80 K indicated that desorption proceeded via second order kinetics at higher hydrogen coverages, which is also consistent with atomic state chemisorption.

Kraemer and Menzel [36] studied the interaction of carbon monoxide and hydrogen on ruthenium with field emission microscopy. They found that a saturated carbon monoxide layer on ruthenium at 300 K did not adsorb any hydrogen. A partially filled carbon monoxide layer adsorbed amounts of hydrogen approximately proportional to the free surface. They also concluded that a saturated hydrogen layer on ruthenium at 300 K was very effectively displaced by carbon monoxide. The displacement probability was not much smaller than the sticking coefficient of carbon monoxide on clean ruthenium.

During displacement of hydrogen by carbon monoxide, a mixed layer was formed which was believed to contain complexes consisting of carbon monoxide and hydrogen. These complexes seemed to suffer a conversion upon heating to above 400 K, which made them more strongly bound than either carbon monoxide or hydrogen alone, and changed their dipole moments. Reactions of carbon monoxide and hydrogen on ruthenium appeared to proceed only at temperatures which destroyed the full carbon monoxide layer, and were most likely to be enhanced by the formation of the more strongly bound complexes. The temperatures at which these reactions occurred, 400 K - 500 K, are those used in practical Fischer-Tropsch catalysis on ruthenium catalysts.

Goodman et al. [35] studied the carbon monoxide and hydrogen interaction on ruthenium ($11\bar{2}0$) by temperature programmed desorption methods. They concluded that coadsorption of hydrogen and carbon monoxide at 300 K resulted in an increase in the hydrogen desorption energy in comparison to desorption from a pure hydrogen layer. This they felt showed that hydrogen and carbon monoxide were interacting. No detectable methane was produced when the ruthenium ($11\bar{2}0$) crystal was heated in a 4:1 H_2/CO mixture at 10^{-3} torr in the temperature range of 300 K - 1400 K.

Ekerdt et al. [14], in thermal desorption spectroscopy experiments used to investigate the chemisorption and reaction of carbon monoxide and hydrogen on ruthenium catalysts, established that carbon monoxide adsorbed in two states with binding energies of 17 and 25 Kcal/mole, while hydrogen chemisorbed in a single state with a binding energy of 28 Kcal/mole. During the desorption of carbon monoxide, a part of the adsorbate dissociated to produce adsorbed carbon atoms. This carbon was removed from the surface by heating in hydrogen.

The formation of H-CO species on the surface has been examined because of interest in intermediates in the interaction of hydrogen and carbon monoxide. Formaldehyde and methanol adsorbed on ruthenium have been studied because of their possible similarity to H-CO intermediates in the hydrogen and carbon monoxide interaction on ruthenium to form methane.

Methenol adsorbed on ruthenium ($11\bar{2}0$) at 120 K and below has been studied by G. B. Fisher et al. [37] using ultraviolet photoemission spectroscopy (UPS). They concluded that chemisorption bonding to the surface was nondissociative, and occurs primarily through lone-pair electrons associated with the oxygen atoms. Heating to $T > 300$ K resulted in decomposition.

G. B. Fisher et al. [38] studied formaldehyde adsorbed at 80 K on ruthenium ($11\bar{2}0$) using UPS and temperature programmed desorption (TPD). They concluded that formaldehyde adsorbed dissociatively on ruthenium ($11\bar{2}0$) at 80 K. TPD and work function data, supported by subtle changes in the UPS spectra, suggested that the formaldehyde-derived surface species included at least some species other than coadsorbed hydrogen and carbon monoxide.

Discussion

In general, the reactor system results indicate that at 225 - 300 °C carbon monoxide-hydrogen mixtures give methane at low pressure and high H_2/CO ratios but long-chain hydrocarbons at high pressures and low H_2/CO ratios. A low H_2/CO ratio inhibits the ruthenium catalyst faster than a high H_2/CO ratio, but the catalyst can be reactivated with hydrogen. Sulfur poisons the catalyst. Ruthenium is the most active group VIII catalyst for methanation and the relative weakness of the carbon monoxide-ruthenium bond is probably an important reason for this.

Rabo et al. [12] claim that carbon monoxide readily dissociates at 300 °C, because they observed carbon dioxide in the effluent when carbon monoxide was passed over ruthenium at 300 °C. They are assuming carbon monoxide is reacting with oxygen on the surface from dissociated carbon monoxide to give carbon dioxide, i.e., $CO + \underset{*}{\underline{O}} \rightarrow CO_2 \uparrow$. However, the carbon dioxide could also be formed by $2CO \rightarrow \underset{*}{\underline{C}} + CO_2 \uparrow$. Therefore formation of carbon dioxide does not mean the carbon monoxide has dissociated. They also observe methane formed from hydrogen reacting with carbon monoxide adsorbed on ruthenium at 300 °C, supposedly dissociated, and no carbon monoxide dissociation or methane formation at room temperature which is all consistent with other results [4].

Rabo et al. [12] observe that hydrogen is taken up by adsorbed carbon monoxide on ruthenium at room temperature in an ambient of greater than 1 atm; McKee [4] also noticed adsorbed carbon monoxide enhancing hydrogen adsorption on ruthenium in an ambient of 100 torr or higher. Bell and Davydov [13] and Ekerdt et al. [14] state that they have conlusively shown that carbon monoxide is linearly bonded to ruthenium. This conclusion is consistent with inorganic chemistry theory [39] and results [40,41], but it has also been shown that carbon monoxide can bridge bond, i.e., $\genfrac{}{}{0pt}{}{\text{Ru}}{\text{Ru}}\!>C = 0$, to ruthenium in metallic clusters [39,42].

The ultrahigh vacuum system results indicate that carbon monoxide has several bonding modes, including possibly dissociation, on ruthenium, and these bonded modes depend on temperature, amount of carbon monoxide, and the ruthenium surface structure. The results also indicate carbon monoxide is mobile on ruthenium above 125 K, completely desorbs by 550 K, and exhibits a sticking coefficient of 0.5 for low doses of carbon monoxide at 300 K.

For hydrogen at least two bonding modes have been observed and it appears that hydrogen is atomically bonded to ruthenium at 80 - 100 K and 300 K. The initial sticking coefficient for hydrogen on ruthenium is high, about 0.5, and hydrogen is completely desorbed from ruthenium at 360 K.

It has been shown that carbon monoxide and hydrogen compete for bonding sites on ruthenium and they do interact to form complexes on ruthenium at 300 K. Neither methanol or formaldehyde adsorption on ruthenium lead to states resembling closely intermediates formed by surface reaction of hydrogen and carbon monoxide. Kraemer and Menzel's [36] more strongly bound complexes formed by heating hydrogen-carbon monoxide mixtures on the ruthenium surface above 400 K, were probably graphitic carbon and surface oxide after the hydrogen had desorbed.

Carbon monoxide and hydrogen interact at low and high pressure and from room temperature up to 300 °C on ruthenium. Carbon monoxide and hydrogen both readily adsorb on ruthenium in several bonding modes depending on temperature and pressure. What is not known is how carbon monoxide and hydrogen interact on ruthenium.

EXPERIMENTAL

Purpose of Experiments

My main objective was to understand how carbon monoxide and hydrogen interact on a ruthenium surface. This surface-adsorbate interaction has not been well resolved in previous results. An understanding of the interaction is necessary for understanding the catalytic function of ruthenium in methanation and Fischer-Tropsch synthesis reactions.

Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) used together can reveal extensive information about how an adsorbate will interact with the substrate surface. I used LEED and AES data for all my conclusions and quadrupole mass spectrometer results to augment these LEED and AES results.

First the carbon monoxide interaction with ruthenium at different temperatures was studied; then the hydrogen interaction with ruthenium at the same temperature was studied. These data were then correlated with data obtained from the interaction of carbon monoxide and hydrogen on ruthenium at the same temperatures. The nature of the carbon monoxide and hydrogen interaction on ruthenium was inferred from these results. The adsorption of oxygen on ruthenium was also studied, mainly for calibrating the Auger oxygen spectra, but also for correlation with the carbon monoxide, hydrogen, and carbon monoxide-hydrogen results.

In order to do a LEED study a single crystalline plane has to be chosen. I chose the $(10\bar{1}0)$ plane of ruthenium because it is a fairly close packed face (8.6×10^{14} atoms/cm^2) and should have a low surface free energy which would indicate good thermal stability to rearrangement or disordering. This $(10\bar{1}0)$ surface has a fairly open structure dominated by troughs that run parallel to the [010] direction. These troughs should play a significant role in adsorption and surface diffusion processes.

Experimental System

The experimental studies were performed in a stainless steel-pyrex ultrahigh vacuum chamber which contained Physical Electronics 4-grid LEED optics and a quadrupole mass spectrometer. The system was pumped with an ion pump, and the base pressure after bakeout was~ 2×10^{-10} torr. The basic system has been described elsewhere [24]; its only significant modification entailed replacing the glass cylinder that housed the LEED electron optics by a stainless steel cylinder with a glass face plate for viewing the LEED electron optics. A description of the Auger electron spectrometer on this system has been given elsewhere [25].

The single crystal ruthenium sample used in this study was cut from a zone refined single crystal supplied by MRC Corporation. It was oriented using Laue x-ray techniques and cut to expose a $(10\bar{1}0)$ plane at its surface. The sample disc was mechanically polished to a mirror finish on both sides. The final thickness was ~ 1.5 mm; the total surface area was 1.1 cm^2.

The sample was spot-welded to a .018" diameter tungsten wire which in turn was welded to the heavier support lead of a glass press seal. The leads of the press seal pass through the top of the system and allow for external electrical connections. The support leads could be immersed in liquid nitrogen which enabled the sample to be cooled to -135 °C. The sample was heated by bombardment with a nominal current, 1 - 50 μA, of 400 eV electrons which were emitted from a thoriated iridium filament suspended directly behind the sample. This technique allowed the sample to be heated to ~ 1150 °C for the purpose of cleaning. Temperatures were measured using a W/Re 5% - W/Re 26% thermocouple (0 °C reference junction) spot-welded to the back of the crystal.

Linde research grade carbon monoxide (99.97% pure) and argon (99.9995% pure) were used without further purification. Oxygen and hydrogen were obtained from Ag and Pd-Ag 25% leak diffusers, respectively.

Procedure

The first requisite, in an ultrahigh vacuum investigation of a catalytic reaction, is a clean surface. Auger spectroscopy on the ruthenium crystal as initially prepared showed that its surface was contaminated with carbon, oxygen, and sulfur. It proved possible to remove the sulfur by heating the crystal to 1200 °C for consecutive thirty minute periods, the oxygen by argon bombarding the crystal, and the carbon by oxygen cleaning the crystal.

The following cleaning regimen was therefore followed before each experiment: oxygen clean to remove the carbon, then argon bombard to remove the oxygen and everything else. The oxygen cleaning regimen consisted of heating the crystal to 1200 °C in 1.5×10^{-6} torr of oxygen for 15 minutes, followed by heating of the crystal to 1200 °C in vacuum for one minute. The crystal was then annealed continuously at 600 °C.

The argon bombarding regimen consisted of bombarding the crystal for 15 minutes with Ar^+ ions and then heating to 1200 °C for 10 minutes. This sequence was repeated several times and then the crystal was annealed at 600 °C. The Ar^+ ions were generated by increasing the pressure in the vacuum chamber to 1×10^{-3} torr with argon, reversing the polarity on the LEED gun anodes, and biasing the sample several hundred volts below ground. The LEED gun was then capable of producing a beam of Ar^+ ions ($\sim 5\,\mu A/cm^2$, 800 eV).

This cleaning regimen produced a clean ruthenium surface as verified by LEED and Auger data. Cleanliness during operation was maintained by continuously heating the ruthenium crystal at 600 °C.

Before starting an experiment, the system ambient pressure was reduced to the 10^{-10} torr range to reduce ambient gas contamination. The pressure was reduced primarily by waiting, outgassing the ion gauge, and outgassing the ruthenium crystal by heating to 1200 °C.

The ruthenium crystal was checked for cleanliness by inspection of LEED patterns and Auger spectra. After numerous Auger spectra and LEED patterns the clean surface parameters were established and were reproduced by LEED and Auger data before each experiment. If the ruthenium crystal was clean, the LEED filament current was turned off to remove the very real possibility of LEED induced changes in the adsorbate on the ruthenium surface.

The temperature of the ruthenium crystal was then established at the desired value. The temperature was established at -135 °C with liquid nitrogen, at 200 °C with a heat lamp, and at 23.5 °C by crystal cooling since the ruthenium is maintained at 600 °C. For the oxygen dose experiments the crystal was heated above 200 °C and allowed to cool below 200 °C before the oxygen was dosed.

Either carbon monoxide, hydrogen, both, or oxygen were dosed for a specified number of Langmuirs (1 Langmuir = 1 X 10^{-6} torr·sec). In the no dose cases 200 seconds were allowed to elapse. 200 seconds was the normal time of a dose. In the experiments where both carbon monoxide and hydrogen were dosed, carbon monoxide was dosed first for the desired number of Langmuirs, 5 minutes elapsed, and then hydrogen was dosed for the desired number of Langmuirs.

Both carbon monoxide and hydrogen from the 10^{-10} torr ambient accumulated on the ruthenium surface while the crystal was approaching 23.5 °C or -135 °C. ~ 0.35 monolayer of carbon monoxide and ~ 0.2 monolayer of hydrogen accumulated. Therefore it made no difference whether carbon monoxide or hydrogen were dosed first in the experiments where both were dosed, since carbon monoxide or hydrogen could never be dosed onto a clean surface at 23.5 °C or -135 °C.

After the dose was stopped, the crystal was maintained in the ambient for 20 minutes with the LEED filament still off to allow structural equilibration of the adsorbed gas without interference from LEED gun electron bombardment.

The LEED filament and emission were turned on and the LEED pattern observed and photographed. Auger spectra were taken after all LEED changes were observed. This finished the experiment and the ruthenium crystal was then cleaned by oxygen cleaning and argon bombardment for the next experiment.

In some of the experiments, the quadrupole mass spectrometer was used to monitor ambient gas changes during the experiment, to help interpret LEED and Auger data from the experiment.

RESULTS

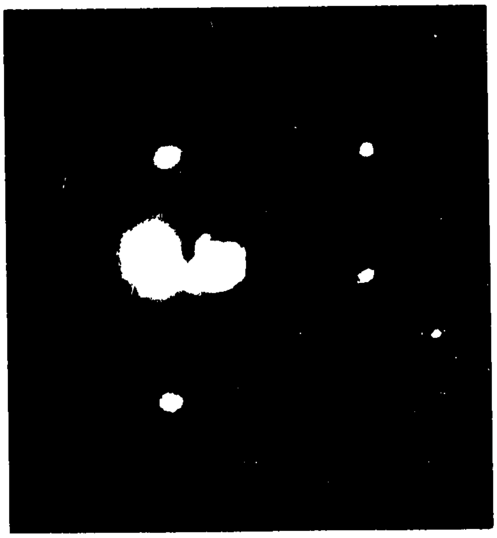
LEED Pattern and Auger Spectrum from Clean Ru(10$\bar{1}$0) Surface

The LEED pattern from the clean Ru(10$\bar{1}$0) surface at a primary beam energy of 38 eV is shown in Figure 1a. The electron beam is approximately 6° off normal incidence. The sample was not positioned at the center of the hemispherical optics; as a result, the LEED beams near the edges of the screen diverged distorting the pattern from the true rectangular symmetry of an hcp (10$\bar{1}$0) plane. The specular beam is masked by visible light from the hot tungsten filament which is reflected off the sample onto the phosphor screen. This light appears as a bright area in the middle of the left side of the photograph. The other bright region is due to the incandescent filament of the LEED electron gun.

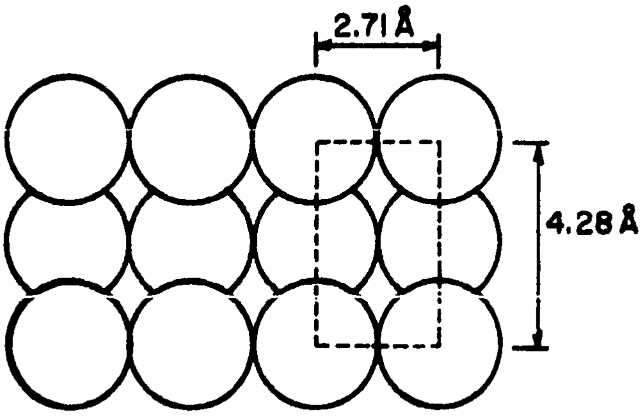
Figure 1b shows the surface unit cell (dotted lines). Figure 1c shows the indexing of the diffraction pattern and the surface unit cell (dotted lines). It should be noted that there is 1 atom per unit cell. The general appearance of the Ru(10$\bar{1}$0) surface is indicated by Figure 1b.

The Auger spectrum of the clean surface is shown in Figure 2. This spectrum was identical to those found by Grant and Haas [27] and Madey et al. [43] for Ru (0001) samples in the Auger electron energy range < 300 eV. In the electron energy range from 300 eV to 500 eV, several small peaks ($\sim$ 2 to 3% of the intensity of the

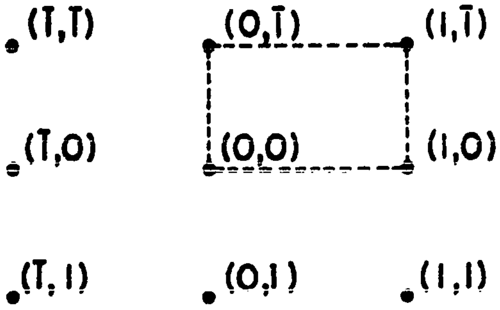
Figure 1. LEED pattern, surface unit cell, and indexing for Ru(10$\bar{1}$0): (a) LEED pattern from the clean surface at 38 eV beam energy, (b) the surface unit cell, and (c) indexing of LEED pattern beams.



(a)

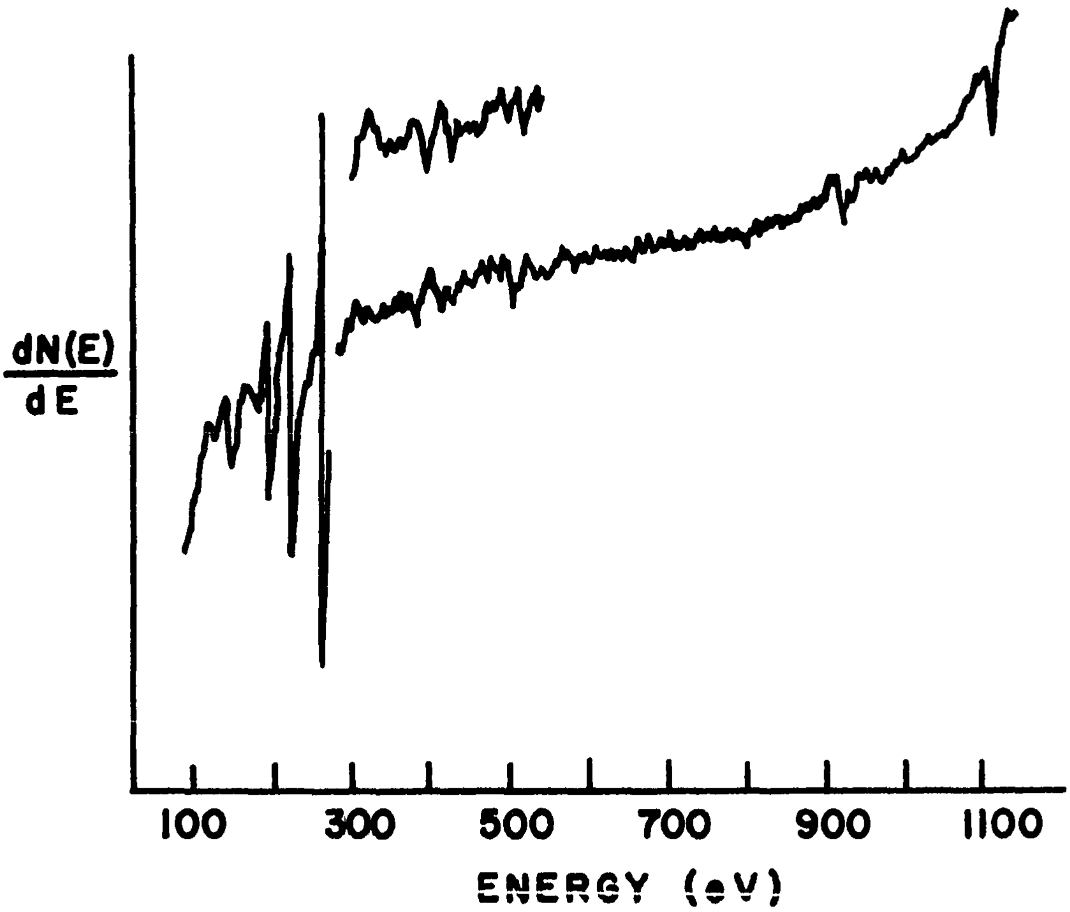


(b)



(c)

Figure 2. Second-derivative Auger spectrum of a clean Ru(10$\bar{1}$0) sample at 500 °C. The insert is a partial spectrum of the same sample at 200 °C. Primary beam energy = 1.4 KeV; beam current = 50 μA; sweep rate = 1.5 eV/s; ac modulation voltage = 2 v (for electron energies below 300 eV) and 4 v (for energies above 300 eV); full scale deflection = 1 X 10^{-10} amperes.


dN(E)
dE
100
300
500
700
900
1100
ENERGY (eV)

Ru_{276} peak) were present. Similar "fine structure" was also observed in the two studies of Ru(0001) samples [27,43], but with peak energies somewhat different from those shown in the insert in Figure 2. There were also features in the spectrum near 950 and 1120 eV.

The dependence of the positions of the features with energies greater than 300 eV on the primary beam energy was examined. It was found that the peaks between 300 and 500 eV were independent of the primary beam energy, but the peaks observed at 950 eV and 1120 eV were linear functions of the primary beam energy. The peak at 1120 eV was found to be a core level ionization edge [25]. An incident electron can transfer part of its energy to a core electron; as a result, the core electron will be ejected with a kinetic energy (with respect to the Fermi level of the sample) of:

$$E_K = E_o - E_B - \varepsilon,$$

where E_B is the binding energy of the core electron, ε is the energy of the scattered incident electron, and E_o is the primary beam energy. The maximum kinetic energy of the ejected electron corresponds to $\varepsilon = 0$. An ionization edge is generally much weaker than an Auger peak since the ejected electron energies are distributed over all values less than the maximum.

The energy of the feature originally observed at 950 eV was equal to 65% of E_o. It was discovered that this anomalous peak was caused by the interaction of the incident beam with the anodes of the electron gun [25].

Examination of Figure 2 will show that the small peaks in the Auger electron energy range 300 to 500 eV have temperature dependent peak heights. This temperature effect was reversible and without noticeable hysteresis. Similar features have been observed for Cu and Co [44], Ni [45], and Ru(0001) [43]. All of these investigators have attributed these peaks to the diffraction of the emitted secondary electrons. Since this is an elastic scattering process, it is reasonable that the energies of the diffraction peaks observed for Ru($10\bar{1}0$) would not coincide necessarily with those found for Ru(0001) samples.

Since this is a diffraction process, it will be dictated by the long range order of the crystal which is reduced (as far as the electrons are concerned in the adiabatic approximation) when the crystal is heated; therefore, the temperature dependence of these features should be characterized by a Debye-Waller factor. Orent [25] has worked through the appropriate theoretical model and shown that the temperature dependent peaks between 300 and 500 eV do indeed increase with decreasing temperature.

Auger Analysis of Adsorbed Gases

The Auger analysis of the chemical composition of the surface was based on the Ru_{151}, Ru_{203}, Ru_{235}, Ru_{276}, and O_{517} peak-to-peak heights in the second derivative spectrum. The clean ruthenium surface was a convenient internal standard. The use of an internal standard avoids the difficulty of absolute calibration, which is important in this case since it is very difficult to reproducibly set the beam current and modulation voltage.

To calculate the oxygen fractional coverage on the ruthenium surface, a standard was needed which could be used to compare results from different experiments. The Ru^o_{235} peak-to-peak height was chosen to scale all the data. An equation developed by Brundle [46] was used to determine Ru^o_{235}. Brundle stated that the substrate signal intensity in the presence of an adsorbate could be expressed as:

$$I = I_o \exp(-\ell/\lambda \cos \phi), \qquad \begin{array}{l} I = Ru_{235} \text{ (covered)} \\ I_o = Ru^o_{235} \text{ (clean)} \end{array}$$

where I is the intensity for an adsorbate covered surface, I_o is the intensity for a clean surface, λ is the emitted electron escape depth, and ϕ is the angle of emission with respect to the surface normal.

This expression is based upon the assumption that the adsorbate forms a uniform layer, there is no contribution from backscattered electrons, and the attenuation is of an exponential form. Therefore values of λ computed from this expression will likely be upper limits. λ was shown to be close to 8 Å by T. Orent [25] and Tracy and Burkstrand [47] for an electron energy of 235 eV.

Since ℓ can be expressed as K times the diameter of the adsorbate and K is proportional to the oxygen peak-to-peak height, the value of I_o, the intensity at zero coverage, can be found from the intercept of a plot of ℓn I versus oxygen peak-to-peak height, $\theta_I = O_{517}$. In Figure 3 ℓn I versus oxygen peak-to-peak height, θ_I, for oxygen dosed at 10L and for the average value of 47 clean Auger spectra of the ruthenium crystal, has been plotted. The intercept at zero coverage was $\ell n\ I = 4.38$. Therefore $I_o = \mathrm{Ru}^{o}_{235}$ was 79.84 divisions. The 10L oxygen dose was done with the ruthenium crystal at < 200 ^{o}C and gave a 2 X 1 LEED pattern. The assumption made was that the heavy dose of oxygen gave the 1/2 monolayer surface coverage indicated by the 2 X 1 LEED pattern.

Having found Ru^{o}_{235}, the data from Figure 3 were then used to make a plot of $\ell n\ I/I_o$ versus θ_I, Figure 4. This plot was used to determine I_o from experimental values of I and θ_I. θ_I was normalized as follows:

$$\mathrm{Ru}^{o}_{235} = 79.84 \text{ divisions (standard)}$$

$$\frac{79.84 \text{ div.}}{I_o} \quad \theta_I = \theta'_I$$

θ'_I = normalized θ_I

I_o = experimentally determined Ru^{o}_{235}

To get the oxygen fractional coverage, the 10L dose of oxygen at < 200 ^{o}C was assumed to have given 1/2 monolayer coverage of oxygen. Therefore doubling θ_I in this experiment gave a full monolayer of oxygen.

Figure 3. Exponential attenuation of the Ru (235 eV) Auger peak intensity (peak-to-peak height) as a function of the O (517 eV) = θ_I intensity (peak-to-peak height).

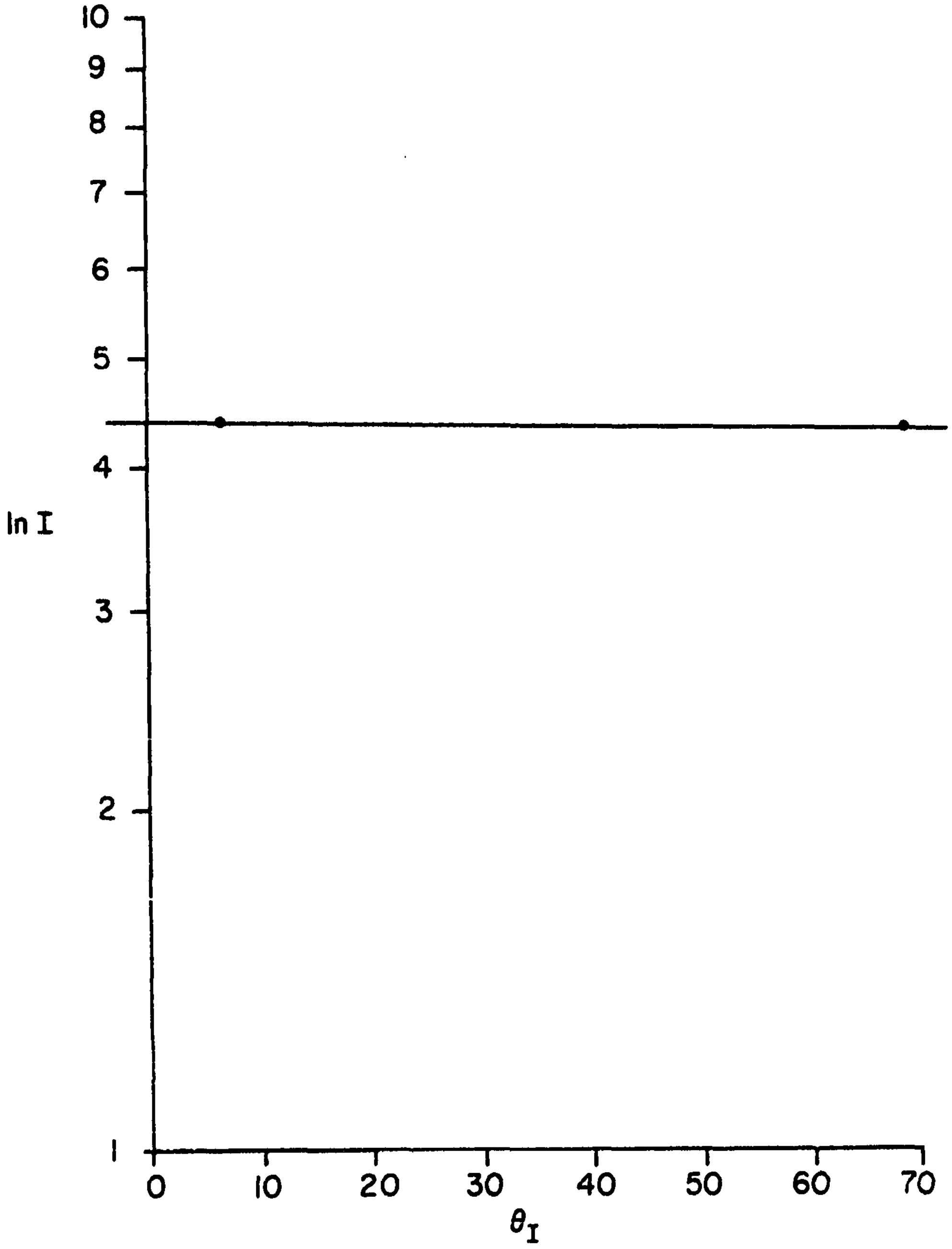
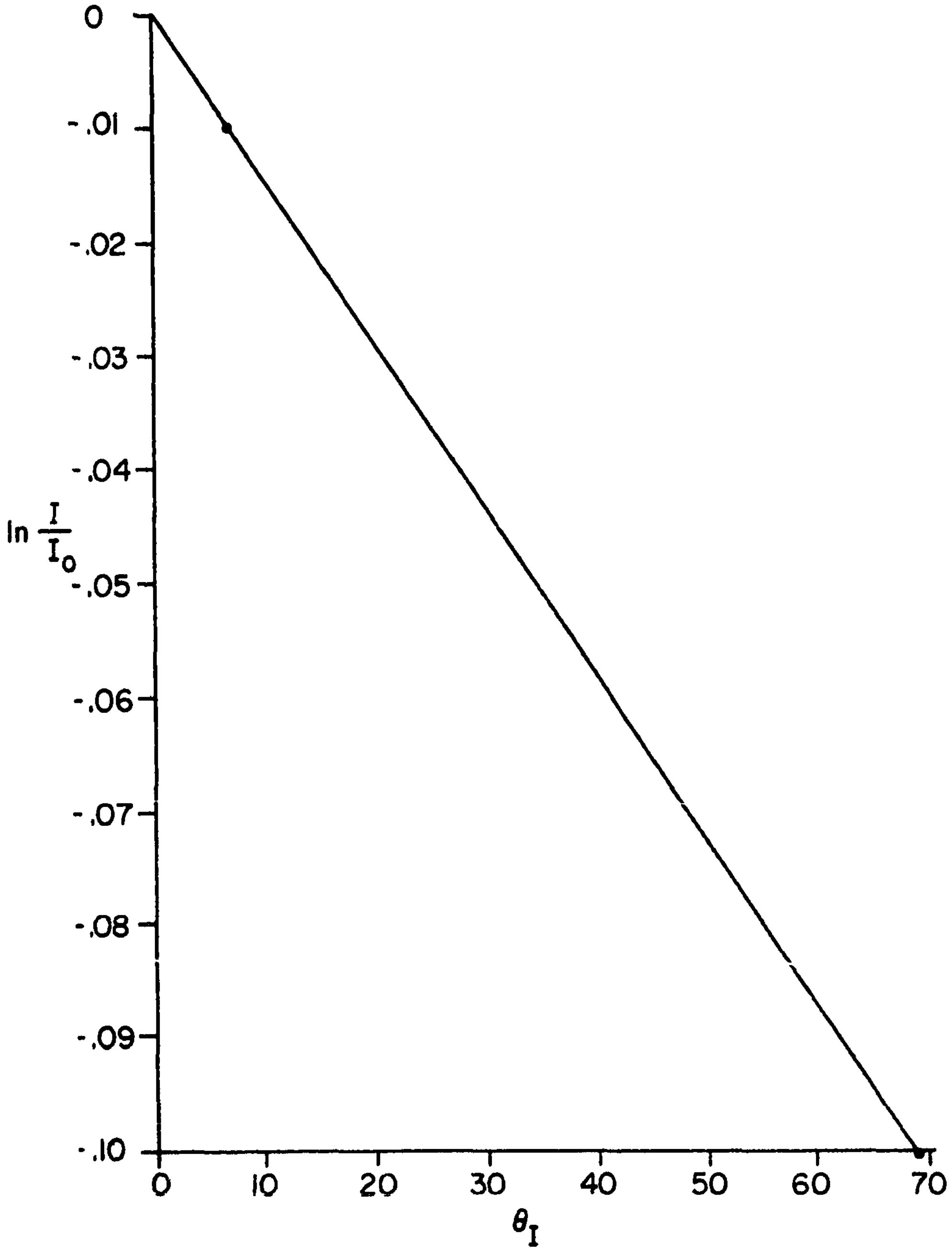

10
9
8
7
6
5
4
3
2
1
ln I
0
10
20
30
40
50
60
70
θ_I

Figure 4. Exponential attenuation of the normalized Ru (235 eV) Auger peak intensity (peak-to-peak height) as a function of the O (517 eV) $\approx \theta_I$ intensity (peak-to-peak height).


0
-.01
-.02
-.03
-.04
-.05
-.06
-.07
-.08
-.09
-.10
$\ln \frac{I}{I_0}$
0
10
20
30
40
50
60
70
θ_I

Finally:

$$\theta_I = 68.85 \text{ divisions } (10L \text{ of } O_2 \text{ at } < 200\ ^{o}C)$$

$$2\ \theta_I = 137.70 \text{ divisions}$$

$$\theta_o = \frac{\theta_I'}{137.7 \text{ divisions}}$$

$$\theta_o = \text{oxygen fractional coverage}$$

The amount of carbon adsorbed on the ruthenium surface was calculated from an analysis of the carbon Auger peak-to-peak intensities in the "clean" and adsorbate covered cases. The analysis was complicated by the fact that the carbon Auger peak, 275 eV, overlaps the principle ruthenium Auger peak, 276 eV. The carbon cannot be calculated by simply subtracting the "clean" carbon-ruthenium peak at 276 eV from the adsorbate covered carbon-ruthenium peak at 276 eV because the adsorbate suppresses the ruthenium substrate peaks. Also the principle ruthenium substrate peaks at 151, 203, 235, and 276 eV are suppressed different amounts by the adsorbate from Auger spectrum to Auger spectrum.

Keeping this in mind, the amount of adsorbed carbon was calculated by first determining the peak-to-peak magnitudes of the ruthenium 151, 203, 235, and 276 eV transitions in the "clean" Auger spectrum from each experiment. Then the adsorbate covered 151, 203, 235, and 276 eV ruthenium transition peak-to-peak magnitudes were calculated from the same experiment. The "clean" to adsorbate ratios were then calculated at each energy, i.e. 151 eV "clean" magnitude ÷ 151 eV adsorbate magnitude. A plot of the ratios (ordinate) versus the energies (abscissa) was then made. A straight line was fitted to the plotted points. At 276 eV the corresponding ratio was determined graphically. The 276 eV "clean" peak-to-peak magnitude was divided by the new 276 eV ratio; this gave a new adsorbate 276 eV peak-to-peak magnitude. This new 276 eV adsorbate peak-to-peak magnitude was subtracted from the original adsorbate peak-to-peak magnitude to determine the approximate carbon adsorbate peak-to-peak magnitude.

The assumptions that were made to calculate the amount of carbon in this way were: the ruthenium 276 eV peak and the carbon 275 eV peak were coincident and the peak-to-peak magnitude depression caused by the adsorbate on the ruthenium substrate peaks was linear for all four peaks. The amount of carbon on the surface was small, therefore the carbon peak-to-peak magnitude was small compared to the ruthenium 276 eV peak-to-peak magnitude which should have reduced errors due to the 1 eV separation of the carbon and ruthenium peaks. Also the shape of the 276 eV peak did not change with the addition of adsorbate containing carbon. The adsorbate peak-to-peak depression of the substrate transitions was not always the same for each substrate transition of ruthenium, but it was consistent enough that a straight line could be fitted in the ratio versus energy plots which approximated the actual peak-to-peak depression closely.

Since the carbon adsorbate peak-to-peak magnitude obtained was approximate, the carbon to oxygen ratio, C:O, was determined and used for the purpose of interpreting results. To determine the C:O ratio the oxygen adsorbate peak-to-peak magnitude had to be determined. Since the oxygen transition of interest, 517 eV, had no overlap problem with another transition, the oxygen adsorbate peak-to-peak magnitude was found by subtracting the "clean" oxygen peak-to-peak magnitude from the adsorbate covered oxygen peak-to-peak magnitude in each experiment. The calculated oxygen adsorbate peak-to-peak magnitude was multiplied by 1.4, to account for instrument resolution [25] and Auger effects due to the different electron binding energies of carbon and oxygen [46], so that the oxygen and carbon intensities were comparable. Then the C:O ratio was determined.

It has been determined by Sickafus [48] using a number of calibration experiments, that there is a linear relationship between Auger signal intensity and adsorbate surface coverages in the submonolayer region. All of the oxygen and carbon coverages determined in this study were smaller than 1 monolayer and it is believed that they indicate very closely the carbon and oxygen coverages on the ruthenium surface.

LEED and Auger Results from Carbon Monoxide Interacting with Ru(10$\bar{1}$0) at 23.5 °C

Table 1 tabulates the LEED and Auger results for carbon monoxide interacting with Ru(10$\bar{1}$0) at 23.5 °C. For very light doses of carbon

Table 1. LEED and Auger results from carbon monoxide interacting with Ru(10$\bar{1}$0) at 23.5 °C

Amount	LEED pattern(s)	θ_o[a]	C:O[b]
0.06L[c]	1 X 1	0.03 ± .01	1:1
0.3L	1 X 1	0.03 ± .01	1:1
0.45L	1 X 1 → C(2 X 2)[d]	0.07 ± .02	1:1
0.6L	1 X 1 → C(2 X 2)	0.18 ± .04	1:1
2L[e]	1 X 1 → C(2 X 2)	0.11 ± .02	1:1
2L[f]	1 X 1 → C(2 X 2)	0.15 ± .03	1:1
3.6L	1 X 1 → C(2 X 2) + C(8 X 4)	0.12 ± .02	1:1
10L	C(8 X 12)	0.16 ± .03	1:1
10L[f]	C(8 X 12)	0.16 ± .03	1:1
50L	C(8 X 12) → C(2 X 2) → C(2 X 2) + C(6 X 4)	0.16 ± .03	1:1
200L[e]	C(8 X 12)	0.21 ± .04	1:1
200L	C(8 X 12)	0.17 ± .03	1:1
200L[f]	C(8 X 12)	0.21 ± .04	1:1

[a] The fraction of the surface covered with oxygen.

[b] The carbon to oxygen ratio.

[c] 1 Langmuir = 10^{-6} torr x sec.

[d] Arrow indicates LEED pattern changed after passage of time.

[e] No 20 minute wait between dose and LEED filament on.

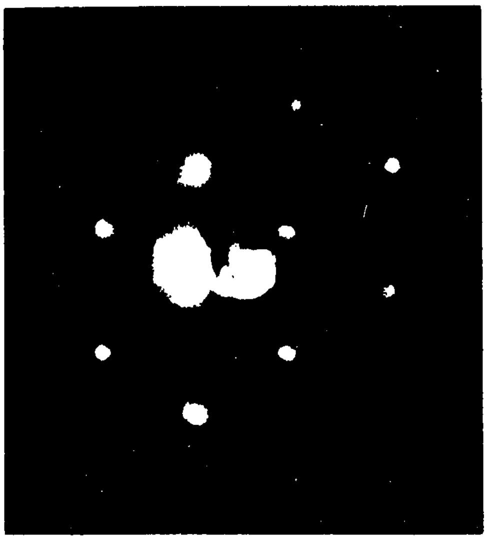
[f] Data taken with hydrogen data.

monoxide the substrate Ru(10$\bar{1}$0) LEED pattern, a 1 X 1, Figure 1, was the only LEED pattern observed. Since the oxygen fractional coverage, hereafter θ_O, was low and the carbon to oxygen ratio, hereafter C:O, was 1:1, it is apparent that very little carbon and oxygen were on the surface when the 1 X 1 LEED pattern was observed.

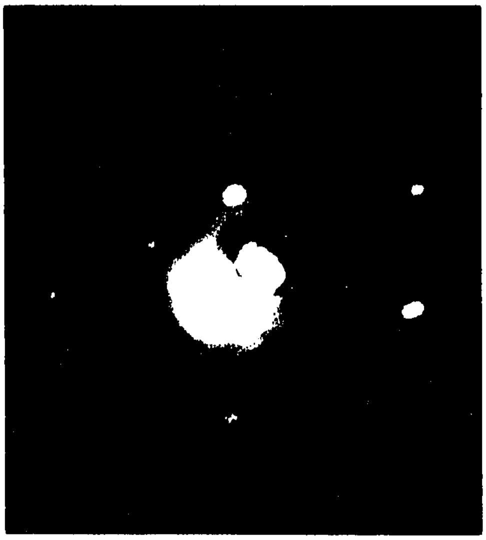
When the carbon monoxide dose was increased to 0.45L a new phenomenon was observed. When the LEED beam was first turned on only a 1 X 1 LEED pattern was observed. After anywhere from 2 to 15 minutes of observation this 1 X 1 changed to a C(2 X 2), Figure 5a. Madey and Menzel [23] observed the same phenomenon when they dosed carbon monoxide on Ru(0001) at 300 K with low doses (~ 3 to 9L) and concluded it was a LEED beam induced effect.

To prove the changing LEED pattern was being caused by the LEED beam, two experiments were run where carbon monoxide was dosed at the number of Langmuirs that gave the changing pattern, 2L. In the first experiment after the dose was finished, the LEED beam was immediately turned on and within a few minutes the second LEED pattern, a C(2 X 2), formed. In the second experiment after the dose was finished, the LEED beam was not turned on for 20 minutes. When the LEED beam was turned on the LEED pattern observed, a 1 X 1, was the same as observed in the first experiment when the LEED beam was turned on. After a few minutes in the second experiment the C(2 X 2) formed. Therefore the formation of the C(2 X 2) was LEED beam induced.

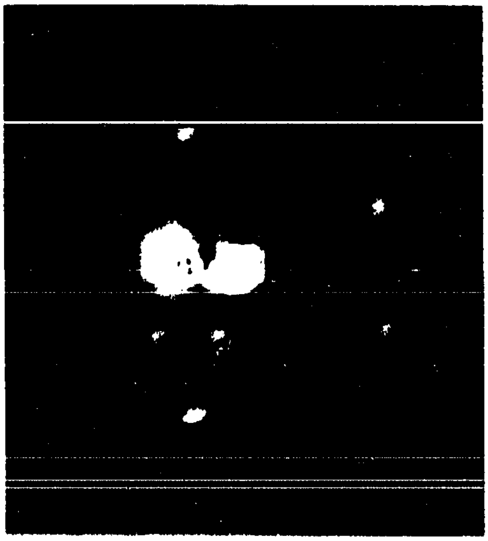
Figure 5. Observed LEED patterns: (a) C(2 X 2), 38 eV beam energy, (b) C(2 X 2) + C(8 X 4), 42 eV beam energy, (c) C(8 X 12), 29 eV beam energy, (d) C(2 X 2) + C(6 X 4), 48 eV beam energy.



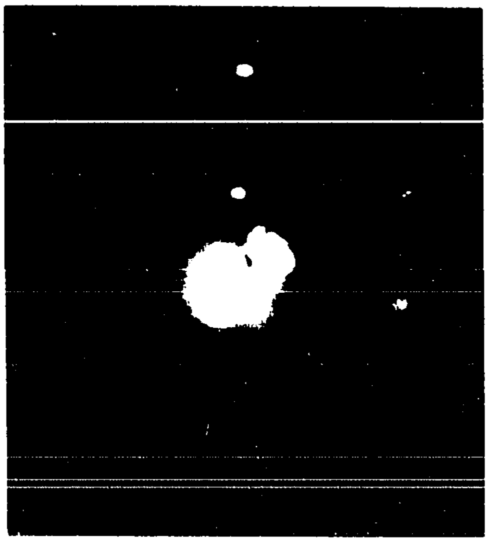
C(2 X 2)
(a)



C(2 X 2) + C(8 X 4)
(b)



C(8 X 12)
(c)



C(2 X 2) + C(6 X 4)
(d)

θ_o varies from 0.07 to 0.18 in the experiments where the C(2 X 2) was LEED beam induced. C:O was 1:1. The C(2 X 2) pattern indicates an adsorbate surface coverage of 50% when the C(2 X 2) domain covers the entire surface. The changing θ_o suggests the C(2 X 2) domain was of a different size in each experiment. With the particular LEED apparatus I utilized, a domain had to be at least 10^4 $\mathring{A}^2$ to produce a LEED pattern.

In the 3.6L dose experiment a compound LEED pattern was LEED beam induced, a C(2 X 2) + C(8 X 4), Figure 5b. This LEED pattern indicated C(2 X 2) and C(8 X 4) domains at least 10^4 $\mathring{A}^2$ in extent.

In the doses of 10L to 200L one LEED structure predominated, a C(8 X 12), Figure 5c. θ_o had values of 0.16 to 0.21 and C:O was 1:1 indicating domains of varying size. To produce a C(8 X 12), a full surface coverage of 0.02 was required if the surface didn't restructure. Obviously from θ_o and C:O there was much more carbon and oxygen on the surface than required for the LEED structure. Therefore the C(8 X 12) reflected some type of complex surface structure. LEED patterns of this type can be rationalized in terms of coincident lattices and restructured surfaces [25,49].

The C(8 X 12) LEED pattern always faded under observation with the LEED beam. When Auger spectra were taken immediately after the LEED beam was turned on, θ_o was always higher than when Auger spectra were taken after 15 minutes. Since C:O was always 1:1, the LEED beam was removing carbon and oxygen from the surface in the same amount, probably as carbon monoxide.

To see if the LEED beam was removing carbon monoxide from the surface at lower dose levels of carbon monoxide, a 3.6L dose of carbon monoxide experiment was run with one difference in the experimental routine. The mass spectrometer was turned on just after the carbon monoxide dose was finished and the ambient in the vacuum system was monitored for the rest of the experiment. When the LEED beam was turned on there was an immediate burst of carbon monoxide and hydrogen noted in the mass spectrometer. This burst could have been caused by the LEED filament being turned on, but the mass spectrometer output did not give the characteristic peak intensity changes for gases desorbing from a surface due to heating [50]. Therefore the carbon monoxide and hydrogen observed came from the Ru(10$\bar{1}$0) surface and was desorbed by the LEED beam. The hydrogen was adsorbed on the crystal from the ambient while the Ru(10$\bar{1}$0) crystal was coming to 23.5 °C.

The electron induced rate of desorption is given by [25]:

$$\frac{dn}{dt} = -n\sigma\Phi,$$

where n is the adatom density, Φ is the incident electron flux, and σ is the total cross section. Hence if n_o is the adatom density at $t = 0$,

$$n = n_o e^{-\sigma\Phi t}$$

and n falls by a factor e every $1/\sigma\Phi$ seconds. Φ is ~ 1 - 3 X 10^{16} electrons/cm^2·sec, and σ has been reported as varying between 10^{-18} and 10^{-20} cm^2 with Orent giving a value of ~ 6 X 10^{-20} cm^2 for oxygen on Ru(10$\bar{1}$0) [25] which compares favorably with my results. Therefore from ~ 8-20 minutes are required for n to fall a factor e in my experiments.

In one instance, 50L of carbon monoxide, a C(8 X 12) was LEED beam induced to a C(2 X 2) and a C(6 X 4), Figure 5d. What is particularly interesting about this structure is that a C(2 X 2) first formed, then the C(6 X 4) formed with the C(2 X 2) in a compound structure. The transition from C(8 X 12) to C(2 X 2) + C(6 X 4) took 25 minutes. Domains of C(2 X 2) and C(6 X 4) were indicated by this structure.

LEED and Auger Results from Carbon Monoxide Interacting with Ru(10$\bar{1}$0) at -135 °C

Table 2 shows the LEED and Auger results for carbon monoxide interacting with Ru(10$\bar{1}$0) at -135 °C. In the 0.6L, and one of the 2L doses of carbon monoxide a 1 X 2, Figure 6a, formed. θ_O was 0.05 and 0.06, respectively. C:O was 1:1. In the other 2L dose a 1 X 1 formed. θ_O was 0.08 and C:O was 1:1. What is interesting is that when 3.6L of carbon monoxide were dosed the 1 X 2 was LEED beam induced and θ_O was 0.05; again C:O was 1:1. It appears that the 1 X 2 would not form when the oxygen and carbon together on the surface was more than ~ 0.12 monolayer.

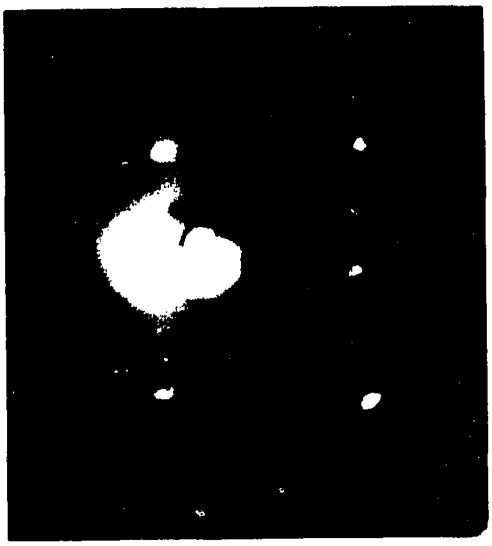
Table 2. LEED and Auger results from carbon monoxide interacting with Ru(10$\bar{1}$0) at -135 °C

Amount	LEED pattern(s)	θ_o	C:O
0.6L	1 X 2	0.05 ± .01	1:1
2L[a]	1 X 2	0.06 ± .01	1:1
2L[b]	1 X 1	0.08 ± .02	1:1
3.6L	1 X 1 → 1 X 2	0.05 ± .01	1:1
10L	C(6 X 4) + C(2 X 2)	0.10 ± .02	1:1
10L[b]	C(8 X 6)	0.16 ± .03	1:1
50L	2 X 1	0.13 ± .03	1:1
200L	2 X 1	0.17 ± .03	1:1
200L[b]	2 X 1	0.13 ± .03	1:1

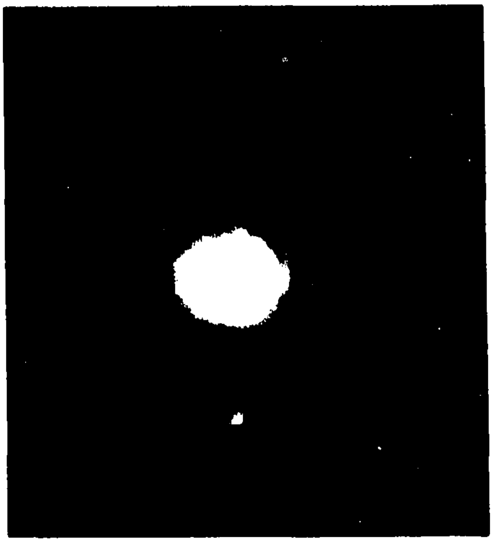
[a] No 20 minute wait between dose and LEED filament on.

[b] Data taken with hydrogen data.

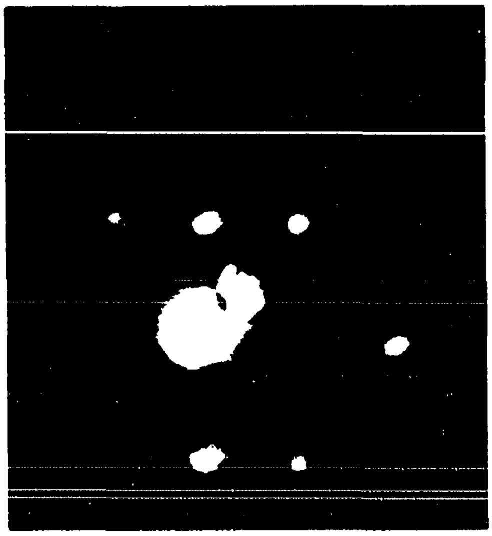
Figure 6. Observed LEED patterns: (a) 1 X 2, 38 eV beam energy, (b) C(8 X 6), 31 eV beam energy, (c) 2 X 1, 39 eV beam energy.



1 X 2
(a)



C(8 X 6)
(b)



2 X 1
(c)

In one 10L dose a C(2 X 2) + C(6 X 4) was observed, Figure 5d. This compound structure was not LEED beam induced. Two domains, one C(2 X 2) and the other C(6 X 4) were implied. The LEED pattern did fade slightly with time during observation with the LEED beam. The other 10L dose produced a C(8 X 6), Figure 6b. To form a C(8 X 6), a surface coverage of 0.04 was required if the surface was not restructured. With $\theta_o = 0.16$ and a C:O of 1:1 there was obviously more carbon and oxygen on the surface than was required for the LEED pattern. Like the C(8 X 12), the C(8 X 6) was a complex surface structure. The C(8 X 6) did fade slightly with time during observation with the LEED beam. To compare the two 10L dose experiments, when more oxygen and carbon were on the surface a more complex structure resulted, while when less carbon and oxygen were on the surface two different LEED structures resulted.

In the heaviest dose cases, 50L and 200L, a 2 X 1 LEED structure formed consistently, Figure 6c. θ_o varied from 0.13 to 0.17 and C:O was 1:1 indicating domains of varying size. Slight fading was observed while the LEED beam was on.

LEED and Auger Results from Carbon Monoxide Interacting with Ru(10$\bar{1}$0) at 200 °C

Table 3 shows the LEED and Auger results for carbon monoxide interacting with Ru(10$\bar{1}$0) at 200 °C. The amounts of carbon monoxide adsorbed at the various doses, as revealed by θ_o and C:O, were evidently small. Only the 200L dose gave a moderate amount of carbon

Table 3. LEED and Auger results from carbon monoxide interacting with Ru(10$\bar{1}$0) at 200 °C

Amount	LEED pattern(s)	θ_o	C:O
0.6L	1 X 1	0.03 ± .01	1:1
2L[a]	1 X 1	0.07 ± .02	1:1
3.6L	1 X 1	0.06 ± .01	1:1
10L	1 X 1 → C(2 X 2)	0.07 ± .02	1:1
50L	1 X 1 → C(2 X 2)	0.08 ± .02	1:1
200L	1 X 1 → C(2 X 2)	0.13 ± .03	1:1

[a] No 20 minute wait between dose and LEED filament on.

monoxide on the surface. To find a reason for this the experimental procedure was changed in the 200L dose experiment by taking Auger spectra of the Ru(10$\bar{1}$0) surface 20 minutes after the dose with the heat lamp on and the Ru(10$\bar{1}$0) crystal at 200 °C. Normally the heat lamp would be turned off 20 minutes after the dose and LEED and Auger data taken. The Auger spectra indicated no carbon monoxide had adsorbed on the Ru(10$\bar{1}$0) surface while the Ru(10$\bar{1}$0) surface was at 200 °C at the dosing pressures used (3 X 10^{-9} to 1 X 10^{-8} torr).

This is consistent with published Flash Decomposition Spectroscopy results [23,33]. The heat lamp was turned off and Auger spectra were taken periodically while the Ru(10$\bar{1}$0) surface cooled. Oxygen and carbon started to appear on the surface. Therefore it was concluded that the carbon and oxygen adsorbed on the surface, once the crystal cooled enough, was from ambient carbon monoxide.

In light dose cases the carbon monoxide left in the ambient after 20 minutes of pumping was not sufficient to produce more than a 1 X 1 LEED pattern. The 10L - 200L doses however left enough carbon monoxide in the ambient after 20 minutes of pumping to adsorb on the crystal, when it cooled enough, and be LEED beam induced to a C(2 X 2). θ_o and C:O for the induced C(2 X 2) experiments indicate the C(2 X 2) domain increased from the 10L experiment to the 200L experiment.

LEED and Auger Results from Hydrogen Interacting with Ru(10$\bar{1}$0) at 23.5 °C

Table 4 shows the LEED and Auger results for hydrogen interacting with Ru(10$\bar{1}$0) at 23.5 °C. The 0.6L dose gave a faint C(2 X 2) which was either being caused by hydrogen or ambient adsorbed carbon monoxide and hydrogen. A blank experiment (background ambient dosed, everything else in the experimental procedure the same) was run at 23.5 °C and gave the same faint C(2 X 2), θ_o = 0.12, and C:O = 1:1. Carbon monoxide has been shown to form an induced C(2 X 2) at 23.5 °C. Kraemer and Menzel [36] with Field Emission microscopy found that carbon monoxide effectively displaces hydrogen on ruthenium at 300 K. They also found that a saturated carbon monoxide layer on ruthenium did not adsorb any hydrogen and a partially filled carbon monoxide layer adsorbed hydrogen approximately proportional to the free space at 300 K. Therefore the evidence points strongly to the C(2 X 2) being formed by carbon monoxide and hydrogen.

In the 10L dose the C(2 X 2) disappeared and only a 1 X 1 was observed. There was more carbon on the surface than oxygen but there was no indication of any adsorbate LEED pattern beside a 1 X 1. The total coverage on the surface indicated by θ_o and C:O was 0.39 of a monolayer. At the 50L dose there was less oxygen on the surface but there was more oxygen than carbon and again the LEED pattern indicated no adsorbate structure. The total surface coverage was 0.14. The

Table 4. LEED and Auger results from hydrogen interacting with Ru(1010) at 23.5 °C

Amount	LEED pattern(s)	θ_o	C:O
0.6L	C(2 X 2) (faint)		
10L	1 X 1	0.11 ± .02	2.5:1
50L	1 X 1	0.08 ± .02	1:1.5
1000L	1 X 1 → C(2 X 2)	0.08 ± .02	1:4

1000L dose gave a LEED beam induced transition to a C(2 X 2), less oxygen on the surface, but much more oxygen than carbon. The total coverage was 0.10.

LEED and Auger Results from Hydrogen Interacting with Ru(10$\bar{1}$0) at -135 °C

Table 5 shows the LEED and Auger results for hydrogen interacting with Ru(10$\bar{1}$0) at -135 °C. The 0.6L dose gave a 1 X 2 which was caused by either hydrogen or ambient adsorbed carbon monoxide and hydrogen. A blank experiment was run at -135 °C and a 1 X 2 was produced which can be attributed to ambient carbon monoxide and hydrogen.

Table 5 shows that a 1 X 2 was formed at 0.6L and 10L doses. In the 10L dose the oxygen coverage was small but the amount of oxygen on the surface was large compared to the amount of carbon. The total surface coverage was 0.06. In the 50L and 1000L doses the total surface coverages were 0.72 and 0.49, respectively, and a 1 X 1 resulted. In Table 2 a 1 X 2 never resulted from carbon monoxide adsorption unless the total surface coverage was less than 0.12. Therefore all the evidence, including Kraemer and Menzel's [36] work for hydrogen and carbon monoxide interacting at 300 K, points to the 1 X 2 being due to adsorbed carbon monoxide and hydrogen. In the 50L and 1000L doses the amount of oxygen on the surface has increased, but in both experiments there was much more carbon on the surface than oxygen.

Table 5. LEED and Auger results from hydrogen interacting with Ru($10\bar{1}0$) at -135 °C

Amount	LEED pattern	θ_o	C:O
0.6L	1 X 2		
10L	1 X 2	0.05 ± .01	1:8
50L	1 X 1	0.08 ± .02	8:1
1000L	1 X 1	0.07 ± .02	6:1

LEED and Auger Results from Carbon Monoxide and Hydrogen Interacting with Ru(10$\bar{1}$0) at 23.5 °C

Table 6 shows the LEED and Auger results for hydrogen and carbon monoxide interacting with Ru(10$\bar{1}$0) at 23.5 °C. For the 2L of carbon monoxide, 10L of hydrogen experiment a compound C(2 X 2) + C(8 X 4) LEED structure was formed, Figure 5b. Domains of C(2 X 2) and C(8 X4) were indicated. In the 10L of carbon monoxide, 50L of hydrogen experiment only a C(8 X 12) was observed. θ_o and C:O indicate the C(8 X 12) was a complex structure. The 200L of carbon monoxide, 1000L of hydrogen experiment produced a compound C(8 X 12) + C(2 X 2) LEED structure, Figure 7a, which indicated domains of C(8 X 12) and C(2 X 2). Slight fading did occur, especially in the C(8 X 12) domain. Fading also occurred in the C(8 X 12) produced in the 10L of carbon monoxide, 50L of hydrogen experiment.

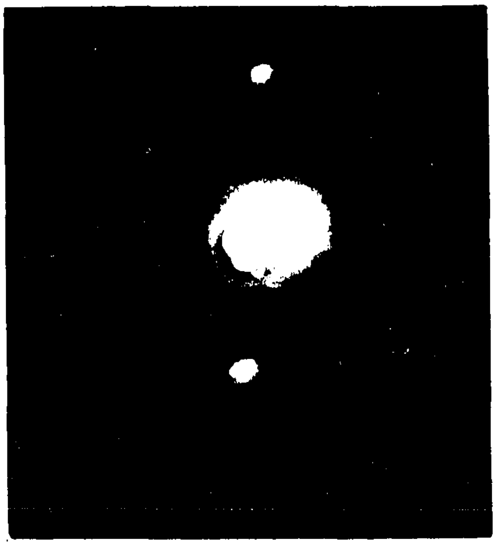
LEED and Auger Results from Carbon Monoxide and Hydrogen Interacting with Ru(10$\bar{1}$0) at -135 °C

Table 7 shows the LEED and Auger results for hydrogen and carbon monoxide interacting with Ru(10$\bar{1}$0) at -135 °C. For the 2L of carbon monoxide, 10L of hydrogen experiment a compound C(2 X 2) + C(6 X 4) LEED structure was formed, Figure 5d. Domains of C(2 X 2) and C(6 X 4) were present. It is of interest that this LEED pattern also formed at 23.5 °C. In both of the remaining experiments a 2 X 1 LEED pattern formed, Figure 6c. θ_o and C:O in both these experiments

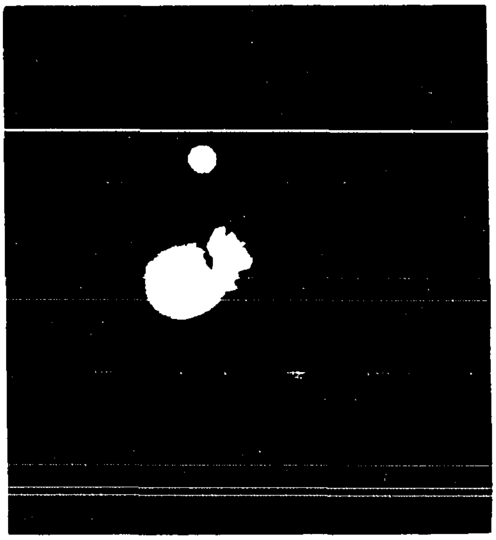
Table 6. LEED and Auger results from carbon monoxide and hydrogen interacting with Ru(10$\bar{1}$0) at 23.5 °C

Gas	Amount	LEED patterns(s)	θ_o	C:O
Carbon Monoxide Hydrogen	2L 10L	1 X 1 → C(2 X 2) + C(8 X 4)	0.12 ± .02	1:1
Carbon Monoxide Hydrogen	10L 50L	C(8 X 12)	0.16 ± .03	1:1
Carbon Monoxide Hydrogen	200L 1000L	C(8 X 12) + C(2 X 2)	0.19 ± .04	1:1

Figure 7. Observed LEED patterns: (a) C(2 X 2) + C(8 X 12), 25 eV beam energy, (b) C(2 X 4), 35 eV beam energy.



C(8 X 12) + C(2 X 2)
(a)



C(2 X 4)
(b)

Table 7. LEED and Auger results from carbon monoxide and hydrogen interacting with Ru(10$\bar{1}$0) at -135 °C

Gas	Amount	LEED Pattern(s)	θ_o	C:O
Carbon Monoxide Hydrogen	2L 10L	C(2 X 2) + C(6 X 4)	0.12 ± .02	1:2
Carbon Monoxide Hydrogen	10L 50L	2 X 1	0.15 ± .03	1:1
Carbon Monoxide Hydrogen	200L 1000L	2 X 1	0.18 ± .04	1:1

indicate that the 2 X 1 domain was larger in the 200L of carbon monoxide, 1000L of hydrogen experiment. Fading of the 2 X 1 occurred during observation of the LEED pattern in both experiments.

LEED and Auger Results from Miscellaneous Experiments of Gases or Background Ambient Gases Interacting with Ru(10$\bar{1}$0) at Different Temperatures

In Table 8 are tabulated the LEED and Auger results for background ambient gases (blanks), oxygen, and hydrogen interacting with Ru(10$\bar{1}$0) at different temperatures. When hydrogen was dosed at 0.6L with the Ru(10$\bar{1}$0) crystal at 200 °C, the LEED pattern observed when the crystal cooled enough was a LEED beam induced faint C(2 X 2). The blank experiment at 200 °C gave exactly the same result.

It was shown previously that no carbon monoxide adsorbed on the Ru(10$\bar{1}$0) surface at 200 °C, but once the Ru(10$\bar{1}$0) surface cooled enough, to about 60 °C, enough carbon monoxide could adsorb from the ambient to be LEED beam induced to a C(2 X 2). In these previous experiments a large carbon monoxide ambient was necessary to provide enough carbon monoxide for a LEED beam induced C(2 X 2).

In these experiments, very little carbon monoxide could be provided from the ambient, but the amount of hydrogen was proportionately larger. Hydrogen adsorbs on a ruthenium surface at 87 °C [34]. Since carbon monoxide displaces hydrogen on a ruthenium surface in the vicinity of 300 K and since hydrogen and carbon monoxide adsorb from the ambient onto a ruthenium surface at 87 °C

Table 8. LEED and Auger results from miscellaneous experiments of gases or background ambient gases interacting with Ru(10$\bar{1}$0) at different temperatures

Gas	Amount	Ru(10$\bar{1}$0) Temperature	LEED pattern(s)	θ_o	C:O
B.A.[a]	~ 0.7 CO ~ 0.4 H_2	23.5 °C	C(2 X 2) (faint)	0.12 ± .02	1:1
B.A.	~ 0.7 CO ~ 0.4 H_2	-135 °C	1 X 2		
B.A.	~ 0.7 CO ~ 0.4 H_2	200 °C	1 X 1 → C(2 X 2) (faint)		
Oxygen	2L[b,c]	< 200 °C	C(2 X 4)	0.20 ± .04	
Oxygen	6L[b,c]	< 200 °C	2 X 1	0.34 ± .06	
Oxygen	10L	< 200 °C	2 X 1	0.50[d] ± .10	
Oxygen	200L	-135 °C	1 X 1	0.31 ± .06	
Hydrogen	0.6L	200 °C	1 X 1 → C(2 X 2) (faint)		

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[a] B.A. = background ambient, ~ 0.7L of carbon monoxide, and ~ 0.4L of hydrogen. Estimated from background gas partial pressures and residence time, ambient partial pressure of hydrogen is ~ 1.1 X 10^{-10} torr, ambient partial pressure of carbon monoxide is ~ 2 X 10^{-10} torr.

[b] No 20 minute wait between dose and LEED filament on.

[c] LEED filament on during dose.

[d] By definition.

[33,34], the 1 X 1 → C(2 X 2) transition at about 60 °C in these two experiments was caused by carbon monoxide and hydrogen adsorbed from the ambient.

I have previously discussed the blank experiments at 23.5 °C and -135 °C. Most of the oxygen experiments were run to check the experimental apparatus by reproducing previously reported experiments and to establish a standard for determining oxygen fractional coverages, θ_o. The 10L of oxygen with Ru(10$\bar{1}$0) at < 200 °C experiment gave a 2 X 1 LEED pattern, as previously reported [25,33], and a maximum oxygen peak-to-peak intensity which was used for the standard 50% surface coverage. The 2L of oxygen with Ru(10$\bar{1}$0) at < 200 °C experiment resulted in a C(2 X 4), Figure 7b, which was previously reported [25,33]. The 200L of oxygen with Ru(10$\bar{1}$0) at -135 °C experiment was run to see what LEED pattern would result. Only a 1 X 1 was observed even though θ_o was 0.31.

DISCUSSION

Structures Resulting from the Interaction of Carbon Monoxide and Hydrogen with Ru(10$\bar{1}$0)

The interpretation of the LEED data is qualitative and it is based solely on the appearance of new diffraction features. Therefore it is not unambiguous for atomic position assignment and it is possible that several structural types could satisfy the LEED results. A LEED intensity study is necessary to fix atomic positions. The proposed surface structures do account for the observed LEED patterns, are consistent with the corresponding Auger results, and have some basis in the literature.

The C(2 X 2) surface structure formed primarily at 23.5 °C, or close to it, except in a few cases at -135 °C, following carbon monoxide, hydrogen, and carbon monoxide plus hydrogen doses. The C(2 X 2) could be formed by LEED beam induction of an adsorbate consisting mostly of carbon monoxide or carbon monoxide and hydrogen. A C(2 X 2) could also be formed by carbon monoxide and hydrogen without LEED beam induction.

The C(2 X 2) structure indicates dissociated carbon monoxide on the ruthenium surface. The main reason for believing this is the oxygen Auger results, θ_O, and the corresponding C:O Auger results. When the C(2 X 2) structure was present in an experiment, θ_O was never more than 25%. Since C:O was 1:1 in most of the experiments where the C(2 X 2) was the only final LEED structure, the only way the 50% maximum surface coverage indicated by the C(2 X 2) structure could be attained was by carbon monoxide being dissociated into carbon and oxygen atoms, i.e., 25% O and 25% C.

Some of the carbon monoxide doses in experiments giving exclusively a C(2 X 2), i.e., 2L of CO at 23.5 °C, have been large enough to ensure one monolayer of coverage of carbon monoxide since the sticking coefficient has been reported to be about 0.5 for doses up to about 2.8L [22,23] at 23.5 °C. Therefore with a C(2 X 2) structure developed from a full monolayer, the oxygen fractional coverage was less than 25%. If carbon monoxide were undissociated the oxygen fraction should have been closer to 50%.

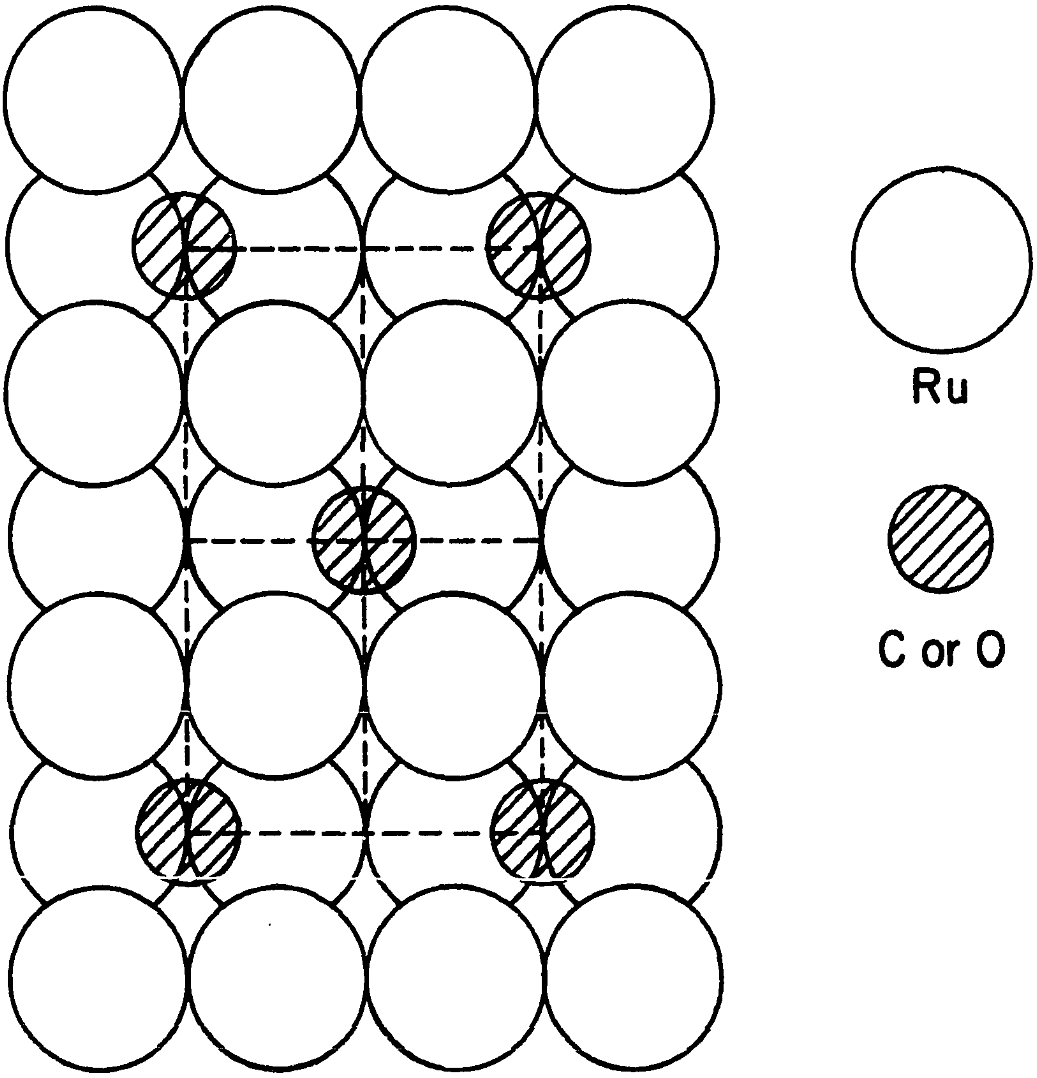
Jona [51] after doing a LEED intensity study of the C(2 X 2) structure of carbon monoxide on Fe (0001), concluded that carbon monoxide was dissociated in this structure and the carbon and oxygen atoms were randomly orientated into 25% C and 25% O. The Fe (0001) structure is similar to the $Ru(10\bar{1}0)$. Felter and Estrup [52] and Riwan, Guillot, and Paigne [53], independently found after studying the Mo(0001) C(2 X 2)-CO structure with LEED and Auger spectroscopy that the oxygen and carbon concentrations were one half those found in the Mo(0001) C(2 X 2)-O and the Mo(0001) C(2 X 2)-C structures, respectively. Felter and Estrup proposed that carbon and oxygen were randomly placed in a C(2 X 2) structure. Mo(0001) is similar to $Ru(10\bar{1}0)$. Further Fuggle et al. [32] believe they have conclusively shown that the LEED beam dissociates carbon monoxide on the Ru(0001) surface.

There are two possibilities for carbon and oxygen distribution on the Ru(10$\bar{1}$0) surface that will result in a C(2 X 2) structure and 25% oxygen and 25% carbon. One is random distribution of carbon and oxygen to give a C(2 X 2). The other is carbon and oxygen separating into domains of carbon and oxygen. An argument against domain formation is that oxygen forms a C(2 X 4), 2 X 1, or no LEED pattern (i.e., the clean surface 1 X 1 pattern), when dosed on Ru(10$\bar{1}$0) at varying doses and temperatures, Table 8. At no time does oxygen form a C(2 X 2) in a domain that is exclusively oxygen. Therefore the carbon must be affecting the oxygen and random distribution of carbon and oxygen looks most appealing.

A model for carbon monoxide randomly dissociated on Ru(10$\bar{1}$0) in a C(2 X 2) structure is given in Figure 8. The chemisorbed species sit in the simple potential minima of the substrate lattice as assumed in the classical approach to chemisorbed structures. Jona et al. [51] and Anders [54] both suggest that carbon and oxygen will be located in these high coordination positions when dissociated from carbon monoxide on iron and tungsten respectively. Ku et al. [33] suggest that in the case of O_2 adsorption, the molecular oxygen dissociates and each oxygen atom resides in the potential well formed by four nearest neighbor ruthenium atoms on Ru(10$\bar{1}$0).

Jona et al. [51] has determined the carbon and oxygen effective radii as 0.67 Å on Fe(0001). In LEED intensity analysis each type of adsorbate atom may be assigned a characteristic effective radius,

Figure 8. Doubly primitive centered-rectangular unit cell of C(2 X 2) overlayer due to carbon monoxide and hydrogen adsorption on Ru(10$\bar{1}$0).


Ru
C or O

which can be calculated by subtracting the atomic radius of the substrate atom from the adsorbate-substrate bond length determined by the surface structure analysis. This value, 0.67 Å, lies below the ranges 0.71-0.78 Å and 0.70-0.88 Å found for oxygen and carbon, respectively, on other surfaces [55], but is larger than the effective radius, 0.48 Å, determined for both oxygen and carbon in the Ti(0001) p (2 X 2)-CO structure [51]. Evidently neither carbon or oxygen will have any problem fitting in the 4-fold potential well on Ru(10$\bar{1}$0).

The C(2 X 2) structure also forms in experiments where hydrogen is dosed or present. Hydrogen has been shown to adsorb from the ambient onto Ru(10$\bar{1}$0) below 87 °C. Since the C(2 X 2) is believed to be formed by carbon and oxygen atoms, and the presence of hydrogen can induce the formation of a C(2 X 2) without the LEED beam on, it seems likely that O-H and/or C-H complexes are also indicated by the C(2 X 2) structure. It also can be concluded from the experiments that a high hydrogen to carbon monoxide ratio (high in hydrogen) helps the formation of the C(2 X 2), i.e., 200L of CO + 1000L of H_2 at 23.5 °C, 1000L of H_2 at 23.5 °C, background ambient gas at 23.5 °C and 200 °C, 0.6L of H_2 at 23.5 °C and 200 °C, 2L of CO + 10L of H_2 at -135 °C and 23.5 °C. For the background ambient gas experiments the estimated doses were 0.4L of hydrogen and 0.7L of carbon monoxide.

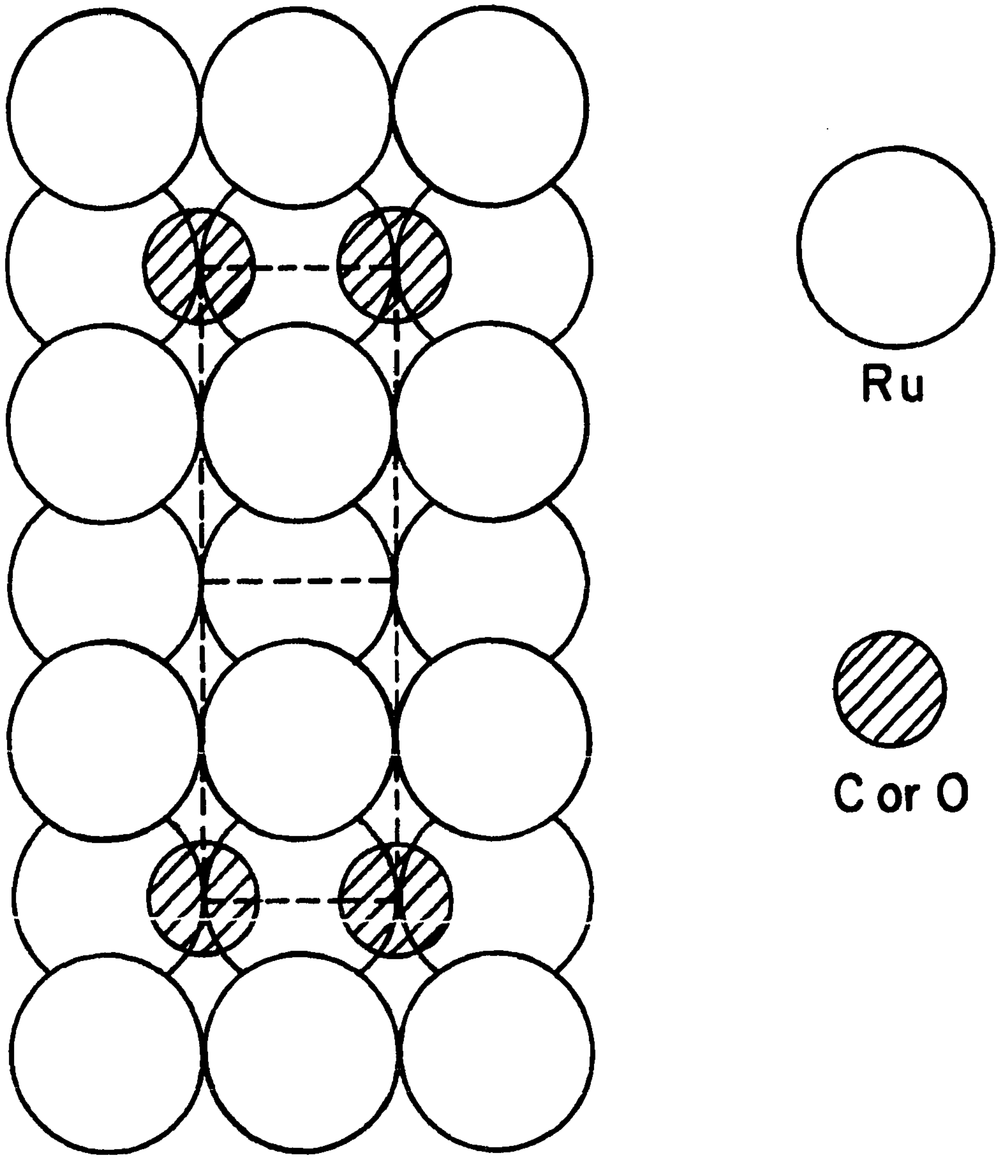
The 1 X 2 structure formed at -135 °C following carbon monoxide, hydrogen, and carbon monoxide plus hydrogen (in the background ambient gas experiments) doses. The 1 X 2 was LEED beam induced from a 1 X 1 after a few minutes of LEED observation in the 3.6L of carbon monoxide dose experiment, Table 2. In all other experiments where the 1 X 2 was observed, the 1 X 2 was present when the LEED beam was first turned on.

The 1 X 2 never formed unless θ_o was equal to 0.06 or below. For heavier carbon monoxide doses, 10L and above, the 1 X 2 was never observed. The 1 X 2 was never observed for heavy hydrogen doses, 50L and above, either. The 1 X 2 therefore is a small domain on the surface at -135 °C.

The 1 X 2 structure with carbon monoxide randomly dissociated is shown in Figure 9. The chemisorbed species are again situated in the simple potential minima of the substrate lattice. The random distribution of carbon and oxygen is implied by C:O being 1:8 in the 10L of H_2 at -135 °C experiment of Table 5. In this experiment ambient carbon monoxide which has adsorbed and hydrogen have interacted and carbon has been removed from the surface, probably as methane. The reaction sequence could well have been carbon monoxide interaction with other carbon monoxide and hydrogen to form surface carbon-hydrogen species and surface oxygen species. The additional hydrogen removes the carbon-hydrogen species as methane. This experiment also implies the 1 X 2 indicates dissociated carbon monoxide.

The Boudouard reaction, i.e., $2CO \rightarrow C + CO_2$, is a well known reaction on group VIII catalysts [7]. On nickel at ≤ 400 K in carbon monoxide pressures as low as 10^{-7} torr, it has been demonstrated that

Figure 9. Primitive unit cell of (1 X 2) overlayer due to carbon monoxide and hydrogen adsorption on Ru(10$\bar{1}$0).


Ru
C or O

the carbon deposited in this reaction can be subsequently hydrogenated to methane [35]. This carbon is not in the same form as in bulk nickel carbide (Ni_3C), which is known to be a poor methane producing catalyst. Therefore for carbon monoxide to react with itself at -135 °C and produce a carbon species that interacts with hydrogen is reasonable. The Boudouard reaction is thermodynamically favorable at -135 °C and carbon dioxide has a vapor pressure of 1 torr at -135 °C. In this experiment it appears the hydrogen interacts in the Boudouard mechanism and instead of forming carbon dioxide forms carbon-hydrogen and oxygen species on the surface. Then the additional hydrogen forms methane. I will discuss the mechanism later. A methanation type mechanism, i.e., $CO + 3H_2 \rightarrow CH_4 + H_2O$, is not appealing because water, actually ice, has a very low vapor pressure at -135 °C and once formed would evaporate very slowly from the surface.

In the 0.6L and 2L carbon monoxide dosed experiments at -135 °C, Table 2, where the 1 X 2 results, adsorbed ambient hydrogen and adsorbed carbon monoxide have interacted to randomly dissociate carbon monoxide, and form the 1 X 2. The fact that carbon monoxide only dissociates is implied by C:O being 1:1. In these experiments carbon monoxide has interacted with itself and hydrogen to form carbon-hydrogen and oxygen species on the surface. No methane was formed and this is reasonable since carbon monoxide was probably in larger quantity on the surface than hydrogen. The LEED beam induced 1 X 2 in the 3.6L dose of carbon monoxide experiment at -135 °C in Table 2 will be discussed later.

Therefore small amounts of carbon monoxide and variable amounts of hydrogen will interact at -135 °C on Ru(10$\bar{1}$0)and form carbon-hydrogen and oxygen species which will form a 1 X 2 LEED structure on the surface, Figure 9. Water might form on the surface at -135 °C but because the vapor pressure of ice at this temperature is very low it would evaporate very slowly.

The 1 X 1 structure is the substrate Ru(10$\bar{1}$0) unit cell LEED pattern. The structure also indicated carbon monoxide, hydrogen, and oxygen surface coverages that didn't form ordered LEED structures, or formed 1 X 1 structures.

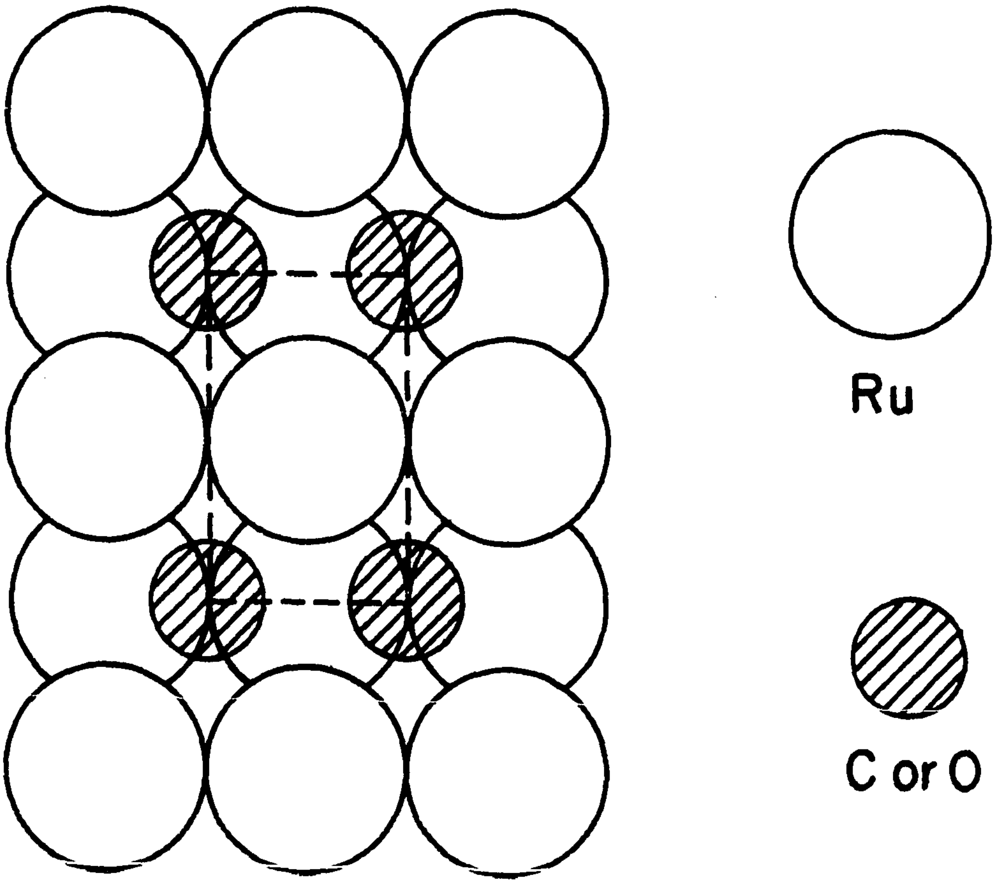
At 23.5 °C flash decomposition spectroscopy results [23,33] have indicated that carbon monoxide bonds to Ru(10$\bar{1}$0) and Ru(0001) associatively. Infrared results [13] have also indicated that carbon monoxide is associatively bonded to ruthenium. Therefore when carbon monoxide was dosed over Ru(10$\bar{1}$0) at 23.5 °C or above the 1 X 1 structure and Auger results suggested associated carbon monoxide adsorbed on the surface. The C:O data in Tables 1 and 3 bear this out for 1 X 1 structures that were not LEED beam induced to another structure.

For oxygen dosed at -135 °C, it is questionable whether the O_2 dissociated. θ_o indicates an oxygen surface coverage of 0.31 which would give a 2 X 1 at higher temperatures when oxygen does dissociate. But the only LEED pattern observed following O_2 dosing at -135 °C was a 1 X 1 pattern, presumably due to the bare surface structure.

For the 1 X 1 structure formed at -135 °C in the hydrogen 50L and 1000L doses, it is evident from θ_o and C:O that there was a high surface coverage of carbon and little oxygen, Table 5. The carbon and oxygen were from ambient carbon monoxide. These experiments indicate randomly dissociated carbon monoxide. The fact that there is more carbon than oxygen on the surface implies that oxygen is coming off the surface. In these interactions the large amount of hydrogen causes the carbon monoxide-carbon monoxide interaction to form carbon dioxide, i.e., $2CO \rightarrow C + CO_2$. I will discuss the mechanism later. There is oxygen on the surface from the hydrogen also causing the carbon monoxide-carbon monoxide interaction to form carbon-hydrogen and oxygen species on the surface.

The 1 X 1 structure with carbon monoxide randomly dissociated is shown in Figure 10. The carbon and oxygen are in the simple potential minima of the substrate lattice. The 1 X 1 formed with 2L of carbon monoxide dosed at -135 °C, Table 2, is the result of dosed carbon monoxide interacting with itself and ambient hydrogen to form a LEED pattern consisting of randomly dissociated carbon monoxide. The amounts of carbon monoxide adsorbed and the θ_o for this LEED structure and the above 1 X 1 structure formed from hydrogen adsorption at -135 °C are very similar. Since there is less hydrogen in this reaction the difference in C:O, i.e., 1:1 instead of ~ 7:1, is reasonable if hydrogen is the primary reason for the carbon monoxide-carbon monoxide reaction forming carbon dioxide which is probably the

Figure 10. Primitive unit cell of (1 X 1) overlayer due to carbon monoxide and hydrogen adsorption on Ru($10\bar{1}0$).


Ru
C or O

case in the hydrogen dosed at -135 °C experiments. The θ_o for this reaction is 0.08, if it had been less than 0.06 a 1 X 2 would probably have resulted, Table 2.

In the 3.6L dose of carbon monoxide at -135 °C experiment, Table 2, the original 1 X 1 was LEED beam induced to a 1 X 2. θ_o = 0.05 and C:O ≈ 1:1 indicate that carbon and oxygen were removed in equal amounts from the surface until the fractional coverage of total carbon and oxygen was lowered enough to form a 1 X 2. The only reasonable way for this to happen was for carbon monoxide to be removed from the surface. Carbon monoxide is always removed from the surface when the LEED beam is turned on, this has been previously shown. Therefore enough carbon monoxide was removed initially by the LEED beam that a 1 X 2 could form with randomly dissociated carbon monoxide after only a few minutes.

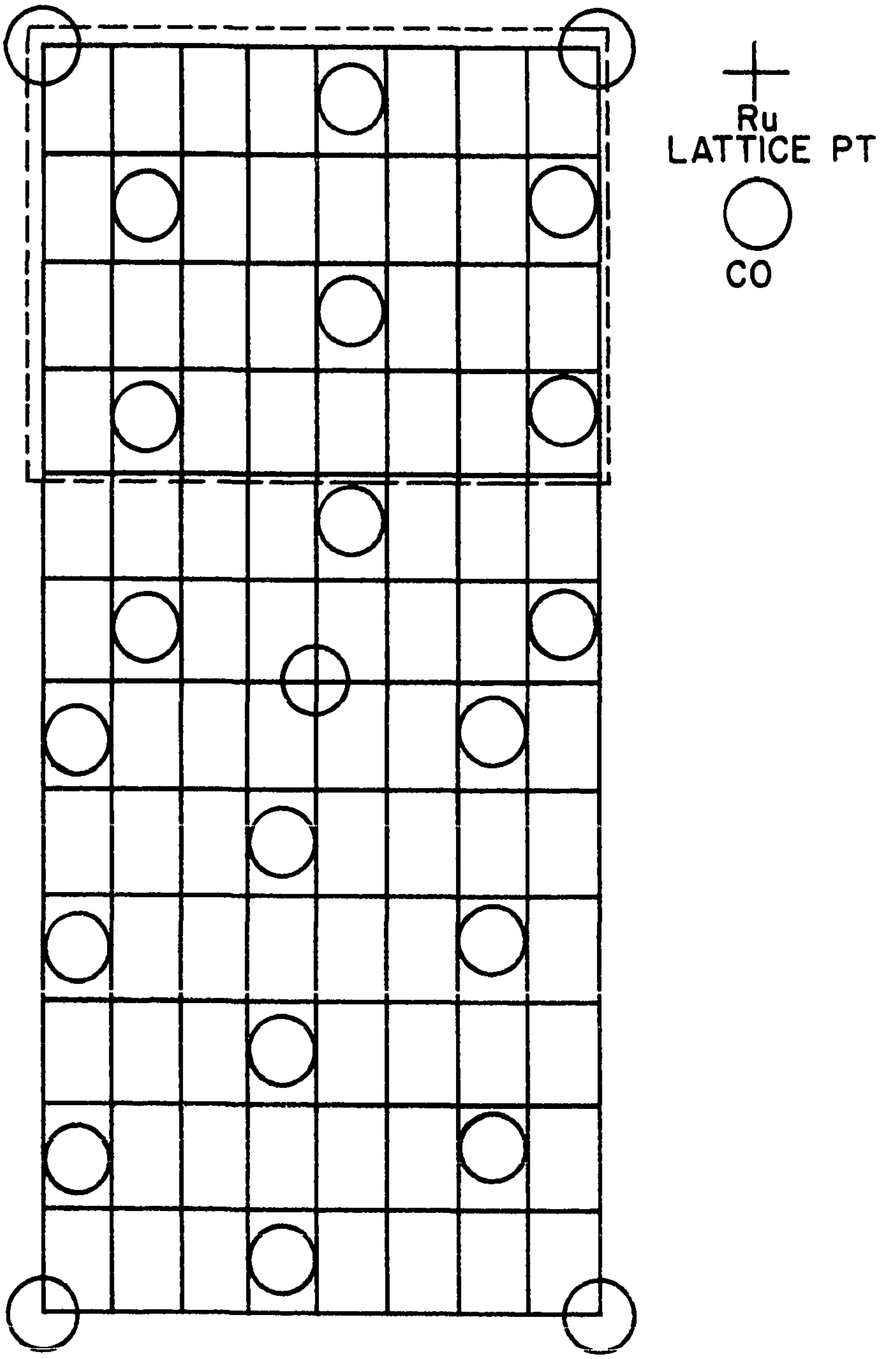
The 1 X 1 structure formed at 23.5 °C in the hydrogen 10L and 50L doses, Table 4, indicates through θ_o and C:O more carbon than oxygen on the surface in the 10L experiment and more oxygen than carbon on the surface in the 50L experiment. Random dissociation of carbon monoxide is indicated by these experiments. Also the 10L experiment indicates a carbon monoxide-carbon monoxide interaction with carbon dioxide probably expelled from the surface, and the 50L experiment indicates a methanation type interaction with methane probably expelled from the surface.

Comparing Tables 4 and 5, it appears the 1 X 2 structure results from a carbon monoxide-carbon monoxide reaction, the 1 X 1 at -135 °C results from a carbon monoxide-carbon monoxide reaction, the 1 X 1 at 23.5 °C results from a carbon monoxide-carbon monoxide reaction and a methanation type reaction, and the 1 X 1 → C(2 X 2) results from a methanation type reaction. From the discussion thus far it is evident that hydrogen interacts strongly with adsorbed carbon monoxide on Ru(10$\bar{1}$0) and dissociates carbon monoxide on Ru(10$\bar{1}$0) at 23.5 °C.

The C(8 X 12) structure formed only at 23.5 °C. The structure formed after at least 10L doses of carbon monoxide, Table 1, and with hydrogen added to the 10L and higher doses of carbon monoxide, Table 6. As stated previously there was more carbon and oxygen on the surface than was necessary for a C(8 X 12) structure with full surface coverage and no restructured surface. To accomodate this fact the C(8 X 12) is modeled as a coincident lattice in which most of the atoms lie in positions of low symmetry with respect to the underlying substrate, Figure 11.

The coincident lattice model [25,56] involves the placement of a simple uniform overlayer structure upon a known substrate geometry. The basic assumption is that the atoms in the surface layer interact with one another in such a manner as to form an overlayer structure that in general ignores the two-dimensional periodicity of the substrate, and, as a result, atoms in the surface overlayer may not

Figure 11. Nonprimitive centered-rectangular unit cell of the C(8 X 12) carbon monoxide overlayer due to carbon monoxide adsorption on Ru($10\bar{1}0$). The dashed line indicates the part of the unit cell that Figure 12 (b) reproduces.


Ru
LATTICE PT
CO

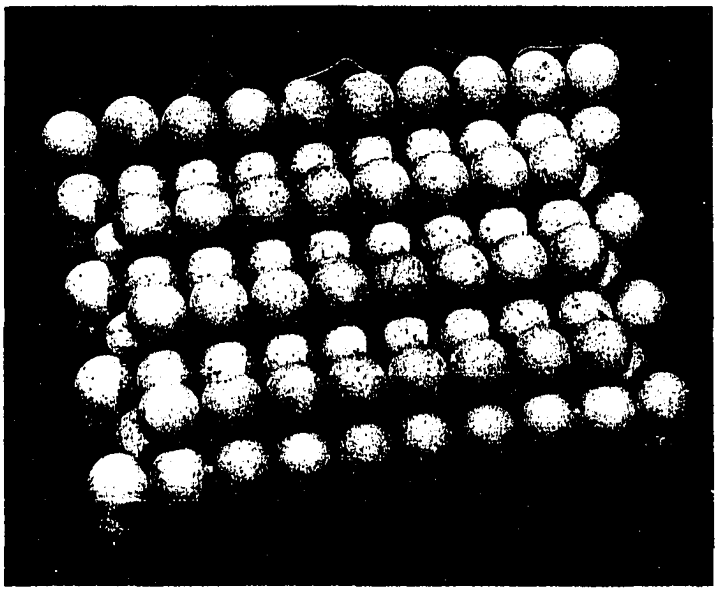
always reside on substrate sites of high symmetry that tend to maximize the bonding coordination of the surface to substrate atoms. In such models there is only an occasional coincidence between lattice points of the surface and substrate structures. The existence of such overlayers was confirmed by the first analysis of LEED intensities. Tucker and Duke [49], found that a Rh(100) C(2 X 8)-O structure was indeed a coincident lattice. Orent [25] postulated from LEED and Auger spectroscopy work that the Ru(10$\bar{1}$0) C(2 X 6)-O, Ru(10$\bar{1}$0) C(4 X 8)-O, and Ru(10$\bar{1}$0) 7 X 1-O structures were all coincident lattices.

A possible configuration for the C(8 X 12) that is consistent with θ_o and C:O values obtained in the experiments is given in Figure 11 and 12b. In this model the Ru(10$\bar{1}$0) surface has restructured to accomodate the coincident lattice. The surface coverage predicted by these figures is 20/96 or 0.21. The maximum surface coverage observed was 0.21 ± .04 in good agreement.

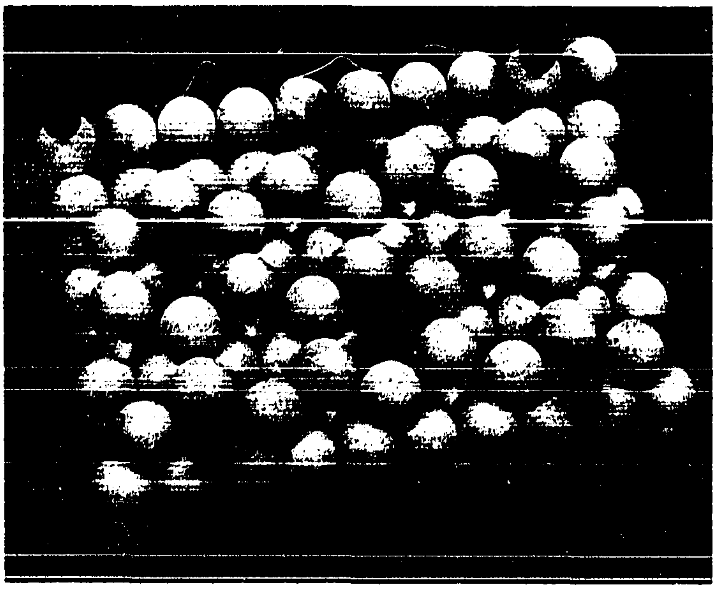
The carbon and oxygen on the surface are still in the form of carbon monoxide because it has been shown by flash decomposition spectroscopy work by Ku et al. [33] that carbon monoxide dosed over Ru(10$\bar{1}$0) at 23.5 ^{o}C is not dissociated on adsorption. Also infrared work [13] has indicated carbon monoxide is associatively adsorbed. The C(8 X 12) was not LEED beam induced and is therefore the adsorption LEED pattern.

From Figure 12b it is apparent that carbon monoxide bonded in two ways to Ru(10$\bar{1}$0) is being postulated. There is linearly bonded

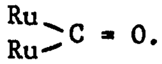
Figure 12. C(8 X 12) overlayer formed by the reconstruction of a Ru(10$\bar{1}$0) surface; (a) ideal Ru(10$\bar{1}$0) surface, (b) carbon monoxide bonded to the reconstructed Ru(10$\bar{1}$0) surface in a C(8 X 12) coincident lattice. The carbon monoxide molecules are not exactly to scale. The white balls are ruthenium, the black balls are carbon monoxide.



(a)



(b)

carbon monoxide, i.e., Ru = C = O, and bridge bonded carbon monoxide, i.e.,  $\begin{matrix}\mathrm{Ru}\\\mathrm{Ru}\end{matrix}\!\!>\!\mathrm{C} = \mathrm{O}$. According to Cotton and Wilkinson [39] linear bonding of carbon monoxide to ruthenium should be the preferred mode of bonding. Infrared work by Bell and Davydov [13] and Brown and Gonzalez [57] for carbon monoxide adsorbed on silica supported ruthenium has also indicated that carbon monoxide prefers being linearly bonded to ruthenium. Churchill et al. [41] have shown by synthesizing $H_2Ru_6(CO)_{18}$ that carbon monoxide will linearly bond to ruthenium in a ruthenium cluster that also contains hydrogen. Therefore the known presence of small amounts of hydrogen on the surface, adsorbed from the ambient, will not inhibit carbon monoxide linearly bonding to ruthenium.

Cotton and Wilkinson [39] also show that a ruthenium carbonyl compound has been formed where carbon monoxide is bridge bonded to two ruthenium atoms. Guerra and Schulman [58] after doing an infrared study of carbon monoxide adsorbed on silica supported ruthenium concluded that carbon monoxide bonds to ruthenium in the linear and bridged configurations. Johnson et al. [42] have shown by synthesizing $Ru_4(CO)_{13}H_2$ that carbon monoxide will bridge bond to two ruthenium atoms in a ruthenium cluster that also contains hydrogen. Again the known presence of small amounts of hydrogen on the surface, adsorbed from the ambient, will not inhibit and may well help carbon monoxide to bridge bond two ruthenium atoms on the surface.

Flash decomposition spectroscopy work for 3L and up doses of carbon monoxide over Ru(0001) and Ru($10\bar{1}0$) at 23.5 °C [23,33], indicated carbon monoxide desorbing at two different temperatures, i.e., about 130 °C and about 240 °C. The 240 °C desorption peak also occurred for carbon monoxide dosed below 3L and probably indicates linearly bonded carbon monoxide, since this is the preferred bonding mode for carbon monoxide bonding to ruthenium. The 130 °C peak occurred only at higher doses of carbon monoxide and was probably due to bridge bonded carbon monoxide. Figure 12b shows that in the postulated model the surface has rearranged to accommodate bridge bonded carbon monoxide and carbon monoxide bonded in this way is not the preferred bonding state for carbon monoxide on ruthenium. Therefore for this state to desorb at 130 °C and before the linearly bonded carbon monoxide state at 240 °C is reasonable.

Besides the correct surface coverage, one of the reasons the model in Figures 11 and 12b is appealing is that a C(2 X 2) structure can be formed from this model. In Table 6 it can be seen that in the 200L carbon monoxide, 1000L hydrogen experiment a C(8 X 12) and C(2 X 2) resulted. The direct implication here is that the C(2 X 2) is being formed from the C(8 X 12) since in the previous experiment, i.e., 10L of CO + 50L of H_2, only a C(8 X 12) was formed. By the surface rearranging back to a simple Ru(10$\bar{1}$0) lattice, Figure 12a, and the hydrogen dissociating the carbon monoxide, a C(2 X 2), Figure 8, can readily be formed from the proposed model for a C(8 X 12).

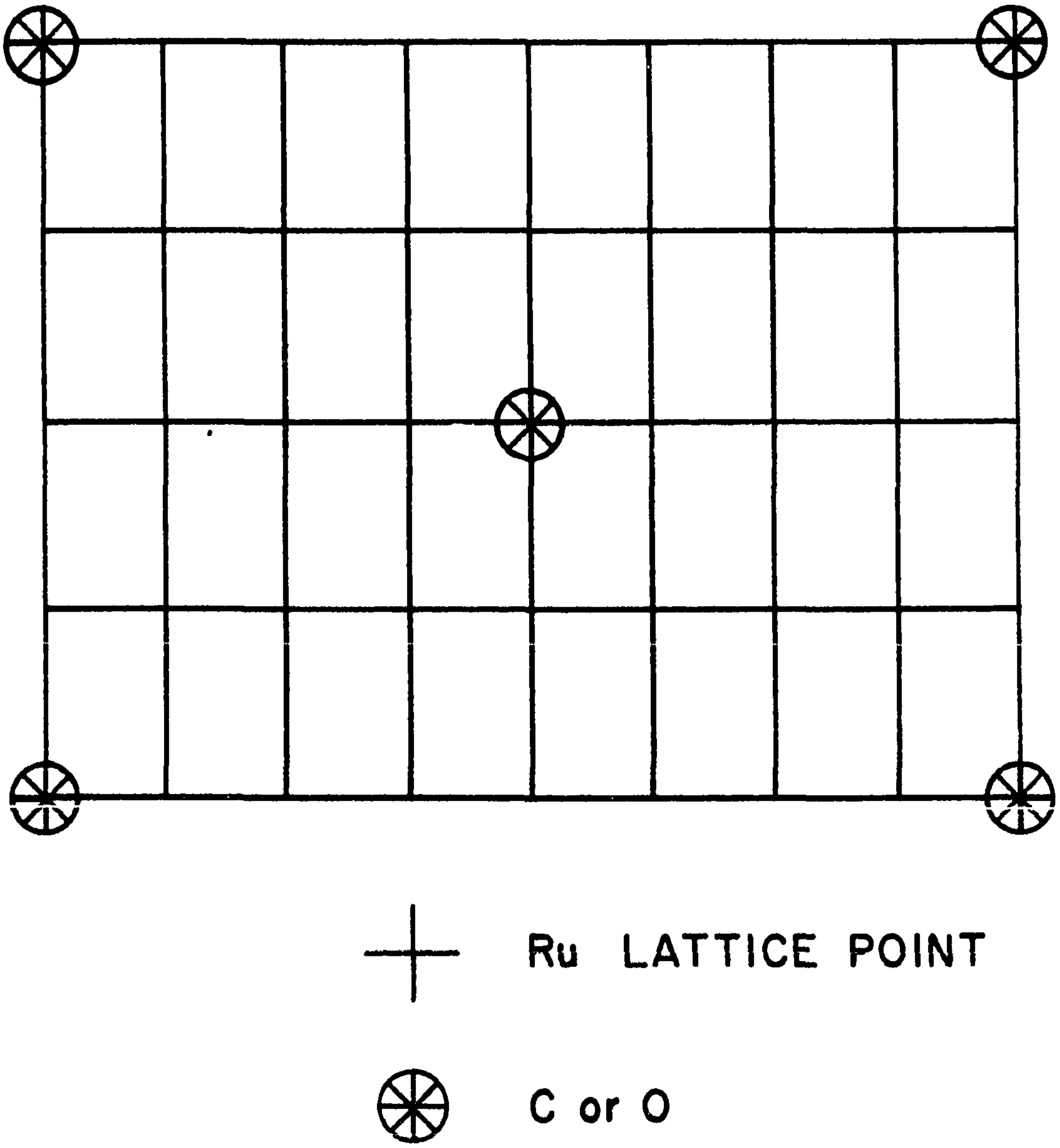
A coincident lattice that would have been consistent with the LEED and Auger results could have been formed without a restructured surface. However if the surface did not restructure it would have been difficult to rationalize why the LEED beam would not have induced a C(2 X 2) as it does in the lighter carbon monoxide doses at 23.5 °C. The restructured surface solves this problem by forming a C(8 X 12) structure that is stable under the LEED beam. The LEED data do not exclude the possibility of surface reconstruction since this reconstruction would cause only variations in diffracted intensities and would not cause the appearance of new fractional-order beams.

The restructured surface is formed by shifting the surface atoms in five adjacent rows from the four-fold holes formed by the underlying metal atoms to the adjacent three-fold holes which are only 1.6 Å away. This reconstruction is accomplished without any change in the density of surface atoms. The reduction in metal-metal coordination accompanying reconstruction is counterbalanced by the carbon monoxide-ruthenium interaction. Orent [25] proposed surface restructure for a coincident lattice of C(2 X 6)-O on Ru(10$\bar{1}$0). The LEED beam will remove some carbon monoxide over a long observation period, 15-25 minutes, but the C(8 X 12) structure will remain though losing some intensity except for one experiment. In the one exception, 50L of carbon monoxide was dosed at 23.5 °C, and the initial C(8 X 12) was beam induced to a C(2 X 2), probably because the LEED beam removed enough carbon monoxide from a particular area of the surface and it became favorable for the surface to form the original simple lattice structure, Figure 12a; the carbon monoxide and ambient hydrogen then reacted with the help of the LEED beam and a C(2 X 2) formed, Figure 8.

The C(2 X 2) + C(8 X 4) surface structure was a LEED beam induced compound structure that formed at 23.5 °C. The structure formed twice, once after a 3.6L dose of carbon monoxide, Table 1, and the other time after a 2L of carbon monoxide, 10L of hydrogen dose, Table 6. The C(2 X 2) domain has been shown to consist of dissociated carbon monoxide. Since hydrogen is a dissociating agent at 23.5 °C and the structure was LEED beam induced, the C(8 X 4) domain very likely is dissociated carbon monoxide too. θ_o was about the same in both experiments. Since C:O was 1:1 in both experiments, the total randomly dissociated surface coverage was 0.24. The maximum surface coverage of a C(2 X 2) covered surface is 50%. The maximum surface coverage of a C(8 X 4) covered unrestructured surface is 6%. Since the actual surface coverage was 0.24 or 24%, the surface was covered by 41% C(2 X 2) and 59% C(8 X 4) assuming the carbon monoxide doses in both experiments were sufficient for a monolayer of coverage. The C(8 X 4) structure is given in Figure 13.

The C(8 X 4) is a more sparsely occupied domain than the C(2 X 2) domain. The LEED beam was probably inducing hydrogen adsorbed from the ambient to interact with the adsorbed carbon monoxide from the dose to form the C(2 X 2) and C(8 X 4) domains in the 3.6L carbon monoxide dose experiment. In the 2L of carbon monoxide, 10L of

Figure 13. Doubly primitive centered-rectangular unit cell of C(8 X 4) overlayer due to carbon monoxide and hydrogen adsorption on Ru(10$\bar{1}$0).


Ru LATTICE POINT
C or O

hydrogen experiment the dosed hydrogen was interacting with the dosed carbon monoxide on the surface to form the C(2 X 2) and C(8 X 4) domains. The 2L of carbon monoxide dose at 23.5 °C, Table 1, only gave a LEED beam induced C(2 X 2) domain. Therefore with more hydrogen available for reaction in the 2L of carbon monoxide, 10L of hydrogen experiment not only was the C(2 X 2) formed, but also an additional C(8 X 4) domain indicating reactivity of carbon monoxide and hydrogen over a larger part of the ruthenium surface and/or methanation, i.e., $CO + 3H_2 \rightarrow CH_4 + H_2O$ going on.

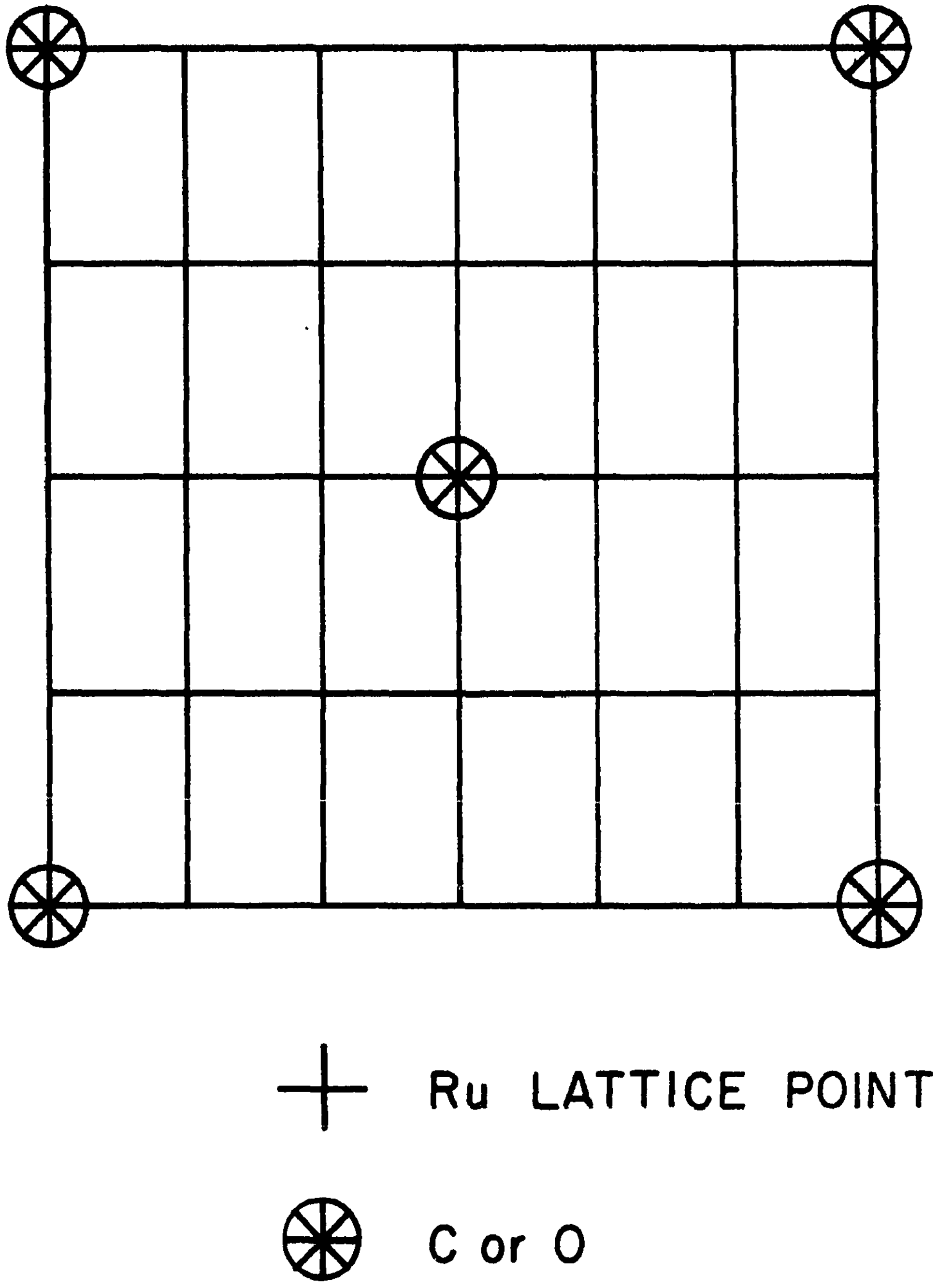
The C(2 X 2) + C(6 X 4) structure was a compound structure that was LEED beam induced at 23.5 °C and was not LEED beam induced at -135 °C. The structure formed after carbon monoxide doses at 23.5 °C, Table 1, and -135 °C, Table 2, and after a carbon monoxide plus hydrogen dose at -135 °C, Table 7.

In the 50L of carbon monoxide dose at 23.5 °C, Table 1, the C(2 X 2) + C(6 X 4) compound structure formed by LEED beam induction after 25 minutes. The C(2 X 2) has been shown to be dissociated carbon monoxide when LEED beam induced at 23.5 °C. Since the C(6 X 4) was LEED beam induced with the C(2 X 2) it was very likely formed from dissociated carbon monoxide. The C(2 X 2) has a maximum surface coverage of 50%. The C(6 X 4) has a maximum unrestructured surface coverage of 0.08 or 8%. θ_o in this experiment was 0.16 or 16%, C:O was 1:1. Therefore assuming 50L of carbon monoxide gave a full surface coverage of randomly dissociated carbon monoxide, the C(2 X 2) domain was 50% of the surface and the C(6 X 4) domain was 41% of the surface. This experiment indicates adsorbed ambient hydrogen reacting with dosed carbon monoxide on the surface to form two domains of dissociated carbon monoxide. The formation of the C(6 X 4) after the C(2 X 2) formed indicates that more of the carbon monoxide on the surface has been dissociated by interaction with hydrogen and/or methanation was going on. The C(6 X 4) is given in Figure 14.

In the 10L of carbon monoxide at -135 °C experiment, Table 2, the C(2 X 2) + C(6 X 4) compound structure was not LEED beam induced. The strongest argument for dissociation of carbon monoxide being indicated by these structures is the 2L of carbon monoxide, 10L of hydrogen experiment at -135 °C, Table 7, which also gives the C(2 X 2) + C(6 X 4) structure. In this experiment the C:O ratio was 1:2. This strongly indicates a methane forming type interaction which would remove carbon from the surface in the form of methane and indicates carbon monoxide was dissociated.

In the 10L of carbon monoxide at -135 °C experiment, hydrogen adsorbed from the ambient was reacting with dosed carbon monoxide to dissociate carbon monoxide. In this experiment carbon monoxide has interacted with itself and hydrogen to form carbon-hydrogen and oxygen species on the surface. No methane was formed and this is reasonable since carbon monoxide was in larger quantities on the surface than hydrogen. If randomly dissociated carbon monoxide is assumed, θ_o and C:O indicate a surface coverage of 0.20 or 20%.

Figure 14. Doubly primitive centered-rectangular unit cell of C(6 X 4) overlayer due to carbon monoxide and hydrogen adsorption on Ru(10$\bar{1}$0).


Ru LATTICE POINT
C or O

Assuming 10L of carbon monoxide gave a full surface coverage, the C(2 X 2) domain was 29% of the surface and the C(6 X 4) domain was 71% of the surface. What is interesting here is that compared to the previous experiment that resulted in a C(2 X 2) + C(6 X 4) at 23.5 °C, the C(2 X 2) domain is much smaller and the C(6 X 4) domain is much larger. This indicates less carbon and oxygen on the surface. It could be that a 10L dose of carbon monoxide at -135 °C did not give a full surface coverage of carbon monoxide.

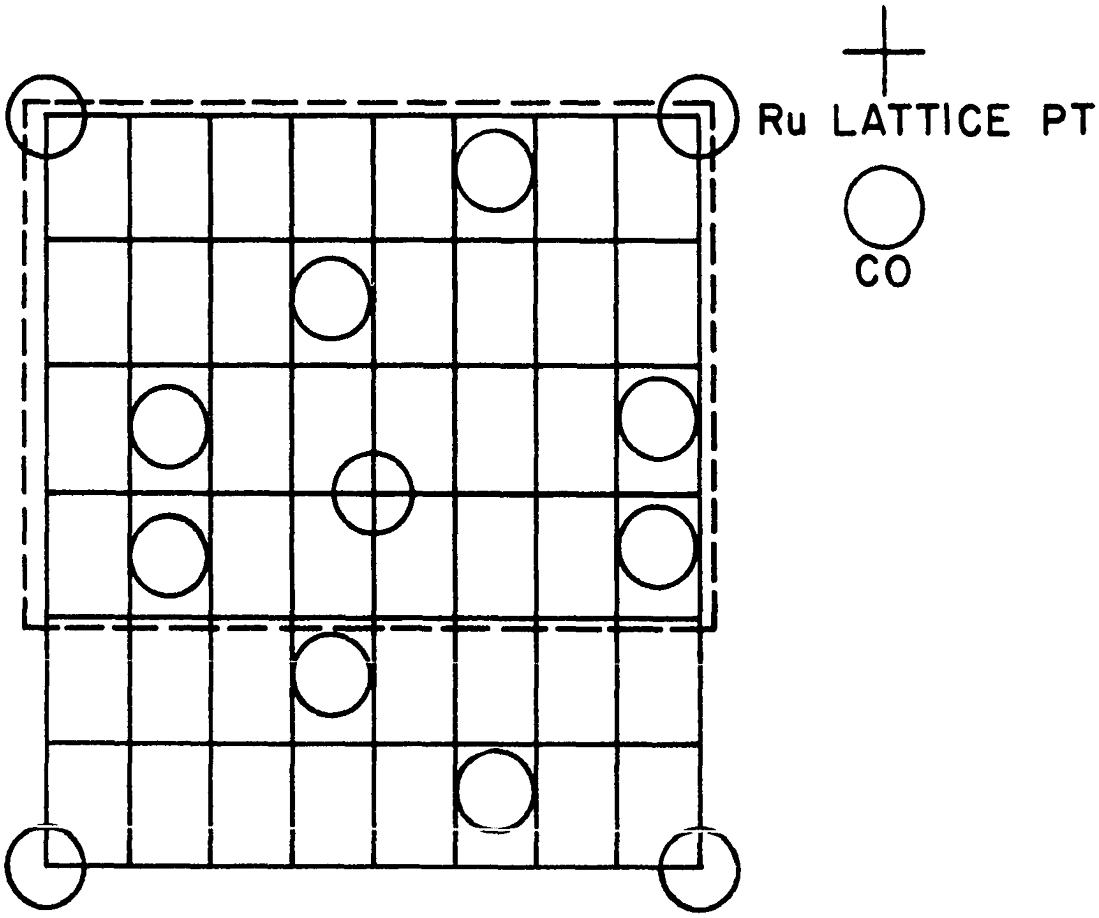
The 2L of carbon monoxide plus 10L of hydrogen at -135 °C experiment also gave a non-LEED beam induced C(2 X 2) + C(6 X 4). This definitely points to hydrogen reactivity as the reason for the formation of this compound LEED structure at -135 °C. The carbon monoxide interaction with itself and hydrogen produced carbon-hydrogen and oxygen species on the surface. Methane was produced from additional hydrogen reacting with some of the carbon-hydrogen species. This explains the C:O ratio of 1:2.

The total surface coverage in this experiment was 0.18 or 18%. Assuming a full monolayer of surface coverage, the C(2 X 2) domain was 23% of the surface and the C(6 X 4) domain was 77% of the surface. Compared to the other two experiments that resulted in a C(2 X 2) + C(6 X 4), the C(2 X 2) covers even less of the surface and more space is available from the C(6 X 4). This tends to indicate that the 2L dose of carbon monoxide did not completely cover the surface and/or methane was being formed.

The C(8 X 6) surface structure was formed after a 10L dose of carbon monoxide at -135 °C, Table 2. θ_o and C:O indicate a total surface coverage of 0.32. Since this is far more than the coverage indicated by a C(8 X 6) on an unreconstructed surface, i.e., 0.04, the C(8 X 6) has been modeled as a coincident lattice, Figure 15. The coincident lattice in Figure 15 gives a surface coverage of 10/48 or 0.21. The surface coverage indicated by the experiment for undissociated carbon monoxide was 0.16. This is reasonably close to the model coverage because fading of the LEED pattern was observed over the LEED observation period, suggesting carbon monoxide being removed from the surface by the LEED beam. The C(8 X 6) was modeled as an undissociated carbon monoxide structure because the 10L dose of carbon monoxide at -135 °C LEED pattern that was dissociated gave a C(2 X 2) + C(6 X 4) structure. Also dissociated LEED patterns have never required coincident lattices in this study. There is precedent in the carbon monoxide dose experiments at 23.5 °C. In 10L carbon monoxide dose experiments at 23.5 °C the C(8 X 12) structure was produced which indicated a coincident lattice made up of undissociated carbon monoxide.

The surface has also been restructured, Figure 16b. The main reason for doing this was to make it more difficult for the C(8 X 6) to reform into a dissociated carbon monoxide LEED structure, i.e., the 2 X 1 or C(2 X 2) + C(6 X 4), by LEED beam inducement. LEED beam inducement does occur at -135 °C as illustrated by the 3.6L of CO at -135 °C experiment, Table 2. The 2 X 1 LEED structure

Figure 15. Nonprimitive centered-rectangular unit cell of the C(8 X 6) carbon monoxide overlayer due to carbon monoxide adsorption on Ru(10$\bar{1}$0). The dashed line indicates the part of the cell that Figure 16(b) reproduces.

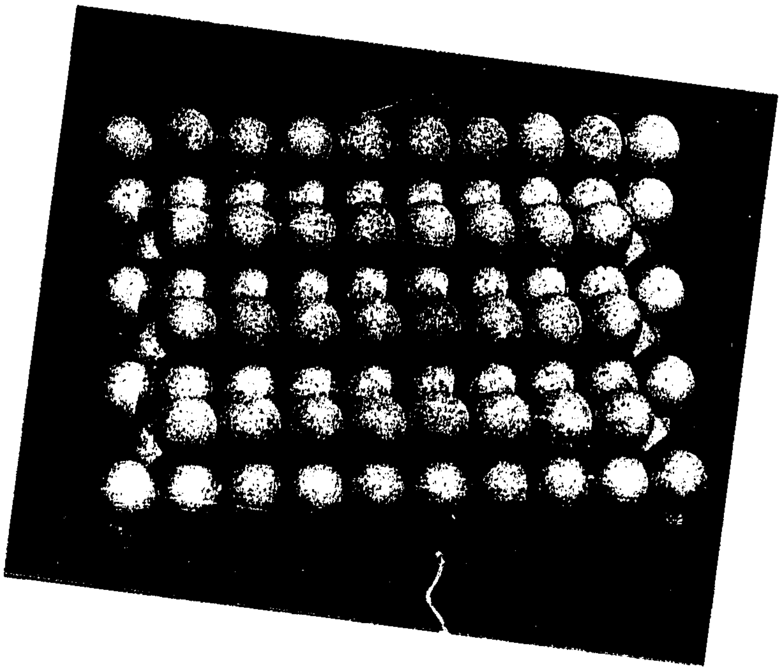

Ru LATTICE PT
CO

will be discussed later and it will be shown that it is a dissociated carbon monoxide LEED structure. The C(8 X 6) did not change under LEED beam inducement after 15 minutes. This indicates a stable coincident lattice structure which directly implies a restructured surface. The C(8 X 6) coincident lattice, Figure 15, is configured so that it would be straight forward for the surface to reform into a simple Ru($10\bar{1}0$) lattice and the carbon monoxide to dissociate to a 2 X 1. This was done because when hydrogen, a known strong dissociating agent, is added to carbon monoxide that has been dosed at 10L, i.e., 10L of CO + 50L of H_2 at -135 °C (Table 7), a 2 X 1 results.

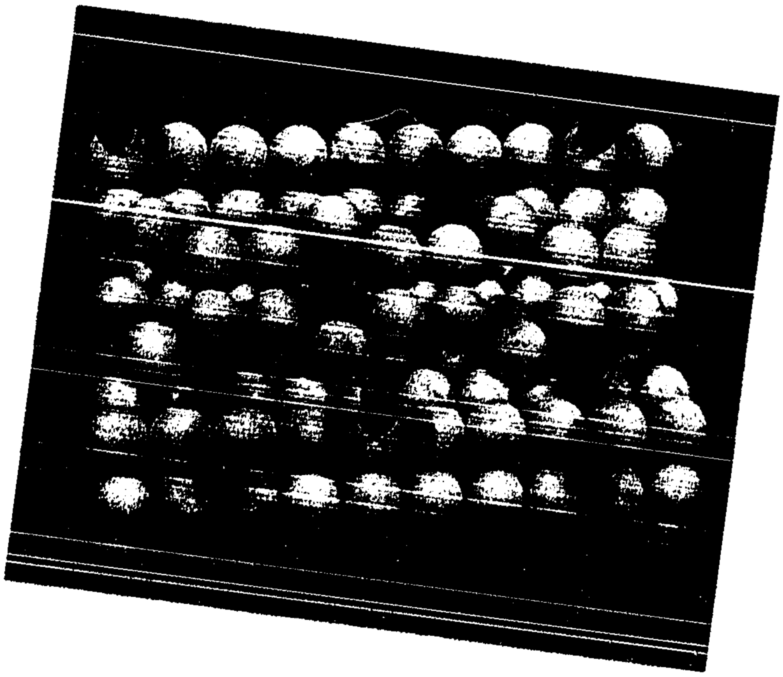
The restructured surface in Figure 16b is formed by shifting the surface atoms in 2 adjacent rows from the four-fold holes formed by the underlying metal atoms to the adjacent three-fold holes which are only 1.6 Å away. This reconstruction is accomplished without any change in the density of surface atoms. The reduction in metal-metal coordination accompanying reconstruction is counterbalanced by the carbon monoxide-ruthenium interaction as in the C(8 X 12). Carbon monoxide has been bridge and linearly bonded in the C(8 X 6) model, Figure 16b. The precedent here was the C(8 X 12) model where both these types of bonding were postulated.

The 2 X 1 surface structure was formed only at -135 °C. The 2 X 1 resulted from 50L and higher doses of carbon monoxide, Table 2, and 10L and higher doses of carbon monoxide with hydrogen, Table 7. The 2 X 1 structure was formed with hydrogen, which interacts strongly

Figure 16. C(8 X 6) overlayer formed by the reconstruction of a Ru($10\bar{1}0$) surface; (a) ideal Ru($10\bar{1}0$) surface, (b) carbon monoxide bonded to the restructured Ru($10\bar{1}0$) surface in a C(8 X 6) coincident lattice. The carbon monoxide molecules are not exactly to scale. The white balls are ruthenium, the black balls are carbon monoxide.



(a)



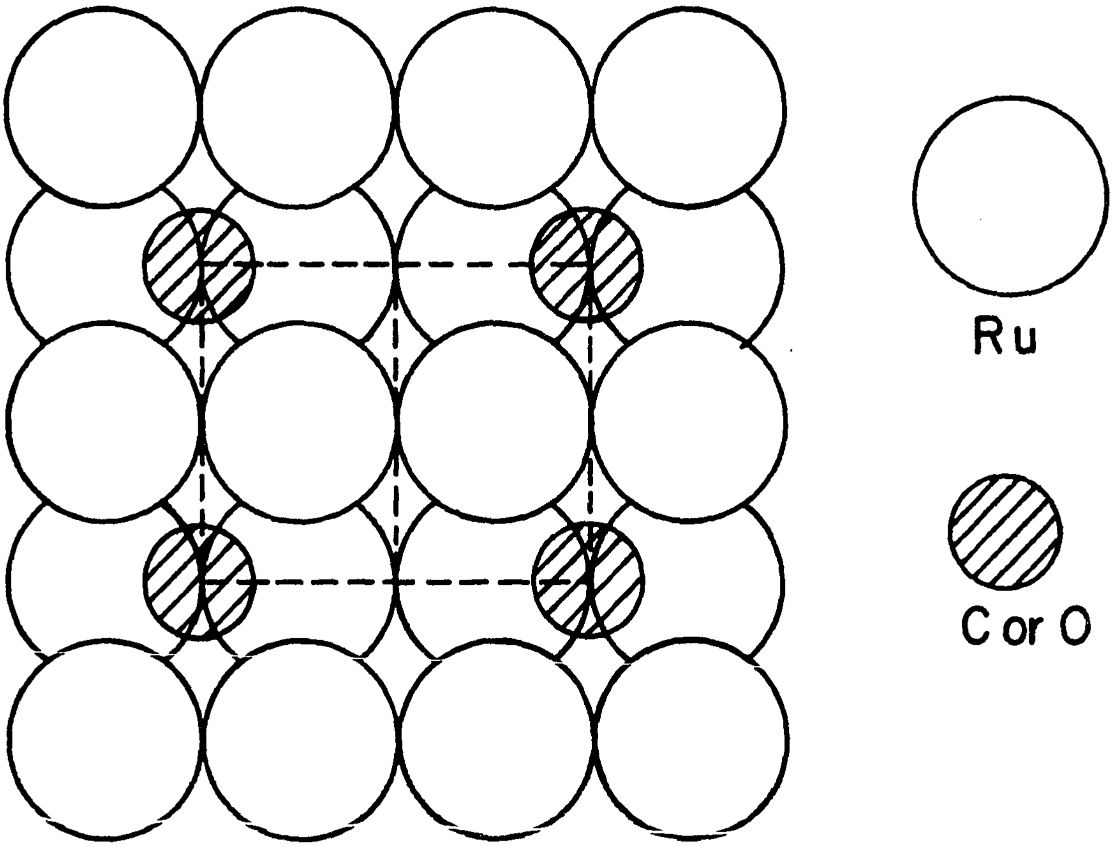
(b)

with carbon monoxide, consistently and this is the strongest reason for associating this structure with dissociated carbon monoxide. The 2 X 1 structure at full coverage of the surface would indicate 50% coverage. θ_o and C:O indicate the highest oxygen and carbon coverage is 0.18. This coverage is much more consistent with a randomly dissociated carbon monoxide surface coverage, i.e. 25% C and 25% O, than an undissociated carbon monoxide surface coverage, i.e. 50% C and 50% O. When the fading of the 2 X 1 under LEED beam observation is taken into account, randomly dissociated carbon monoxide surface coverage is reasonable. Carbon monoxide interacting with itself and hydrogen adsorbed from the ambient and dosed is postulated to produce carbon-hydrogen and oxygen species on the surface. These species form a stable configuration and not enough hydrogen is present relative to the amount of carbon monoxide to produce methane or carbon dioxide. The 2 X 1 structure with carbon and oxygen randomly orientated is shown in Figure 17. The carbon and oxygen are in the simple potential minima.

The Interaction of Carbon Monoxide and Hydrogen with Ru(10$\bar{1}$0) as Implied by the LEED and Auger Results

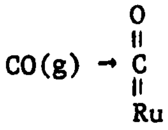
The experimental results indicate that hydrogen and carbon monoxide are interacting at 23.5 °C, or close to it, and carbon monoxide is interacting with itself and hydrogen at -135 °C and 23.5 °C. The Boudouard reaction, i.e., $2CO \rightarrow C + CO_2$, appears to occur at -135 °C

Figure 17. Primitive unit cell of (2 X 1) overlayer due to carbon monoxide and hydrogen adsorption on Ru(10$\bar{1}$0).


Ru
C or O

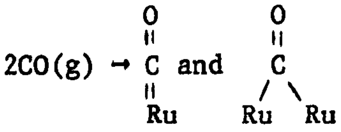
and 23.5 °C producing carbon dioxide, and hydrogen appears to promote this reaction. Methane appears to be produced at 23.5 °C via a methanation type reaction, i.e., $CO + 3H_2 \rightarrow CH_4 + H_2O$, and produced at -135 °C via carbon monoxide interacting with itself and hydrogen. The LEED beam will help hydrogen induce dissociation of carbon monoxide at 23.5 °C and will remove adsorbed carbon monoxide and hydrogen from the surface at 23.5 °C and -135 °C.

At 23.5 °C and -135 °C carbon monoxide will adsorb on the surface associatively. In light doses, i.e., 3.6L and below, carbon monoxide will probably adsorb linearly [39]:



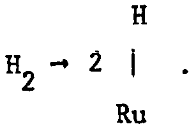
$$CO(g) \rightarrow \begin{array}{c} O \\ \| \\ C \\ \| \\ Ru \end{array}$$

In heavy doses, i.e., 10L and up, carbon monoxide will adsorb linearly and in the bridged position:



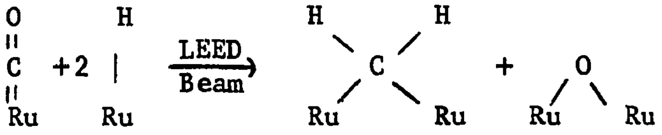
$$2CO(g) \rightarrow \begin{array}{c} O \\ \| \\ C \\ \| \\ Ru \end{array} \text{ and } \begin{array}{c} O \\ \| \\ C \\ / \ \backslash \\ Ru \quad Ru \end{array}$$

Hydrogen will adsorb and dissociate into atomic hydrogen [34,35]:

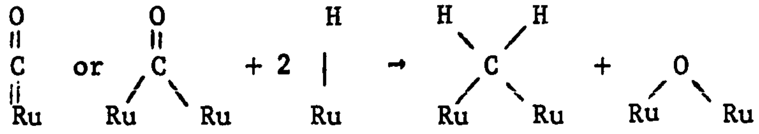


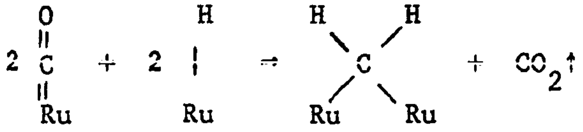
$$H_2 \rightarrow 2 \begin{array}{c} H \\ | \\ Ru \end{array} .$$

In light doses of carbon monoxide at 23.5 °C the LEED beam will help ambient adsorbed or dosed hydrogen to dissociate carbon monoxide:

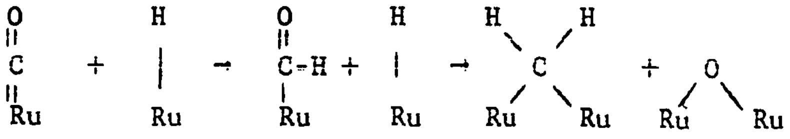


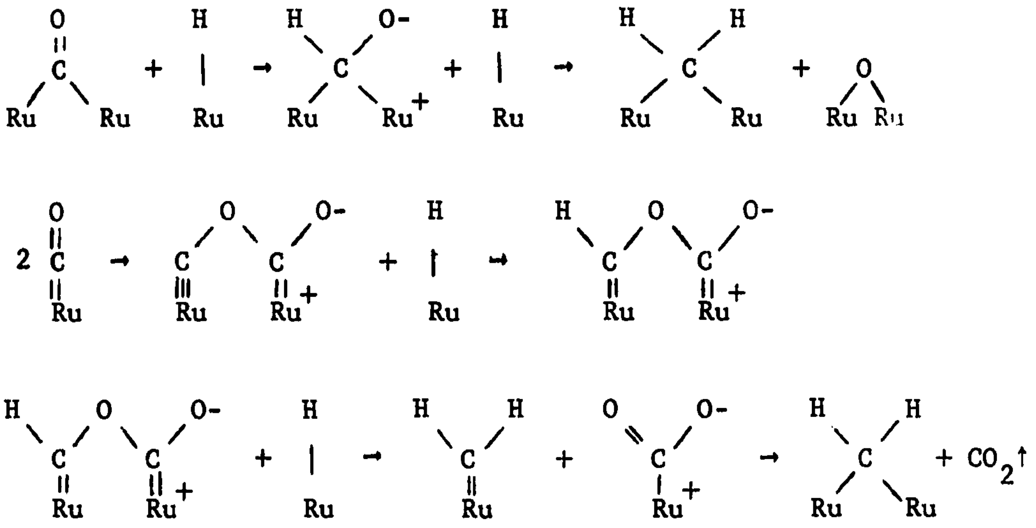
When hydrogen is present on the surface in high enough quantity relative to carbon monoxide, it will react with the associatively adsorbed carbon monoxide without the aid of the LEED beam and dissociate carbon monoxide at 23.5 °C, or facilitate carbon monoxide reacting with itself to form carbon dioxide at 23.5 °C and -135 °C.



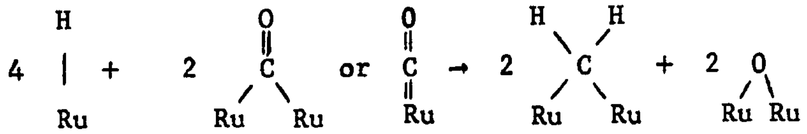


It is postulated that the mechanism for these reactions involves hydrogen attack at the carbon atom:

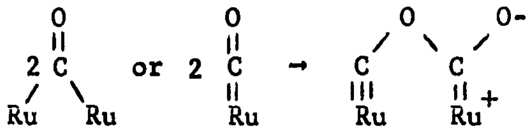


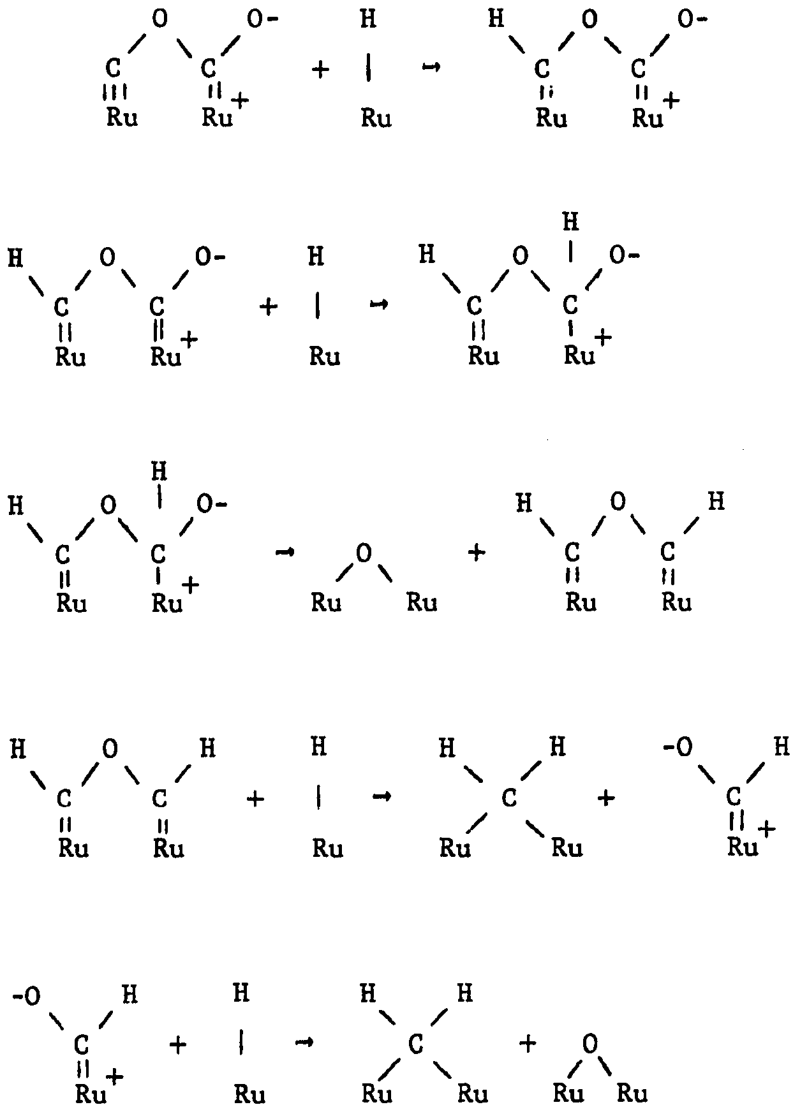


When hydrogen is more or less than the carbon monoxide dose at -135 °C a carbon monoxide-carbon monoxide interaction results that hydrogen facilitates:

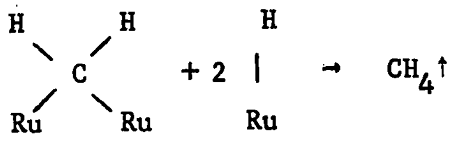


It is postulated that the mechanism for this reaction involves hydrogen attack at the carbon atoms:

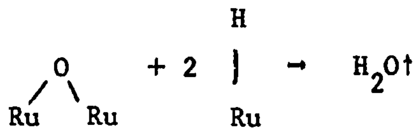




Additional hydrogen at 23.5 °C and -135 °C, and/or LEED beam inducement at 23.5 °C, will remove carbon-hydrogen compounds, probably methane, from the surface:



Additional hydrogen and/or LEED beam inducement at 23.5 °C, will also remove oxygen-hydrogen compounds, probably water, from the surface:



The results indicate that carbon monoxide molecules show a strong preference for interacting at -135 °C and much less of a tendency to interact at 23.5 °C. Hydrogen and carbon monoxide are reluctant to react at 23.5 °C. Large amounts of hydrogen relative to carbon monoxide or the LEED beam is necessary for hydrogen and carbon monoxide to interact at 23.5 °C. Methane is produced via carbon monoxide interacting with itself and hydrogen at -135 °C and via a methanation type interaction at 23.5 °C.

FUTURE INVESTIGATIONS

The immediate project would be to study the LEED patterns formed with some other electronic techniques. A LEED intensity study would be a large help to firmly establish the atomic positions of the adsorbate carbon and oxygen atoms on the $Ru(10\bar{1}0)$ surface. An XPS X-ray induced photoelectron spectroscopy, study of the LEED patterns would hopefully give chemical bonding information which would be very helpful in determining whether the carbon monoxide was dissociatively or undissociatively adsorbed.

One of the major problems in the study was ambient hydrogen and carbon monoxide. A system that could pump hydrogen and carbon monoxide better, and where the $Ru(10\bar{1}0)$ crystal could be brought to 23.5 °C and -135 °C more quickly, could be well utilized. Then experiments where hydrogen was dosed before carbon monoxide could be run and the results would be most illuminating. A flash decomposition spectroscopy kinetic study could also be undertaken, in particular at -135 °C, to provide rates and desorption products for carbon monoxide, hydrogen, and carbon monoxide plus hydrogen interactions with $Ru(10\bar{1}0)$.

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