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Molecular Phenomena at Electrode Surfaces

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Structural, Catalytic, Electronic, and Electrochemical Properties of Strained-Copper Overlayers on Ruthenium(0001)

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The chemical behavior of monolayer coverages of one metal on the surface of another, i.e. Cu/Ru, Ni/Ru, Ni/W, Pd/W, has recently been shown to be dramatically different from that seen for either of the metallic components separately. These chemical alterations, which modify the chemisorption and catalytic properties of the overlayers, have been correlated with changes in the structural and electronic properties of the bimetallic system. The films are found to grow in a manner which causes them to be strained with respect to their bulk lattice configuration. Earlier studies have addressed the adsorption of CO and H₂ on copper overlayers on Ru(0001) as well as the measurement of the elevated pressure kinetics of the methanation, ethane hydrogenolysis, and cyclohexane dehydrogenation reactions. In addition, unique electronic interface states have been identified for this bimetallic system. A comparison of electrochemical (EC) and ultrahigh vacuum (UHV) deposition methods has been made via a series of co-characterization experiments in which Cu was deposited in one environment (UHV or EC) and characterized in the other (EC or UHV). Both EC stripping and temperature programmed desorption (TPD) in vacuum of the Cu show that the difference in the heat of desorption between multilayer and monolayer Cu is ~6 kcal/mole and identical for both methods.

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It has long been recognized that the addition of impurities to metal catalysts can produce large effects on the activity, selectivity, and resistance to poisoning of the pure metal (1). For example, the catalytic properties of metals can be altered greatly by the addition of a second metal (2). A long-standing question regarding such bimetallic systems is the nature of the properties of the mixed metal system which give rise to its enhanced catalytic performance relative to either of its individual metal components. These enhanced properties (improved stability, selectivity and/or activity) can be accounted for by one or more of several possibilities. First, the addition of one metal to a second may lead to an electronic modification of either or both of the metal constituents. This electronic perturbation can result from direct bonding (charge transfer) or from a structural modification induced by one metal upon the other. Secondly, a metal additive can promote a particular step in the reaction sequence and, thus, act synergistically with the host metal. Thirdly, the additive metal can serve to block the availability of certain active sites, or ensembles, prerequisite for a particular reaction step. If this "poisoned" reaction step involves an undesirable reaction product, then the net effect is an enhanced overall selectivity. Further, the attenuation by this mechanism of a reaction step leading to undesirable surface contamination will promote catalyst activity and durability.

The present studies are part of a continuing effort (3-12) to identify those properties of bimetallic systems which can be related to their superior catalytic properties. A pivotal question to be addressed of bimetallic systems (and of surface impurities in general) is the relative importance of ensemble (steric or local) versus electronic (nonlocal or extended) effects in the modification of catalytic properties. A complete understanding of surface impurity effects (including alloying) in catalysis will likely include components of both electronic and ensemble effects, the relative importance of each to be assessed for a given reaction and reaction conditions. An emphasis of our research has been in the area of addressing and partitioning the importance of these two effects in the influence of alloying and surface additives on surface reactions.

**Experimental**

The studies described other than the combined ultrahigh vacuum (UHV)-electrochemical (EC) studies involve the use of an experimental apparatus of the type described in references 14 and 15. This device consists of a surface analysis chamber vacuum interlocked to a microcatalytic reactor. Both regions are of ultrahigh vacuum construction and capable of ultimate pressures of less than 2 times $10^{-10}$ torr. In the surface analysis chamber, techniques such as Auger spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED), and temperature programmed desorption (TPD) are available for sample preparation and for sample characterization before and after reaction. The sample support assembly allows the metal single-crystal catalyst to be transferred in vacuo from the
surface analysis region to the microcatalytic reactor. In the microcatalytic reactor, reaction kinetics can be measured for single crystal catalysts having surface areas of less than 1 cm$^2$ at reactant pressures up to several atmospheres.

The single crystal catalysts, \(-1\) cm in diameter and \(1\) mm thick, are typically aligned within 0.5° of the desired orientation. Thermocouples are generally spot-welded to the edge of the crystal for temperature measurement. Details of sample mounting, cleaning procedures, reactant purification, and product detection techniques are given in the related references. The catalytic rate normalized to the number of exposed metal sites is the specific activity, which can be expressed as a turnover frequency (TOF), or number of molecules of product produced per metal atom site per second.

The electrochemical experiments were conducted in an apparatus consisting of an electrochemical cell attached directly to a UHV system and has been described in detail elsewhere (16). The transfer between UHV and the EC was accomplished via a stainless steel air lock vented with ultra-pure Ar. Differentially pumped sliding teflon seals provided the isolation between UHV and atmospheric pressure. The sample was mounted on a polished stainless steel rod around which the teflon seals were compressed. All valves in the air lock were stainless steel gate valves with Viton seals. Details of the electrochemical cell and conditions are contained in reference 16. Electrochemical potentials are referred to a saturated calomel electrode (SCE).

Results and Discussion

Structural, Catalytic, and Electronic Properties. Interest in bimetallic catalysts has increased steadily because of the commercial success of these systems, which allow an enhanced ability to control the catalytic activity and selectivity by tailoring the catalyst composition (17-29). A key point in these investigations, as with the studies involving other impurities, has been determining the relative importance of ensemble and electronic effects in defining catalytic behavior (29-32). It is advantageous to simplify the problem by utilizing models of a bimetallic catalyst, which have been made by deposition of metals on single-crystal substrates in a UHV environment. A combination that has been studied extensively in supported catalyst research is copper on ruthenium (Cu/Ru). The immiscibility of copper in ruthenium circumvents the complication of determining the three-dimensional composition. Furthermore, distinct TPD features exist for the first monolayer of copper relative to multilayer coverages (3). Thus the copper coverage can be calibrated accurately by TPD measurements as discussed in Section II.

A comparison of CO desorption from ruthenium (6), and from multilayer (10 ML) and monolayer copper covered ruthenium is shown in Figure 1. The CO coverage is at saturation. The TPD features of the 1 ML copper (peaks at 160 and 210 K) on ruthenium are at temperatures intermediate between those found for adsorption on surfaces of bulk ruthenium and copper, respectively. This suggests that the copper monolayer is perturbed electronically and that this perturbation is manifested in the bonding of CO. An increase in the
desorption temperature relative to bulk copper indicates a stabilization of the CO on the copper monolayer which suggests an electronic coupling of the CO through the copper to the ruthenium.

Model kinetic studies of these Cu/Ru(0001) catalysts have been performed for methanation (7), cyclohexane hydrogenolysis (9), and cyclohexane dehydrogenation (10) reactions. For the first two reactions, copper serves as an inactive diluent, blocking sites on a one-to-one basis. The latter reaction is quite different. Figure 2 shows the effect, caused by addition of copper onto ruthenium on the rate of dehydrogenation of cyclohexane to benzene. The overall rate of this reaction increases by approximately an order of magnitude at a copper coverage of 0.75 ML. This translates into a specific rate enhancement for ruthenium of ~40. At higher coverages, the rate decreases to an activity approximately equal to that of copper-free ruthenium.

The rate enhancement for cyclohexane dehydrogenation observed for submonolayer copper deposits may result from changes in the geometric (6) and the electronic (8) properties of the copper overlayer relative to bulk copper. Alternatively, the two metals may catalyze different steps of the reaction cooperatively. For example, dissociative H₂ adsorption on bulk copper is unfavorable because of an activation barrier of approximately 5 kcal/mol (33). In the Cu/Ru system, ruthenium may function as a reservoir for atomic hydrogen, which is accessible via spillover to neighboring copper. Kinetically controlled spillover of hydrogen from ruthenium to copper (5) is consistent with the observed optimum reaction rate at an intermediate copper coverage.

The unique chemical behavior seen in CO adsorption and for certain catalytic reactions is mirrored in unique physical and electronic properties. For example, the adsorption and growth of copper films on the Ru(0001) surface have been studied (3,6,34-41) by work function measurements, LEED, AES, and TPD. The results from recent studies (3,6,8) indicate that for submonolayer depositions at 100 K the copper grows in a highly dispersed mode, subsequently forming two-dimensional islands pseudomorphic to the Ru(0001) substrate upon annealing to 300 K. Pseudomorphic growth of the copper during the first monolayer indicates that the copper-copper bond distances are strained by almost 6% beyond the equilibrium bond distances found for bulk copper. Thermal annealing to 600 K of copper films at coverages in excess of 2 ML results in the agglomeration of copper into three-dimensional islands. The particles formed expose primarily Cu(111) surfaces and partially uncover the underlying ruthenium surface. This is the origin of the residual activity of the copper films at coverages greater than 1 ML.

In terms of the electronic properties, recent angle-resolved photoemission (ARUPS) studies (8) also reveal unique structure, an interface state that is related to the altered bonding of copper films intimate to ruthenium. The ARUPS data, shown in Figure 3, are using HeI photon radiation (21.2 eV) at normal incidence and at an electron emission angle corresponding to the excitation of electrons from states of a particular symmetry character with respect to the crystal structure. The spectra correspond to the energy distribution of photoelectrons, and are shown as a function of the coverage of copper overlayer. The zero of electron binding energy is the
Figure 1. TPD results for CO adsorbed to saturation levels on clean Ru(0001), on multilayer Cu, and on a 1 ML Cu covered Ru(0001). (Data from ref. 6.) (Reprinted with permission from ref. 42. Copyright 1986 Annual Reviews, Inc.)

Figure 2. Relative rate of reaction vs. surface Cu coverage on Ru(0001) for cyclohexane dehydrogenation to benzene. $P_T = 101$ Torr. $H_2/cyclohexane = 100$. $T = 650$ K. (Data from ref. 10.) (Reprinted with permission from ref. 42. Copyright 1986 Annual Reviews, Inc.)
Figure 3. ARUPS energy distribution curves taken with HeI radiation at normal incidence and an electron emission angle of 52° shown as a function of copper coverage. The intensity of the various curves has been normalized at the Fermi level $E_F$. The individual curves are matched to their corresponding copper coverages in monolayers by the solid lines and the saturation behavior of the interface state at approximately $-1.5$ eV is identified by the dashed lines. (Data from ref. 8.) (Reprinted with permission from ref. 43. Copyright 1987 American Association for the Advancement of Science.)
abrupt rise in photoemission intensity, at the Fermi level. Over-
layer copper does not alter appreciably the ruthenium electronic
structure at binding energies less than \(-1\) eV except for an
intensity attenuation. Hence, the spectra can be normalized so that
they have equal intensity at the Fermi level. The fingerprint of
bulk copper is the narrow d-band peak just below 2 eV for copper
coverages greater than 1 ML. Below this coverage the overlayer
copper causes an increase in intensity in narrow regions centered at
\(-1.5\) and \(-3.6\) eV. These states remain unchanged in energy and
relative intensity for copper overlayer of a dozen monolayers.
These two features exemplify the behavior of interface states, which
are states that are not seen for either component of a bimetallic
surface alloy but which exist because of the abrupt change in elec-
tronic properties at the interface.

The interface nature of the states shown in Figure 3 have been
corroborated in recent theoretical calculations (8). The calculated
energy position of these states is in close agreement with the
experimental results. Their orbital character has been determined
as well. These results indicate that the interface states at about
1.5 eV are of appropriate character and energy to be active in
environmental chemical reactions involving sub- and monolayer copper
films on ruthenium.

**Vacuum Desorption and Electrochemical Properties** Figures 4a-4d
shows a series of TPD spectra of Cu from Ru(0001) (16) corresponding
to three regions of Cu coverage—-low, medium, and high. The TPD
traces were independent of the deposition parameters such as evapora-
tion rate or temperature of the anneal subsequent to evaporation.
In the low coverage region (Figure 4a) the initial buildup of Cu can
be seen. The initial stage of Cu growth is indicated by the
appearance of an approximately zero order desorption peak and,
following the notation of Christmann and co-workers (34), is noted
as \(\beta_2\). This state reflects Cu coverages up to approximately one
monolayer (one Cu atom per surface Ru atom). The saturated \(\beta_2\) state
has a desorption maximum at \(-1210\) K.

Higher Cu exposures (Figures 4b, 4c, and 4d) cause the
appearance of a second binding state, \(\beta_1\), with a desorption maximum
at a temperature below that of the \(\beta_2\) state. The kinetics of the
desorption process of the \(\beta_1\) state are approximately zero order,
indicating that the rate of the desorption is independent of the Cu
concentration on the surface. The general adsorption behavior and
peak temperatures in Figure 4 are completely in agreement with the
work of Christmann, et al. (34).

The evolution of the Cu desorption first entails filling of the
\(\beta_2\) state followed by filling of the \(\beta_1\) state. As the \(\beta_1\) state
grows, the \(\beta_2\) state remains essentially unchanged. This is consist-
ent with the assignment of the \(\beta_2\) state to Cu-Ru interactions and
the \(\beta_1\) state to three-dimensional Cu-Cu interactions (34). The
ordering of these TPD features imply Cu-Ru interactions which are \(-6\)
kcal/mole more stable than Cu-Cu interactions (16). The growth
mechanism of the Cu overlayer in either case of preparation is
suggested by the TPD results which are consistent with a Frank-van
der Merve or layer-by-layer mechanism. Furthermore, the filling of
the \(\beta_2\) TPD peak provides an accurate calibration point for a single
Figure 4. Left, copper TPD from a Ru(0001) surface at copper coverages corresponding to a, 0.6 ML, b, 1.5 ML, c, 2.5 ML, and d, 5.2 ML. (Data from ref. 3.) Right, electrochemical stripping curves as a function of Cu coverage (determined by AES) for vacuum deposited Cu on Ru(0001). (Data from ref. 16.)
monolayer of Cu, which, assuming purely epitaxial growth, is $1.59 \times 10^{15}$ Cu atom/cm$^2$\textsuperscript{35}.

A Ru(0001) sample, with vacuum deposited Cu, has been characterized by cyclic voltammetry by transferring to an electrochemical cell\textsuperscript{(16)}. Figures 4e-4h shows the anodic stripping curves for four different coverages of Cu. A single stripping peak was observed at +110 mV for 0.6 ML Cu and shifted to +145 mV for 5.2 ML Cu. This peak represents the removal of the first monolayer of Cu or Cu in direct contact with the Ru surface. The curve for 5.2 ML Cu shows an additional peak at -20 mV for the stripping of multilayer Cu.

The splitting between the multilayer and monolayer stripping peaks of 140 mV is equivalent to an absolute energy difference of 6.4 kcal/mole, essentially the same value found for the difference in apparent activation energy for monolayer versus multilayer Cu removal by TPD techniques described above. Auger spectra recorded after electrochemical stripping and removal of the electrode at +400 mV showed no signs of Cu remaining on the surface.

There is a good correlation between determination of the Cu coverage by UHV (AES or TPD) and electrochemical methods\textsuperscript{(16)}. Figure 5 compares the Cu coverage measured by AES and CV. The CV data were calculated from the integrated charge under the monolayer and multilayer stripping peaks assuming that the stripping reaction was

$$\text{Cu}_{\text{ads}} \rightarrow \text{Cu}^{2+}_{\text{ads}} + 2 \text{e}^-$$

The error in the CV determinations was estimated to be ±25%. That the line does not go through the origin and its slope deviates from unity is attributed to ambiguities in determining the proper baseline for integrating the charge under the CV peaks.

A typical Auger spectrum of the sample following electrodeposition of Cu is shown in Figure 6\textsuperscript{(16)}. For this experiment the sample was immersed in a solution of 0.2 M HClO$_4$ and 0.96 mM Cu$^{2+}$ at +400 mV, cycled to -100 mV, and then back to +40 mV at a sweep rate of 20 mV s$^{-1}$. The sample was held at +40 mV for 2 min and emersed under potential control. It was not rinsed before transfer to vacuum; the small droplet which remained on the electrode was allowed to evaporate in vacuum. Under these conditions, one would expect that the Cu coverage was approximately one monolayer. This is approximately the case as the Cu/Ru ratio in Figure 6 is 0.048 corresponding to about one monolayer of Cu (see Figure 5).

**Conclusions**

These studies have shown that:

1. Cu deposited onto Ru(0001) at 100K grows in 2-d islands via a Frank-van der Merwe (layer by layer growth) mechanism up to 2 ML. The island sizes but not the basic growth mode are altered by a post-deposition anneal at 900 K.

2. The structure of the first monolayer of Cu is pseudomorphic with respect to the Ru(0001) substrate whereas successive Cu layers grow epitaxially with a Cu(111) structure.
Figure 5. Correlation of electrochemical vs. Auger determination of Cu coverage. The electrochemical measurements were taken from the area under the Cu stripping peaks. (Data from ref. 16.)

Figure 6. Auger spectrum after electrodeposition of Cu on Ru(0001) from an electrolyte of 0.2 M HClO₄ and 0.96 mM Cu²⁺. The sample was emersed without rinsing at 40 mV (SCE). (Data from ref. 16.)
3. The adsorptive properties of 1 ML of Cu on Ru(0001) toward CO is markedly different than either corresponding to CO on Ru(0001) or CO on bulk Cu(111).
4. The addition of Cu to Ru(0001) results in a dramatic enhancement of the rate of cyclohexane dehydrogenation, despite the fact that Cu is much less active for this reaction than is Ru.
5. ARUPS results have identified unique electronic interface states for the Cu/Ru(0001) system. These states are not present in either metal separately but exist because of the abrupt change in properties at the interface.
6. The difference in desorption energy between multilayer and monolayer Cu is essentially the same for Cu desorption from Ru in vacuum or by electrochemical stripping.

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References


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