Calorimetric Measurement of Adsorption and Adhesion Energies of Cu on Pt(111)

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Abstract

The adsorption energies of submonolayer amounts of one metal on the surface of another metal have been measured for decades by temperature programmed desorption. However, that method fails for metals that alloy. We report here the first measurement of the adsorption energy for any such metal-on-metal combination that forms a bulk alloy. The adsorption and interfacial energetics of vapor deposited Cu onto Pt(111) at 300 K has been studied using single crystal adsorption calorimetry (SCAC) and X-ray photoelectron spectroscopy (XPS). The Cu grows as 2D pseudomorphic islands in the first layer and its heat of adsorption decreased linearly from 358 to 339 kJ/mol. This is attributed to increasing lattice strain with island size, associated with the small lattice mismatch (8%). It adsorbs ~2 kJ/mol more weakly in the 2nd layer than above 3 ML, where it reaches the bulk heat of sublimation of Cu(solid), 337 kJ/mol. The adhesion energy of multilayer Cu onto Pt(111) is 3.76 J/m². The extra stability of the first Cu monolayer compared to bulk Cu measured here is ~12 kJ/mol, compared to a difference of ~83 kJ/mol for underpotential deposition of Cu on a Pt(111) electrode, with the difference attributed to stronger bonding of Cu to the solvent and double layer compared to Pt.

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1. Introduction

Bimetallic catalysts generally have physical, chemical, electronic, and catalytic properties unique from their individual parent metals[1-6] and thus often have superior performance as catalysts and electrocatalysts.[1-9] In order to understand how the choice of metal influences catalytic properties, a variety of detailed surface science studies have been performed where the system structure, the total concentration of each metal, and cleanliness of the system can be controlled.[3-6, 9]. Fundamental studies of this type can help lead to ideas for more efficient, environmentally friendly catalysts. While true alloys are often excellent catalysts and have been used for decades, a newer class of bimetallic catalysts that has shown particular promise involve core-shell nanoparticles, where one metal element exists as a single monolayer coating the surface of the second metal.[10-12] While the energetic and thermodynamics of alloy formation have been well studied,[6] much less is known about the energetics of such monolayer metal films on other metal's surfaces. For two metals which are immiscible in the bulk, the heat of adsorption of one metal on another has been measured by temperature programmed desorption (TPD) in many cases,[6] and once by SCAC.[13] However, the heat of adsorption of a single monolayer of adsorbed metal has never been measured on another metal with which it can make a bulk alloy, since TPD does not work for such systems. This is because the metals intermix (diffuse into each other) before reaching the desorption temperature. We report here the first measurement of the heat of metal adsorption for such a system, Cu adsorption on Pt(111), using calorimetry to *directly* measure the heats.

Alloying Cu with Pt has proven to be an effective way to tune the catalytic properties of Pt, and was a very thoroughly studied prototype system in basic research aimed at elucidating the relative importance of electronic effects versus ensemble effects in bimetallic catalysis.[1, 6, 14, 15] Thus, well-ordered Cu overlayers and thin-film CuPt alloys on Pt(111) have been studied extensively in the past to further elucidate those effects and to clarify their unique adsorption and catalytic properties of small molecules such as oxygen,[16] CO,[17, 18] CO₂,[19, 20] and formate.[21]

To gain the first insight into the energetics of metal – metal bonding at the interface of core-shell bimetallic catalysts particles consisting of *miscible* metals in general, and Cu/Pt in particular, we study the adsorption and adhesion energies of Cu vapor deposited onto clean, well-ordered Pt(111) at 300K by single crystal adsorption calorimetry (SCAC). We interpret these

adsorption energies in light of previous detailed structural studies of Cu adsorbed on Pt(111).[22-25] This is only the second bimetallic system adsorption directly measured by SCAC.[26] Adsorption energies of Cu onto other transition metals have been previously been reported using temperature programmed desorption (TPD),[6] but could not be measured for Cu on Pt since annealing causes Cu/Pt to alloy before Cu desorbs.[27-30]

The growth of vapor-deposited Cu on Pt(111) has been studied in detail by Auger electron spectroscopy (AES),[23-25] low energy electron diffraction (LEED),[23-25] thermal desorption spectroscopy (TDS) of H₂ and CO,[23, 25] and scanning tunneling microscopy (STM).[22] Copper grows layer-by-layer on Pt(111) in the first monolayer (ML) as evidenced by a linear decrease in the saturation coverage of H and CO (by TPD) with Cu coverage to nearly zero in the first ML, as well as a distinct break in the Cu and Pt AES signals at 1 ML.[23, 25] STM results also show Cu growing layer-by-layer with nucleation occurring primarily at Pt step edges followed by the formation of branched Cu islands.[22] The branching was attributed to large diffusion lengths of Cu monomers on Pt(111) terraces, but slow diffusion of Cu atoms along the edges of the Cu islands which nucleate and grow. During the growth of the first layer, no nucleation was seen on terraces, but only at Pt(111) steps edges, indicating Cu-Pt bonds are stronger than Cu-Cu bonds.[22] LEED results show Cu growth is pseudomorphic with Pt(111) as evidenced by the appearance of no new LEED spots at the highest submonolayer coverage studied (~1/2 ML).[23, 25] By the second Cu layer, new LEED spots were observed with an ~8% smaller lattice parameter indicating Cu grew with the ideal Cu(111) lattice spacing in the second and subsequent layers.[23] Nowicki et al.[24] found using LEED and directional elastic peak electron spectroscopy (DEPES) that Cu forms a misfit Cu(13x13) layer on Pt(12x12) at just over 1 ML and 330K, consistent with a lattice parameter very near that of Cu(111). (Note that the Cu coverages in that paper were all reported as 1/2 of their true values, based on comparison of the Cu/Pt peak ratio in AES to those reported in,[23] where CO and H chemisorptions clearly identified monolayer completion.

2. Experimental

The calorimetry apparatus has been described in detail previously.[31] The calorimeter was housed in an ultrahigh vacuum chamber (UHV) with a base pressure $>2 \times 10^{-10}$ torr. The chamber was equipped with low energy electron diffraction (LEED), X-ray photoelectron

spectroscopy (XPS), a quadrupole mass spectrometer (QMS), and several quartz crystal microbalances (QCM). XPS was operated using 12 kV 200 W and Al K α emission with normal detection.

The 1 μm Pt(111) single crystal sample, purchased from Jacques Chevallier of Aarhus University, was cleaned by successive cycles of 1 keV Ar⁺ sputtering in 6×10^{-6} background Ar followed by annealing in to 1173K in UHV then to 873K in 1×10^{-6} torr O₂ until no C was present in XPS. A final flash to 1173K in UHV for 1 minute immediately before calorimetry experiments removed any residual oxygen. Sample order was verified by sharp Pt(111) LEED spots. After Cu deposition, the sample was first cleaned by 1 keV Ar⁺ sputtering in 6×10^{-6} Ar until no Cu was present in XPS to avoid Cu alloying with Pt during the annealing steps.

The single crystal adsorption calorimetry experiments were performed as described in detail elsewhere.[31, 32] Briefly, the calorimeter heat detector is a pyroelectric polyvinylidene fluoride ribbon that can be translated into gentle thermal and mechanical contact to the backside of the Pt(111) single crystal sample. A 4-mm diameter beam of Cu atoms is generated using an electron beam evaporator and is chopped and collimated through a series of apertures to produce a spatially and temporally well-defined 100 ms pulse every 2 seconds which is directionally dosed onto the front of the single crystal sample. Upon adsorption, a transient temperature rise results from the exothermic adsorption, giving a transient signal whose magnitude is proportional to the total heat released upon metal adsorption. The detector response is normally calibrated with pulses from a HeNe laser that is chopped and collimated through the same series of apertures as the calorimetry pulse, but the laser power output was not stable over the duration of a calorimetry experiment. Therefore, we scaled the absolute calibration factor slightly so that the multilayer heat of adsorption in the high-coverage limit equals the literature value for the heat of sublimation of bulk Cu(solid) from Ref.[33].

The absolute flux of Cu atoms during each pulse is measured using a calibrated QCM that translates into the sample position (along the central axis of the atomic beam) before and after the calorimetry experiment. Another, off-axis QCM monitors the flux of metal atoms during the entire duration of the experiment. The beginning and ending fluxes measured by the on-axis QCM were used to scale the flux measured by this off-axis QCM so that it provided the Cu flux at the sample position during heat measurements. The fraction of metal atoms that transiently adsorb, but do not stick permanently to the surface, are measured using a QMS at the

magic angle and compared to a reference zero sticking pulse from a hot Ta flag. The total Cu coverage is recorded in monolayer (ML) Cu coverage, where 1 ML = 1.5×10^{15} atoms/cm² which is the atomic density of Pt atoms in the (111) surface. Since the Cu atoms are generated from a hot source, a fraction of the heat signal is due to radiation. To subtract the signal contribution due to thermal radiation, a BaF₂ flag is translated into the beam path so all metal atoms are blocked and a known fraction of radiation impinges on the sample, the resulting peak, corrected for the BaF₂ transmission, can be subtracted from the calorimetry peak to give the total heat signal from metal atom adsorption. See[32, 34, 35] for more details of these procedures.

3. Results

The heat of adsorption of vapor deposited Cu onto Pt(111) as a function of Cu coverage at 300K is shown in Figure 1. All heats of adsorption reported here have been corrected slightly for the hot temperature and directed nature of the Cu atomic beam, so that they correspond to Cu atoms in a Boltzmann distribution at the surface temperature, and RT has been subtracted from the measured energies, as we always do in calorimetry. This is done so that the values in Figure 1 (and 2) correspond to the standard enthalpy of adsorption (ΔH_{ad}) at the sample temperature (multiplied by -1, so it corresponds to a heat at 1 bar). The heat of adsorption data in Figure 1 was divided into three distinct regions based on the growth of Cu on Pt(111) described above. In region 1 (0-1 ML, where 1 ML is defined by the density of Pt atoms in the (111) plane, 1.52×10^{15} atoms/cm²), Cu adsorbs with an initial heat of adsorption of 357 kJ/mol, the heat of adsorption decreases over the first 1 ML to 339 kJ/mol. Figure 2 shows the heat of adsorption in region 1 in more detail. The decrease in heat of adsorption is well fit as a linear decrease that follows the equation $\Delta H_{ad} = (358 - 19\theta)$ kJ/mol where θ is the total Cu coverage in ML. In region 2 (1-3 ML), the heat of adsorption continues to decrease, and reaches a minimum of ~335 kJ/mol between 1.5 and 2.5 ML. The heat then increases to the heat of sublimation of bulk Cu(s), 337 kJ/mol,[33] by 3 ML. Above 3 ML, the heat of adsorption remained constant at this value.

From the heats versus coverage in Fig. 1, the adhesion energy of Cu(solid) to Pt(111) can be calculated. This is done using the energy-balance equation derived in Ref.[36]:

$$n \cdot \sum_n \Delta H_{adsorption} = -n \cdot \Delta H_{sublimation} + A \cdot [(1+f)\gamma_{v/m} - E_{adhesion}],$$

where $\gamma_{v/m}$ is the surface free energy of bulk Cu(solid), f is the surface roughness factor (~ 1 here), $\sum_n \Delta H_{\text{adsorption}}$ is the integral (average) molar heat of adsorption of Cu up to some multilayer coverage, n is the number of moles of Cu on the surface at that coverage, A is the total area covered by the Cu film, and $\Delta H_{\text{sublimation}}$ is the molar heat of sublimation of bulk Cu(solid). The adhesion energy determined in this way is 3.78 J/m^2 for 3 ML and above. (Small inaccuracies in absolute heat calibration make results at 5 ML and above less reliable, so we use here only the values found at 3 and 4 ML, both 3.78 J/m^2 .) This adhesion of Cu on Pt(111) is slightly stronger than the adhesion of two Cu(111) planes in bulk Cu(solid) which is just two times the surface free energy ($2 \times 1.79 = 3.58 \text{ J/m}^2$).[36]

4. Discussion

Since the growth Cu overlayers on Pt(111) have been extensively described in the literature[22-25] and summarized above, we use these results to analyze the shape of our heat curves in Figures 1 and 2. STM by Allison et al.[22] has shown that Cu grows as pseudomorphic 2D islands in the first monolayer, which nucleate at Pt step edges and then grow outward from the step edges onto terraces in a tendril pattern via step flow growth.[37] We therefore assign the initial heat of adsorption of 357 kJ/mol to Cu adsorbing primarily as small 2D islands attached to Pt step edges. The average heat in the first ML (349 kJ/mol) is 12 kJ/mol larger than the heat when Cu adsorbs onto bulk Cu(solid) (337 kJ/mol), indicating that Cu-Pt bonds are stronger than Cu-Cu bonds. The nearly linear decrease in heat with coverage in the first ML (Fig. 2) indicates that the decrease is not mainly due to the expected effect of stronger bonding at step edges, which are preferentially populated at low coverage. The step density seems to be so low here that the effect of step edges is not clearly seen. Therefore, we will instead attribute the decrease in heat in the first ML to the effect of increasing lattice strain as the Cu island size increases within a pseudomorphic growth model.

Figure 3 illustrates an idealized situation where a 2D Cu(111) island lies flat on a Pt(111) surface and both the Pt and Cu have their ideal (111) lattice spacings. The central Cu atom in the island is aligned to sit in its most favorable adsorption site on Pt(111), furthest down one well of the periodic potential shown (bottom part of Figure 3), which represents the potential energy versus x distance for an isolated Cu adatom. As the island size increases (beyond this one atom), the Cu atoms are displaced out of the ideal binding site due to an 8% lattice mismatch with

Pt(111), and sit higher and higher up the potential energy curve, thus energetically less and less favorable sites than the initial Cu atom. As discussed previously, Cu grows pseudomorphically, adopting the Pt(111) lattice spacing, in the first layer so that all Cu atoms sit in the most favorable adsorption site. However, this comes at an energy penalty of increasing the length of Cu-Cu bonds which are energetically less favorable than in bulk Cu(solid) causing a decrease in the heat of adsorption in region 1. The islands will also repel each other as they grow closer together due to strain induced in the Pt that acts in opposite directions on neighboring islands.[38] This will cause further decrease in the heat of adsorption.

The heat of adsorption ultimately becomes equal to the bulk heat of sublimation of Cu(solid) at multilayer coverage as expected, but it is lower than this by 1 to 4 kJ/mol in region 2 (i.e., where most of the Cu add into the 2nd Cu layer). We attribute this smaller heat in layer 2 to the much stronger bonding of Cu to Pt in layer 1. That stronger bonding in layer 1 means that the Cu in layer 1 has lower chemical potential than in bulk Cu. Consequently it cannot bond as aggressively to the next Cu layer, since lower “chemical potential” usually means just what that name implies: less bonding capacity to the next neighbor that approaches it.[39] This explains the lower heat of adsorption in layer 2 observed. This lower heat extends slightly above 2 ML coverage, which we attribute to Cu atoms which randomly land on layer 2 islands and thus populate layer 3(which is more stable than layer 2) before layer 2 completes, thus leaving sites in layer 2 beyond 2 ML. This broadens out the transition from layer 2 heats to the higher heats in layer 3 and beyond, as observed.

A similar broadening happens in the transition from layer 1 to layer 2 heats. Paffett et al.[23] saw CO uptake up to 1.2 ML Cu on Pt(111), indicating holes in the first Cu layer may still be present after 1 ML. The initial decrease in heat just beyond 1 ML is therefore attributed to a small fraction of Cu atoms filling in the remainder of the first Cu layer which would form more energetically favorable Cu-Pt bonds.

Paffett et al.[23] new Cu (1x1) LEED spots at ~1.6 ML, indicating layer 2 in the Cu islands already has a lattice parameter very close to that of Cu(111). Nowicki et al.,[24] who grew their films at 330K, did not see the ideal Cu(111) spacing until 5 ML Cu so it unlikely the films are perfectly ordered here, but the lattice strain is relaxed enough to not affect the heat of adsorption.

Previous work by Bruckenstein et al.[40] and Goodman et al.[41] measured the difference in binding energy of the first Cu layer on polycrystalline Pt and Pt(111) compared to all other layers using underpotential deposition respectively. In underpotential deposition, Cu is electrochemically deposited and removed from a Pt electrode, the voltage difference necessary to remove the outer Cu layers and the first Cu layer can be used to calculate the difference in binding energy of Cu to Pt compared to bulk Cu. Cu was observed to bind 39 kJ/mol more strongly to a polycrystalline Pt electrode in the first layer than itself (i.e., compared to making multilayer Cu instead),[23] which would correspond to a heat of adsorption of 376 kJ/mol (heat of Cu(bulk) sublimation plus the measured electrochemical difference). Similarly, Cu was found to bind 83 kJ/mol more strongly to a Pt(111) electrode than to multilayer Cu.[41] These numbers are the average heat of adsorption of all Cu atoms in the first monolayer (in the presence of solvent). To compare this value to our heat of adsorption data in Figure 1, we must use the integral (average) heat of adsorption in region 1 (the first ML), which is 349 kJ/mol, just 12 kJ/mol stronger than the heat of sublimation of bulk Cu. This is much weaker than the binding of Cu in the first ML observed for electrochemical deposition on both types of Pt electrodes.

The ~70 kJ/mol stronger adsorption energy for Cu on Pt(111) in underpotential deposition must be due to the fact that when Cu adsorbs on a Pt electrode, the attractive bonding between Pt surface atoms and the electrochemical solution is replaced with even more attractive bonding between Cu surface atoms and the electrochemical solution. This is not surprising, since Cu is less noble than Pt. The bonding of surface metal atoms to the electrochemical solution involves attractions to the solvent molecules, solvated ions near the electrode, and the corresponding electric double layer. When Cu adsorbs onto multilayers of Cu already on the electrode, there is no change in the strength of these interactions. These differences in Cu versus Pt attractions to the electrochemical solution that appear during underpotential deposition are not present in the UHV calorimetry measurements here. Since the Cu^+ ions in the bulk solution have a fixed energy difference compared to Cu gas atoms, they do not contribute to this *difference* in energy between Cu adsorption on Pt(111) and Cu adsorption on multilayer Cu seen in the electrochemical environment versus the *difference* we see here in UHV.

The measured adsorption energies here are important benchmarks to test the accuracy of theoretical calculations. To our knowledge the only DFT calculation of the adsorption energy of Cu onto Pt(111) has been done by Mentus et al.[42] using the Perdew–Burke–Ernzerhof (PBE)

functional within the generalized gradient approximation (GGA) approximation. The adsorption energies were determined for 5 different coverages ranging from 0.25 to 1 ML and corrected here for the difference between energy and enthalpy by adding 0.8 kJ/mol (RT) to compare to our calorimetric heats of adsorption measurements in figure 1 and 2. The DFT calculations of Mentus et al.[42] gave the integral heat of adsorption to be 338 kJ/mol at 0.25 ML (single atom based on the (2x2) unit cell used in the calculations), increasing to 377 kJ/mol by 1 ML. This value at 1 ML can be compared to our integral heat of adsorption at 1 ML of 349 kJ/mol from Figs. 1-2, indicating that DFT overestimates the stability of the first ML of Cu by ~28 kJ/mol. The increased heat of adsorption with coverage in this DFT calculation is due to the increasing Cu-Cu lateral attractions in Cu islands, also seen in calculations of a free-standing Cu layer. Results in Figures 1 and 2 show that the heat of adsorption of Cu versus coverage behaves opposite of this prediction by DFT, decreasing with increasing Cu coverage. This is because the DFT assumes a structure at $\frac{1}{4}$ ML that is incorrect, with the Cu in a 2x2 overlayer and not in 1x1 islands as observed.

5. Conclusions

Using single crystal adsorption calorimetry, Cu was found to adsorb onto Pt(111) with heat of adsorption which decreases linearly with coverage in the first monolayer as (358 - 19.3 θ) kJ/mol, while growing pseudomorphic 2D islands. This decrease is attributed to increasing lattice strain with increasing Cu 2D island size, due to lattice mismatch between the (111) crystal faces of these two metals. The average heat of Cu adsorption in the first ML is 12 kJ/mol larger than the heat of sublimation of bulk Cu(solid). This extra bonding stability of a Cu monolayer on Pt(111) compared to bulk Cu is consistent with the reported underpotential deposition of Cu on a Pt(111) electrode, although the added stability in the monolayer is ~70 kJ/mol larger in that electrochemical environment than in vacuum here. The heat of Cu adsorption between 1 and 3 ML is slightly lower than the heat of sublimation of bulk Cu(solid). After 3 ML the Cu heat of adsorption reached Cu(metal) heat of sublimation. The adhesion energy of a multilayer film of Cu to Pt(111) at 300K was determined to be 3.76 J/m².

6. Acknowledgements

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7. References

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Figure 1: Heat of adsorption of Cu atoms onto clean Pt(111) (average of 3 experiments) at 300 K versus Cu coverage. The data will be discussed in terms of three distinct regions of coverage. Region 1 (0-1 ML) where 2D Cu islands grow pseudomorphically on Pt(111). Region 2 (1-3 ML) where a large fraction of the Cu film is 2 layers thick. Region 3 (>3 ML) where bulk-like Cu(111) grow in islands that are at least 3 layers thick.

Figure 2: The Cu heat of adsorption in the first ML on Pt(111) from Fig. 1. Despite Cu islanding (attractive Cu-Cu interaction), a decrease in the heat of adsorption is observed due to lattice strain in the first Pt(111) layer and Cu overlayer, associated with the 8% lattice mismatch between bulk Cu(111) and Pt(111). The data from Region 1 is well fit as a linear decrease in heat of adsorption with Cu coverage as shown.

Figure 3: Schematic illustration of the energetics of adsorbed Cu atoms for small 2D Cu island growth on the Pt(111) surface, showing a hypothetical situation (not observed) where Cu does not adopt pseudomorphic growth but instead grows with a bulk-like Cu(111) lattice spacing. Note that this would cause Cu to sit in less and less stable adsorption sites as the Cu island size grows. Note that the energy for the Cu atoms near the edges of the island would decrease if the Pt atoms in the top layer moved slightly toward the island center and if the Cu atoms near the edges of the islands moved outward from the island center. This gives rise to forces that increase with island size (i.e., with coverage for a fixed number density of 2D islands), so the lattice strain grows with island size. The decrease in heat of adsorption with coverage in the 1st monolayer is attributed to this island-size effect.

TOC Image: