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Publication Date
1983-06-01
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June 1983
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This work was supported by the Division of Material Sciences,
Office of Basic Energy Sciences of the U. S. Department of Energy
under Contract No. DE-AC03-76SF00098
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ABSTRACT

Epitaxial layers of copper were formed on Pt(111) and Pt(553) single crystal surfaces by condensation of copper atoms from the vapor. Surface alloys were formed by diffusing the copper atoms into the platinum substrate at temperatures above 550 K. The activation energy for this process was found to be -120 KJ/mole. These Pt/Cu surfaces were characterized by LEED, AES, and TDS of CO. The copper grows in islands on the Pt(111) surface and one monolayer is completed before another begins. There is an apparent repulsive interaction between the copper atoms and the step sites of the Pt(553) surface which causes a second layer of copper to begin forming before the first layer is complete. Epitaxial copper atoms block CO adsorption sites on the platinum surface without effecting the CO desorption energy. When the copper is alloyed with the platinum however, the energy of desorption of CO from the platinum was reduced by as much as 20 KJ/mole. This reduction in the desorption energy suggests an electronic modification that weakens the Pt-CO bond.
INTRODUCTION

Studies of the deposition and growth of one transition metal on the ordered surface of another transition metal are important to understand the nature of epitaxy and the mechanism of metal crystal growth. Investigations of how alloys form by the diffusion of one of the constituents into the other from the surface reveal the mechanism of the initial stages of alloying. The copper-platinum system is a good choice for both of these studies. The interatomic distance of the metals is similar (copper is 8% smaller than platinum). Their heat of mixing is exothermic (-10 kcal/mole) and they form several ordered alloy structures (Pt₃Cu, PtCu, and PtCu₃).

The catalytic properties of a transition metal surface can also be drastically altered by the addition of another metal which may not itself catalyze the reaction of interest. The catalytic properties of Cu/Pt alloys supported on silica in the hydrocarbon conversion reaction have been studied [1-3]. These investigations showed an increased selectivity for cracking for the alloys as compared to pure platinum, a rather surprising result since copper itself does not exhibit activity for cracking. Because of the poor characterization of the alloy surface, interpretation of these results is difficult. Impurities such as oxygen, which would have a profound effect on the reaction [4], could not be detected if present. Since copper tends to segregate to the surface of Cu/Pt alloys [5], the bulk compositions reported are not representative of the composition of the catalytic surface. Also, ordering and structure of the alloy surface can effect the selectivity of the catalyst, again impossible to detect using supported alloys.
In order to better understand the novel selectivity and activity of the Cu/Pt system, the surface properties of the alloy need to be better characterized. In this paper we report the results of experiments directed toward understanding the composition, structure, and chemisorption characteristics of this alloy surface. The atomically flat, hexagonally closest packed Pt(111) surface and the stepped Pt(553) surface were studied. Copper was deposited by evaporation onto the crystal surface. Surface alloys were formed by heating the sample to temperatures at or above 550 K, allowing the copper to diffuse into the platinum substrate. Surface structure was studied using low energy electron diffraction (LEED), surface composition was determined using Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS) of CO was used to probe the changes in bonding characteristics of the platinum at the alloy surface.
EXPERIMENTAL

Experiments were carried out in an ion-pumped stainless steel ultrahigh vacuum chamber equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and a UTI-100C mass spectrometer placed -6 cm away from the crystal face. LEED spot patterns were analyzed but no attempt was made to analyze the diffraction spot intensities. A 2000 V electron beam with an incidence angle of -70° from the surface normal was used as the excitation source for AES. Auger electron energies were analyzed with the 4-grid LEED optics used as a retarding field analyzer. The platinum crystal could be heated by conduction from a resistively heated 0.5 mm Ta wire which was spot welded around the edges of the sample. Cooling of the crystal to -250 K was achieved by passing liquid nitrogen over the copper feedthroughs leading to the sample. Temperatures were determined using a chromel-alumel thermocouple spot welded to the back of the crystal. Samples were cleaned with a combination of argon ion bombardment and heat treatment in $10^{-7}$ torr of oxygen. The crystal was cleaned after each thermal desorption when working with epitaxial copper. Deposition of copper was performed by evaporation from a resistively heated tungsten wire. The evaporation source was encased in a tantalum housing with an exit slit which collimated the beam of copper atoms. Fluxes obtained were on the order of $10^{14}$ copper atoms/cm² min. The flux of copper atoms could be interrupted by means of a rotatable shutter.
RESULTS

a) The Growth of Copper Layers on Pt(111)

AES has been used to determine the growth mechanism of one metal deposited on a single crystal substrate of another metal [6]. In this procedure, the Auger signal of both the substrate and the adsorbate are plotted versus the deposition time of the adsorbate. If a constant sticking coefficient is assumed for the adsorbate, the time of deposition from a constant flux source is proportional to the coverage of the adsorbate. The abscissa can then be labeled in units of deposited metal monolayers. In Fig. 1 the Auger signal is normalized to the peak-to-peak height of the pure platinum \(N_6\) Auger transition at 150 eV (Pt-150 V). The Pt-150 V signal drops off sharply and linearly with copper coverage, with a change of slope at a coverage assigned to one monolayer of copper. Another change of slope is observed after an equal period of deposition indicating the completion of a second monolayer of copper. At low copper coverages the signal of the copper \(M_{2,3}V\) Auger transition at 105 eV (Cu-105 V) is buried in the background of the platinum Auger spectra. However, once the Cu-105 V signal is resolved the growth of the signal is linear with coverage with breaks at the same coverages as the breaks that occur in the Pt-150 V signal versus copper coverage plot. This behavior is indicative of a layer-by-layer growth [6] mechanism in which one monolayer of copper is formed before the second begins and the growth continues layer-by-layer.

The clean Pt(111) single crystal surface showed the expected hexagonal LEED pattern. As copper was deposited neither the spot positions nor their sharpness changed and no new spots appeared up to one
monolayer copper coverage. Relative diffraction spot intensities changed somewhat but no attempt was made to analyze this behavior. After more than one monolayer of copper had been deposited, the diffraction spots began to lose their sharpness and intensity. When four monolayer had been deposited a (12×12) coincidence pattern was observed after slight annealing at 450 K. This type of pattern has been observed for silver deposited on a Cu(111) substrate [7]. Upon heating the platinum crystal which had several monolayers of copper deposited onto it to 500 K, the diffraction spots initially lost intensity and sharpness. After further annealing at this temperature a (2×2) pattern was observed on several occasions.

The TDS of CO from the Pt(111) surface with several different coverages of copper are shown in Fig. 2. The sample was exposed to CO to obtain a saturation coverage of CO(12L) at 250 K. At this temperature the CO will adsorb only on the platinum sites. The TDS is therefore representative of desorption from the platinum surface atoms. Figure 3 shows a plot of the area under these curves, which is proportional to the amount of CO desorbed, versus the copper coverage. The amount of CO desorbed falls off linearly with copper coverage and levels off at a copper coverage corresponding to the first break in the plot of the Auger signal versus copper coverage, confirming the assignment of one monolayer of copper to this coverage. The residual CO desorption at this and higher copper coverages is due to desorption from the platinum crystal edges (which were not exposed to copper or masked in any other way) and from the tantalum support wires. The position (temperature) of the desorption peak remains constant until high copper coverages. In
addition to the main desorption peak, a low temperature shoulder is present. The saturation coverage of CO on the Pt(111) surface at 250 K is 0.5. Since one complete monolayer of copper is required to block all CO adsorption sites on the platinum surface, two copper atoms are required to block one CO adsorption site on the platinum.

b) Diffusion of Surface Copper into the Platinum Substrate

When copper is deposited onto the platinum substrate and subsequently heated, it diffuses into the platinum bulk. The extent of diffusion was monitored by following the Pt-150 V Auger signal with time at a constant temperature and assuming a direct proportionality of this signal to the fraction of the surface covered with platinum. The change in the amount of copper at the surface with time was calculated from this data. The diffusion was studied at temperatures between 520 K and 580 K. The diffusion process was modeled as described by Schouten for the dissolution of carbon into nickel [8]. The model has also been successfully used to obtain the activation energy for the diffusion of rubidium into silver [9]. Briefly, the model utilizes a constant plane source solution to Fick's second law for diffusion in one dimension. Integrating this solution with respect to time gives the total amount of copper diffused into the bulk and can be equated to the amount of copper depleted from the surface. It was found that

$$\Delta \theta_{Cu} = -mt^{1/2}$$

where m is a constant proportional to the square root of the diffusion coefficient, D^{1/2}. If Arrhenius type behavior is assumed, the activation energy for this process can be determined from the slope of the
plot of $\ln m$ versus $T^{-1}$. Such a plot is shown in Fig. 4. A linear fit was obtained with an activation energy of 120 KJ/mole. This value falls between values for the activation energy for copper surface diffusion [10] and bulk diffusion for copper in a Cu/Pt alloy [11].

c) Thermal Desorption of CO from Cu/Pt Alloy Surfaces

TDS of CO from the alloy surfaces are shown in Fig. 5. Two monolayers of copper were deposited onto the Pt(111) surface and then exposed to 12 L of CO. No desorption was seen since CO does not adsorb on copper at 250 K and $10^{-8}$ torr. The crystal was heated to 600 K during this thermal desorption. This temperature rise resulted in the diffusion of some of the surface copper into the platinum bulk. This alloyed surface was exposed to 12 L of CO and the TDS showed a small, broad peak. The shape and position of the desorption peak changed noticeably with each successive heat treatment until a surface composition of $X_{Cu} = 0.85$ was reached. (Surface composition was determined from the CO desorption yield from the CO saturated alloy surface relative to the yield from the CO saturated pure platinum surface. This will be considered further in the discussion section.) This surface was relatively stable. The temperature at which the CO desorption rate from this alloy surface reached a maximum was shifted down -100 K from the temperature of maximum CO desorption rate from a pure Pt(111) surface. The fraction of copper in the surface alloy could further be reduced by flashing the crystal to increasingly higher temperatures. Using the standard Redhead formula [12] and assuming a pre-exponential factor of $10^{13}$ s$^{-1}$, the temperature at which the rate of desorption is greatest can be used to calculate an energy of desorption. The energy of
desorption of CO from the alloy surfaces is plotted versus the surface composition in Fig. 6. The energy of desorption decreases smoothly with increasing copper concentration at the surface. In all cases only one desorption peak was observed with no shoulders present.

Usually, the repulsive interaction between CO molecules adsorbed on the surface results in a shift to lower temperature of the desorption peak as the CO coverage is increased. This effect is seen in Fig. 7, where a series of TDS of CO from a Pt(111) surface after various CO exposures is shown. Figure 8 shows a similar series of TDS of CO from an alloy surface containing 76% copper. The behavior observed for the alloy surfaces was the same as that for the pure platinum surface. In Fig. 9 the calculated energy of desorption of CO is plotted versus the amount of CO desorbed relative to the amount of CO desorbed from the CO-saturated pure platinum surface. The energy of desorption decreases with increasing CO coverage for both the pure platinum and the alloy surfaces. Extrapolation to an initial CO coverage of zero gives the CO desorption energy without any contribution from CO intermolecular repulsions, i.e., a desorption energy which is dependent only on the Pt-CO bond strength. The energy of desorption from the alloy surface containing 76% copper at an initial CO coverage of zero is 24 kcal/mole lower than the energy of desorption of CO from the pure platinum surface.

d) The Growth of Copper on Pt(553)

The growth of copper on the Pt(553) surface, which is a stepped surface with terraces of (111) orientation, is somewhat different than copper growth on the (111) surface of platinum. The Auger signal versus copper coverage plot for this surface is shown in Fig. 10. As was the
case with the Pt(111) surface, the Pt-150 V signal drops off rapidly with copper coverage. However, unlike the Pt(111) surface, the signal is not linear with copper coverage and there are no breaks in the curve. It would seem from this behavior that the copper almost forms a complete monolayer, but before completion a second layer begins.

The TDS of CO from the Pt(553) surface with various coverages of copper (Fig. 9) show a decrease in the desorption yield with increased copper coverage. In Fig. 12 it can been seen that again the CO desorption yield decreases linearly with the copper coverage until coverages near one monolayer are reached. At near monolayer coverage the curve is rounded, again indicating that a second layer begins to form before the first is complete. Closer inspection of Fig. 11 reveals a cause for this behavior. In the TDS of CO from clean Pt(553) there is a peak around 400 K and a high temperature shoulder. The main desorption peak is due to desorption of CO from the terrace sites and the high temperature shoulder is due to desorption from the step sites. As copper is deposited onto the surface the desorption of CO from the terrace sites is attenuated whereas the desorption from the step sites remains unchanged. This trend continues until high copper coverages. This site selectivity of the copper atoms adsorbing only onto the platinum terrace sites is responsible for the growth mechanism observed.
Copper growth on Pt(111) was seen to proceed by a layer-by-layer mechanism. This is partly due to the lower surface free energy of copper, but is also the result of a relatively strong interaction between the copper and the platinum. This favorable interaction would be expected since the bulk alloy has an exothermic heat of mixing [13]. The LEED results show that copper, which has a bulk lattice constant that is 8% smaller than platinum's, takes on the platinum lattice spacing for the first few monolayers of copper, also indicating a strong interaction between the two metals. The sharpness of the LEED spots and low background intensity for copper coverages up to one monolayer of copper suggest that the copper is growing in islands. If this was not the case and the copper atoms were randomly scattered across the platinum surface, the TDS of CO would show an increase in the temperature of the desorption peak with increasing copper coverage due to a separation of the CO molecules, resulting in less of a repulsive interaction. This increase in the temperature of the desorption peak was not observed. The position of the desorption peak remained constant until near monolayer coverages of copper. The new feature which did appear when copper was deposited is a low temperature shoulder. This is probably due to desorption from the edge of the copper islands. It may also indicate some alloy formation although this would be a minor contribution since the rate of diffusion is negligible at 250 K, the temperature at which the copper was deposited. The TDS also shows a linear decrease in the amount of CO desorbed with copper coverage and that two copper atoms are
required to block one CO molecule, a behavior that requires island formation.

The Pt(553) surface is a stepped surface with terraces of (111) orientation five atoms wide and steps of monatomic height. The behavior of copper on the terraces would be expected to be similar to that described for the Pt(111) surface and any changes in the behavior of the copper atoms on the surface as a whole to be induced by the steps. As was seen, the plot of the Auger signal versus copper coverage for this surface indicates that the growth mechanism is no longer layer-by-layer. The sharp decrease in the Pt-150 V signal with copper coverage and the linear decrease in the desorption yield of CO to near monolayer coverages of copper suggests that the first monolayer is nearly completed before a second begins. The TDS of CO from the Pt(553) surface shows that the copper preferentially adsorbs at sites away from the step site where CO adsorbs. Since it would be energetically favorable for the copper atoms to increase their coordination with the platinum, it seems reasonable the copper growth begins at the bottom of the steps and moves out onto the terraces. The energetically least favorable copper adsorption site would be at the top of a step where the coordination with the platinum is low. The energy of adsorption of copper at the top of a step appears to be close to the energy of adsorption of copper on top of the first layer of copper. Thus the second monolayer begins forming before the first is complete. These results would suggest that the adsorption site for the CO is located at the top of the step and that the presence of a copper atom at the bottom of the step has little effect on the bonding of that CO molecule.
The low temperature shoulder in the TDS of CO is much more pronounced for the Pt(553) with sub-monolayer copper coverages than for the Pt(111) with sub-monolayer copper coverages and the desorption yield of this shoulder is nearly constant over a broad range of copper coverages on the Pt(553) surface. This behavior can be rationalized in the following way. The copper is preferentially adsorbed at the bottom of the platinum steps creating one-dimensional islands of copper. The desorption from the edges of these copper islands gives the low temperature shoulder in the TDS. As more copper is deposited it adds to the edge of the copper islands already formed, resulting in a nearly constant copper island edge site concentration.

The TDS of CO from the alloy surfaces show a significant decrease in the temperature of the desorption peak. We believe that this shift of the CO desorption peak is indicative of a decrease in the energy of desorption of CO from the platinum at the surface of the Cu/Pt alloys brought about by a copper induced electronic change in the platinum. UPS studies carried out by Shek et al. [14] on Cu/Pt alloys indicates an electronic modification of the constituents of the alloy. Using 150 eV synchrotron radiation, an energy at which platinum has a Cooper minimum, they were able to selectively study the electronic structure of copper in the alloy. An increase in the intensity between $E_F$ and -1.4 eV was attributed to significant Cu3d-Pt5d hybridization. XPS studies have shown that there is little or no charge transferred between the copper and platinum atoms when alloyed [15]. This would imply that the weakening of the CO-Pt bond at the alloy surface is due to a rehybridization of the platinum orbitals. Infrared spectroscopy studies of CO adsorbed
on Cu/Pt alloy surfaces [16] show that changes in the C-O stretching frequency can be correlated with changes in the dipole-dipole interactions of the adsorbed CO molecules. This would indicate that the presence of copper causes a weakening of the Pt-C bond without effecting the back donation into the 2π orbital of CO. High resolution electron energy loss spectroscopy (HREELS) would help to clarify the nature of the Pt-CO bond at the alloy surface. These experiments will be carried out in our laboratory in the near future.

There are several other factors which could possibly result in the observed shift of the CO desorption peak upon alloying platinum with copper. These are: 1) An increase in the pre-exponential factor; 2) CO adsorption at mixed Cu-Pt sites; 3) closer packing of the CO molecules on the alloy surface. Several orders of magnitude increase in the pre-exponential factor would be needed to cause the observed 100 K decrease in the position of the CO desorption peak. This could be explained by a decrease in the mobility of CO adsorbed on the alloy surface relative to the pure platinum surface or an increased mobility of the transition state. However, as has been discussed by Weinberg [17], the decrease in the temperature of the desorption peak would be accompanied by a narrowing of the desorption peak if the shift is caused by a change in the pre-exponential factor. This narrowing was not observed, arguing against any significant change in the pre-exponential factor. Mixed adsorption sites have been proposed for several alloy surfaces [1,10]. It has been argued that desorption from a site consisting of two different metal atoms would have a desorption energy somewhere between the desorption energies for the pure component surfaces. If mixed sites
were responsible for the decrease in desorption energy of CO from the alloy surface, two desorption peaks should be present at low copper concentration. One peak due to desorption from mixed sites and another due to desorption from platinum sites. Two desorption peaks were never observed in the TDS of CO from the alloy surfaces. As can be seen in Fig. 6, the energy of desorption decreases smoothly with increasing copper concentration. Another possibility is that the CO molecules are being forced closer together by the copper atoms, with the increased intermolecular repulsion resulting in a lower desorption energy. In this case, extrapolating the energy of desorption back to an initial CO coverage of zero should give the same energy of desorption for both the alloy surface and the pure platinum surface. Inspection of Fig. 9 shows that this is not the case.

Bulk Cu/Pt alloys form several ordered structures at temperatures below 1100 K [18]. It seems likely that the surfaces of these alloys would also be ordered. Only one ordered structure was observed by LEED. This was a (2X2) pattern and it was seen for a high concentration of copper at the surface. The structure of Cu₃Pt is essentially fcc with copper at the faces and platinum at the corners. The (111) face of this structure would produce the (2X2) LEED pattern observed. This structure is particularly interesting because it consists of platinum atoms completely surrounded by copper atoms. It may be possible to use this surface to test reaction mechanisms which are proposed to proceed on a single platinum atom. Further studies of the surface order of these alloys will have to be postponed until single crystals of the bulk alloys can be obtained. This is because there is a large concentration gradient
for copper at the surface of the system presently being studied and any
energy input to further order the alloy surface also results in the dif­
fusion of copper into the bulk.

In determining the surface composition of the alloy with thermal
desorption, the ordering of the alloy can be very important. CO adsorbs
on the clean Pt(111) surface in a one-to-two ratio (one CO molecule per
two platinum atoms). However, on a surface with isolated platinum atoms
the CO would be able to adsorb in a one-to-one ratio. The solid line in
Fig. 13 shows the relationship between the CO desorption yield from an
alloy surface saturated with CO and the composition of the surface. At
copper concentrations ≥75% the CO-to-platinum ratio is one. At copper
concentrations ≤25% the ratio of CO-to-platinum is 1/2. Until further
information is available on the ordering at intermediate compositions,
we assume a linear transition between the conditions at the two
extremes.

ACKNOWLEDGMENTS

We would like to thank the Division of Material Sciences and the
Office of Basic Energy Sciences of the U. S. Department of Energy under
Contract No. DE-AC03-76SF00098 for supporting this work.
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FIGURE CAPTIONS

Fig. 1. Plot of Auger peak-to-peak intensities of the Pt-150 V peak and the Cu-105 V peak versus copper coverage for copper deposited on Pt(111).

Fig. 2. Thermal desorption spectra for CO adsorbed on Pt(111) covered with varying amounts of copper, after a saturation exposure of 12 L CO.

Fig. 3. Plot of the relative CO desorption yield from Pt(111) with varying coverages of copper after a saturation exposure of 12 L CO, versus the copper coverage.

Fig. 4. Arrhenius plot for an estimation of the activation energy for surface-to-alloy diffusion of copper on platinum.

Fig. 5. Thermal desorption spectra for CO adsorbed on Cu/Pt(111) surface alloys of varying composition after a saturation exposure of 12 L CO.

Fig. 6. Surface composition dependence of the energy of desorption of CO from Cu/Pt(111) alloy surfaces.

Fig. 7. Thermal desorption spectra for CO adsorbed on Pt(111) after varying CO exposures.

Fig. 8. Thermal desorption spectra for CO adsorbed on 76% Cu/Pt(111) surface alloy after varying CO exposures.

Fig. 9. A plot of the energy of desorption of CO adsorbed on Pt(111), 53% Cu/Pt(111), and 76% Cu/Pt(111), versus the relative CO desorption yield.
Fig. 10. Plot of Auger peak-to-peak intensities of the Pt-150 V peak and the Cu-105 V peak versus copper coverage for copper deposited on Pt(553).

Fig. 11. Thermal desorption spectra for CO adsorbed on Pt(553) covered with varying amounts of copper, after a saturation exposure of 12 L CO.

Fig. 12. Plot of the relative CO desorption yield from Pt(111) with varying coverages of copper after a saturation exposure of 12 L CO, versus the copper coverage.

Fig. 13. Plot of the desorption yield of CO adsorbed on Cu/Pt(111) alloy surfaces versus the surface fraction of copper.
Fig. 1
Pt(III)/Epitaxial Cu
CO Thermal Desorption
Saturation CO Coverage (12 L)

CO Partial Pressure (Mass 28 Signal)

Crystal Temperature (K)

Fig. 2
Fig. 3

Pt(III)/Epitaxial Cu CO Uptake

Relative CO Desorption Peak Area

Cu Coverage (Monolayers)
$E_q = 120 \text{ KJ/mol}$

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Fig. 4
PT(III)/Cu Alloy
CO Thermal Desorption
Saturation CO Coverage (12 L)

Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10
Fig. 11
Fig. 12
Fig. 13

Fractional Cu Surface Composition

Relative CO Coverage at Saturation

\[ n = \frac{\text{CO}}{\text{Pt atoms}} \]
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