

Energetics of Au Adsorption and Film Growth on Pt(111)

by Single-Crystal Adsorption Calorimetry

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Abstract

Bimetallic catalysts are an important class of heterogeneous catalysts with catalytic properties distinct from either of their bulk metal constituents. The structural, electronic, chemisorptive and catalytic properties of bimetallic surfaces have been widely studied. Surface reactivity often correlates with adsorption energy of one metal on a single-crystal surface of the other as measured using temperature programmed desorption (TPD). However, TPD only works for systems where the metals are immiscible. For bimetallic systems that form an alloy or intermetallic compound, TPD generally fails since the adsorbed metal penetrates into the bulk upon heating. The metal-on-metal adsorption energy is unmeasured for all but one such system previously, but often calculated since these adlayers often have interesting catalytic properties. We report here calorimetric measurements of the adsorption energy versus coverage of an adlayer of one metal on another for such a bimetallic system where the metals prefer to alloy: Au on Pt(111). This bimetallic combination is important in catalysis and electrocatalysis. The first monolayer (ML) of Au grows pseudomorphically with the Pt(111) surface at 300 K, with an average heat of adsorption of 389 kJ/mol, ~21 kJ/mol greater than the bulk heat of sublimation of Au. The heat increases with coverage by ~11 kJ/mol in the first 0.03 ML and then by another ~2 kJ/mol up to a maximum of 395 kJ/mol at 0.7 ML, and it then decreases to near the bulk heat of sublimation (368 kJ/mol) at 1 ML. The increase in heat is attributed to the increase in size of the two-dimensional (2D) Au islands that nucleate at very low coverage, and their corresponding increase in the average number of Au-Au nearest neighbor bonds. The high-coverage decrease in heat is attributed to the buildup of strain associated with the 4% Au/Pt lattice mismatch. The

second and third layers of Au show similar but much smaller oscillations in heat around 370 kJ/mol, attributed to the same two effects.

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1. Introduction

Bimetallic nanomaterials are an important class of heterogeneous catalysts. Core-shell nanoparticles are a new class of bimetallic catalysts where the 2nd metal exists as a monolayer coating (“shell”) on the surface of the other “core” metal. They have shown exceptional activity for some important catalytic and electrocatalytic applications.¹⁻⁹ The surface reactivity of such bimetallic solids, specifically the strength with which they bind small adsorbed molecules like CO, has been shown to correlate with the chemical potential of the metal element that binds the adsorbate.^{10,11} Thus, it is important to know the strength of binding between the two metal elements near the surface, since it determines this chemical potential. For core-shell systems, this requires knowing the heat of adsorption of the shell metal onto the surface of the core metal element.

While the energetics and thermodynamics of alloy formation have been well studied, much less is known about the energetics of monolayer metal films on other metal 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) for decades.¹² However, the heat of adsorption cannot be measured by TPD for one metal on any other metal with which it makes a bulk alloy or intermetallic compound. This is because the metals intermix (diffuse into each other) before reaching the desorption temperature. We recently reported the first measurement of the heat of metal adsorption for any such bimetallic system, using single crystal adsorption calorimetry to *directly* measure the heat of Cu adsorption on Pt(111) at 300 K.¹³ Here we report a similar study of the adsorption energy for the second such system, Au on Pt(111). This is a much less stable alloy than CuPt, with a maximum solubility of only ~20% Pt in Au at 400°C.¹⁴ This is still soluble enough to allow mixing upon heating, and prevent clean desorption of submonolayer coverages of Au adatoms on Pt(111) for the purposes of determining their desorption energy by TPD. (They would not desorb in TPD until above 400°C, where the solubility is even higher.) Here, we use calorimetry to study this, and find that the first monolayer of Au on Pt(111) is ~21 kJ/mol more stable than multilayer Au(solid), with interesting changes in the heat of adsorption with coverage which we associate with the increase 2D Au island size (at low coverage) and the buildup of lattice strain (at high coverage).

Alloying Au with Pt often markedly improves the catalytic and electrocatalytic properties of Pt,^{4,15-21} and is a prototype bimetallic catalyst that has been well studied to elucidate the

relative importance of electronic effects versus ensemble effects in bimetallic catalysts.^{12, 22-27} Core-shell AuPt bimetallic catalysts have also been studied and show improved catalytic and electrocatalytic performance.⁵⁻⁹

The growth of vapor-deposited Au thin films on Pt(111) at room temperature has been studied using Auger Electron Spectroscopy (AES),²⁶ Low Energy Electron Diffraction (LEED),^{26, 28, 29} Scanning Tunneling Microscopy (STM),²⁹ Temperature Programmed Desorption (TPD) of CO,²⁶ X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS)³⁰ and photoemission of adsorbed Xenon (PAX).^{28, 31} The AES intensities versus coverage shows distinct breaks at the successive completions of the first three monolayers in the Auger signal, indicating layer-by-layer growth. The amount of adsorbed CO measured by TPD decreased linearly with Au dose, indicating the growth of two-dimensional (2D) islands of Au, with a break in slope of CO coverage versus Au dose that agreed with the ML coverage point determined by AES.²⁶ Further, the TPD peak temperature for CO desorption remained constant with Au coverage and equal to that of clean Pt(111),²⁶ also indicating that Au grows as 2D islands. Also consistent with 2D islands is the STM image at ~0.8 ML Au coverage by Krupski et al.,²⁹ where islands of Au voids are seen, consistent with 2D Au island coalescence.²⁹ In addition, the hexagonal Pt(111) LEED pattern remained throughout Au deposition, and no new LEED spots were observed.^{26, 28} The lattice constant of the surface layer calculated from the spot-to-spot distances indicated that the first layer of Au grows pseudomorphically with the Pt(111) surface, and by 5 ML it relaxed to the bulk lattice constant of Au(111).²⁶ Upon heating ~3 ML of Au on Pt(111), PAX showed the onset of fast lateral mobility of gold atoms on the surface (i.e., 2D islanding) between 250 and 350 K, and their intermixing (alloying) by 750 K.²⁸

2. Experimental

The experimental apparatus and methods are essentially identical to those reported in our similar study of the heats of adsorption versus coverage of Cu on Pt(111).¹³ Specific differences related to dosing Au rather than Cu can be found in our similar study of Au adsorption energies on thin films of CeO₂(111) grown on Pt(111).³²

To convert the measured adsorption energies to heats of adsorption requires a small correction to account for the energy difference between the experimental reaction conditions and the reference reaction conditions used here to define “heat of adsorption.” The heat of adsorption

is defined here as the negative of the *standard* enthalpy change for the adsorption process with both gas and surface at the surface temperature. The correction accounts for the extra translational energy of metal atoms in a molecular beam pulse from a hot evaporation source relative to these gas atoms in a Boltzmann distribution at the Pt(111) temperature, as described elsewhere.³³ All heats of adsorptions reported here have been corrected in this fashion.

3. Results

The differential heat of Au atom adsorption versus coverage on clean Pt(111) at 300 K is shown in Figure 1. The Au coverage is given in monolayer (ML) units, where 1 ML is defined as the surface atom density of the (111) plane of the Pt substrate, 1.52×10^{15} atom/cm². The heat is high in the first monolayer (ML), but by 4 ML it drops to the bulk heat of sublimation of Au (indicated by a horizontal line) and remains constant thereafter. The sticking probability of Au onto Pt(111) at 300K was >0.99 at all coverages.

The first ML is shown in expanded scale in Figure 2. The heat of adsorption is initially 382 kJ/mol, but increases quickly to 393 kJ/mol by 0.03 ML, and then more slowly to a maximum of 395 kJ/mol at 0.6 ML. Above 0.7 ML, the heat decreases steeply to 370 kJ/mol at 1 ML (nearly equal to the bulk heat of sublimation of Au). The coverage-averaged (i.e., integral) heat of adsorption in the first ML of Figure 2 is 389 kJ/mol.

Returning to Figure 1, the heat shows a small (~ 4 kJ/mol) increase and then decrease between 1 and 2 ML and again between 2 and 3.3 ML. From ~ 3.5 ML to the highest coverage studied, the heat has stabilized at the bulk heat of sublimation of Au (368 kJ/mol³⁴).

The Au/ Pt(111) differential heat of adsorption given above, when integrated up to multilayer coverage (4.5 ML), can be used to determine the Au(111)/Pt(111) adhesion energy using the thermodynamic cycle described previously.³⁵ This gives a value of 3.7 J/m² assuming a flat Au(111) film. This is substantially larger than the adhesion energy of two Au(111) planes to each other, which equals twice the Au(111) surface energy (1.5 J/m² from ref. ³⁶), or 3.0 J/m², as expected for the complete film wetting observed experimentally.

4. Discussion

As described in the Introduction, the growth of Au films on the Pt(111) surface by vapor deposition has received considerable attention in the literature. To summarize those results, the Au film grows layer-by-layer for several layers, and the first layer grows pseudomorphically with Pt(111), in 2D islands. We use those previous results together with the unique calorimetry results above to establish a more complete picture of the film's structural properties and the energetics that drive these structures to form.

The heat of adsorption is 382 kJ/mol initially, and it increases to 393 kJ/mol by ~ 0.03 ML. We attribute this initial steep rise to an increase in the average particle size of the growing 2D islands, and the resulting increase in the number of new Au-Au nearest-neighbor (NN) bonds per added Au atom. For example, as a triangular Au₃ trimer adds 4 Au atoms to make a Au₇ hexagon, 9 new Au-Au NN bonds are formed, or 2.25 such bonds per atom, but as this Au₇ hexagon grows to a 2D Au₁₉ hexagon, the 12 added Au atoms make 30 new Au-Au NN bonds, or 2.5 bonds per atom. Assuming that bulk Au solid and 2D Au islands are held together mainly by Au-Au NN bonds, then each Au-Au NN bond energy is 1/6 of the heat of sublimation ($1/6 \times 368$ kJ/mol) or 61.3 kJ/mol, and the average heat of Au adsorption as Au₇ grows to Au₁₉ should be larger than that as Au₃ grows to Au₇ by $(2.5-2.25)(61.3) = \sim 15$ kJ/mol. As the 2D islands grow to infinite size, the average number of Au-Au NN bonds reaches a limit of 3 per added Au atom, corresponding to another increase in heat of adsorption of $(3.0-2.5)(61.3) = \sim 30$ kJ/mol compared to that when Au₇ grew to Au₁₉. This effect qualitatively explains the continued but much slower increase in heat from 0.03 to 0.6 ML in Figures 1-2. However, as shown below, the buildup of lattice strain with island size causes a change in the opposite direction at very large island sizes, slowing down the increase in heat, and finally causing the heat to decrease with coverage above 0.7 ML.

Due to similar effects of NN bonding, but in this case due to the Au-Pt bonds formed at the surface, the most energetically favorable adsorption site for a Au monomer is certainly at the bottom of a Pt step edge. Therefore, the 2D clusters discussed above probably nucleate at step edges and grow from there. This increases the heats of adsorption for the smallest Au clusters, thus changing the quantitative values compared to above. However, the qualitative explanation for the steep initial increase in heat of adsorption up to 0.03 ML, and the much slower increase up to 0.6 ML, is still certainly valid.

The ~ 24 kJ/mol drop in adsorption energy from 0.7 - 1 ML in Figures 1-2 can be attributed to the lattice mismatch between Au and Pt (Au is 4% larger than Pt in lattice constant) and the resulting buildup of lattice strain within any Au island, as well as the strain-induced repulsion between neighboring 2D Au islands.¹³ A similar drop (19 kJ/mol) was also reported by James et al.¹³ for Cu adsorption on Pt(111), where the lattice mismatch is larger (Cu is 8% smaller than Pt). That paper¹³ provides a detailed explanation of the physical reasons why the heat decreases with increasing 2D island size due to lattice strain. Briefly, as the island size increases, the Au adatoms must sit farther and farther away from the ideal binding site energy minima (which are periodically separated by the Pt(111) lattice distance), due to this lattice mismatch. Also, the islands repel each other as they grow closer together due to the resulting strain induced in the Pt that acts in opposite directions on neighboring islands. That explanation is equally valid here, even though the lattice mismatch is in the opposite direction.

This effect of lattice strain on the heat of adsorption is clearly much stronger at high coverages (>0.6 ML, Figure 2). This is because the islands will begin to coalesce at high coverages, e.g., resulting in a sudden doubling of their size when two islands of similar size coalesce. This faster increase in island size with coverage will increase the energy cost of lattice strain more rapidly.

The average heat of adsorption in the first layer is 389 kJ/mol, 21 kJ/mol higher than the saturation heat at high coverage, indicating that Au/Pt(111) bonds are stronger than Au/Au(111) bonds by ~ 21 kJ/mol on average. This small difference could explain why underpotential deposition of Au monolayers on Pt electrodes has never been reported (to our knowledge). This small extra stability seen in the first ML in vacuum here is probably more than overcome by the expected stronger attraction of the electrolyte to the Pt surface than to an added Au layer, rendering the first layer of Au on Pt unstable relative to 3D particles of bulk Au(solid) when in electrolyte.

As seen in Figure 1, the second and third monolayers grow with a heat that is slightly greater than the bulk heat of sublimation of Au(s), and the second layer shows a heat maximum in the middle (i.e., at ~ 1.5 ML). The growth in the second layer is probably similar to that for the first monolayer, with 2D islands first nucleating and growing in size and finally coalescing as the layer nears completion. This causes the heat to increase and then decrease for the same reasons as in the first ML: increasing numbers NN Au-Au bonds per added atom with increasing 2D

island size and then buildup of lattice strain. These heat oscillations seen in layers 1 and 2 are damped out at higher coverage, probably because new layers start before the last layer is completed, such that the oscillations on different parts of the surface get increasingly out-of-phase, as is very common in homoepitaxy.³⁷ There may be some evidence for this oscillation still seen in layer 3, but it is not clear. Above ~ 4 ML, the heat of adsorption stabilizes at the bulk heat of sublimation of Au(s) as the Au relaxes to the Au bulk lattice parameter (as reported to occur by ~ 5 ML²⁶). The (111) surface of bulk Au undergoes herringbone reconstruction at room temperature.³⁸ We do not know if that occurs for the thin films studied here, nor if it affects the energetics described above.

5. Conclusions

The heat of adsorption of Au on Pt(111) at 300K to make a pseudomorphic monolayer is 389 kJ/mol, compared to 368 kJ/mol at Au coverages above 4 ML (equal to the bulk heat of sublimation of Au). The heat increases with coverage from 382 kJ/mol initially to a maximum of 395 kJ/mol at 0.6-0.7 ML, with most of this change occurring in the first 0.03 ML. This is attributed to the effect of increasing 2D Au island size on the number of Au-Au bonds parallel to the surface. The heat then decreases to 368 kJ/mol at 1 ML, attributed to the buildup of lattice strain with 2D Au island size (arising from the 4% Au/Pt lattice mismatch). Small (~ 4 kJ/mol) oscillations in heat of adsorption with coverage are seen in the second and third Au layers as well. The Au(111)/Pt(111) adhesion energy was estimated from the heat of adsorption versus coverage up to 4.5 ML, and found to be 3.7 J/m^2 .

6. Acknowledgements

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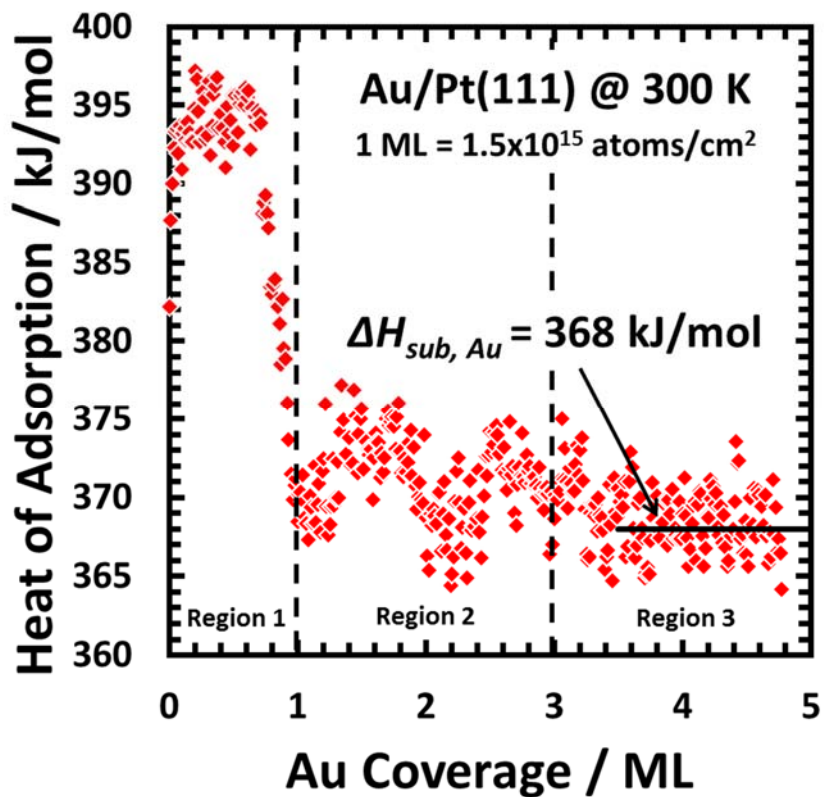


Figure 1. Differential heat of adsorption of Au atoms onto the clean Pt(111) surface at 300 K as a function of Au coverage. (This is the average of three experiments.) Coverage is marked by three regions, corresponding to different general behaviors (see text). A coverage of one ML is defined as one Au atom per Pt(111) surface atom.

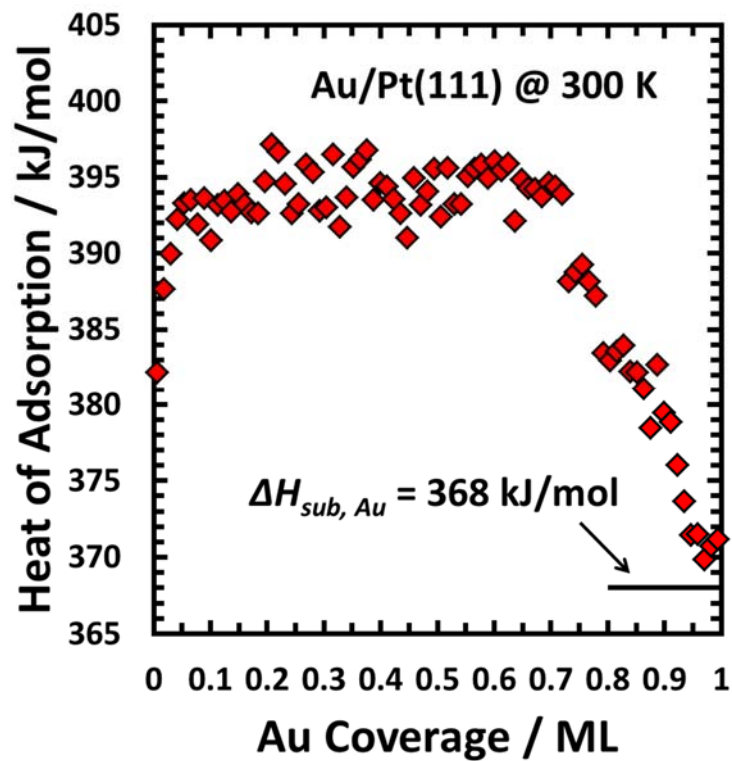


Figure 2. The differential heat of Au atom adsorption versus coverage in the first ML of Au on Pt(111) from Fig. 1. At low coverage, the increasing 2D Au island size results in an increasing heat due to the additional metal-metal bonds formed per added Au atom. Above 0.7 ML, the 2D islands begin to merge, exacting increasingly larger energy penalty due to lattice strain from lattice mismatch.

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