Structure-reactivity relationship for bimetallic electrodes: Pt overlayers and PtAu surface alloys on Au(111)

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We report calculations based on density functional theory of the adsorption properties of CO on pseudomorphic Pt overlayers and PtAu surface alloys on the Au(111) surface. Similar to the Pd/Au system, electrodes consisting of pseudomorphic Pt overlayers on Au show a higher reactivity than pure Pt electrodes due to a combination of geometric strain and electronic interaction effects. Furthermore, we find a significant second-layer effect for CO adsorption at the ontop site of the Pt/Au(111) overlayers which is much smaller for the fcc-hollow site. We have clarified that this second-layer effect for the ontop-site adsorption essentially comes from the highly-directional chemical bonding of C and Pt atoms in the direction perpendicular to the surface, where bonding orbitals have significant overlap with the second-layer atoms. In the case of monolayer PtAu surface alloys, the binding energy on the most stable adsorption sites becomes remarkably larger as the number of Pt atom in the topmost layer increases.

Keywords: electronic structure calculations, thin layer, chemisorption, electrocatalysis, CO, platinum, gold

I. INTRODUCTION

Bimetallic surfaces are recently attracting much attention in heterogeneous and electrocatalysis since they allow to tailor the reactivity by modifying their composition or structure [1, 2]. In order to systematically investigate the relationship between structure and reactivity in bimetallic systems, pseudomorphic overlayers are particularly well-suited since lattice strain effects can be separated from electronic ligand effects by increasing the number of overlayers [3, 4]. As for the strain effects in overlayers due to the lattice mismatch with the underlying substrate [5], it has been known that the lattice expansion can lead to larger binding energies because of an induced upshift of the *d*-band of the overlayer transition metal [6]; it should be noted that there are also exceptions [7]. However, electronic effects depending on the thickness of ultrathin overlayers and the composition of surface alloys are not sufficiently understood yet. A promising approach to understand these effects is to analyze the dependence of the overlayer electronic structures on the thickness by performing total energy electronic structure calculations. The insights from these studies can then also be used to understand the properties of surface alloys.

In particular, the adsorption of CO on Pt surfaces or bimetallic surfaces including Pt has been intensively investigated both experimentally [3, 8–11] as well as theoretically [3, 12–19] where the interaction strength of CO with the metallic substrates has been used as a probe of the reactivity of the bimetallic electrode. As for the PtAu system, it is of current interest in the context of the electrocatalytic methanol oxidation reaction [20–22]. Theoretically, the electronic structure of PtAu surface alloys has been studied by electronic structure calculations [9] which showed that the expansion of the pseudomorphic Pt overlayer on Au by about 5% due to the lattice mismatch together with the relatively weak Pt-Au interaction leads to an upshift of the local *d*-band which is associated with a higher reactivity [23]. Another recent theoretical study addressed the interaction of bimetallic PtAu clusters with CO [24]. The calculations showed that the CO adsorption strength on the PtAu clusters is enhanced compared to pure Pt or Au clusters. The CO adsorption energy on one Pt monolayer on Au(111) has also been calculated before [13] showing a stronger CO binding on the Pt/Au(111) surface than on pure Pt(111).

We have recently studied the CO adsorption on Pt/Ru [3] and Pd/Au [25–27] overlayer systems as a function of the number of overlayers by performing calculations based on density functional theory (DFT). Interestingly, these bimetallic systems exhibit properties that are beyond those of the single components. The more reactive metal becomes even more reactive and the more inert metal becomes more inert. In the case of the PtRu system, the same has also been found for surface alloys [17]. A careful analysis of the calculations yielded that both geometric strain effects as well as the electronic interaction contribute significantly to the modified reactivity. On the other hand, PdCu overlayer systems show a behavior that is intermediate between those of Pd and Cu [28] because of the strong mutual interaction between Pd and Cu.

Furthermore, for the Pd/Au system we found a nonmonotonic behavior of CO and hydrogen adsorption energies as a function of the number of Pd monolayers on Au with the maximum binding energies for a two-monolayer thick Pd overlayer on Au [25, 26]. These results can be explained by second-layer effects in the adsorbate-substrate interaction. In the meantime, the predictions of

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the strain and electronic interaction effects in bimetallic overlayer electrodes have been confirmed experimentally in an electrochemical setup [29]. In contrast, insights on geometric strain and electronic effects of the Pt/Au system are yet to be obtained.

In the present study, we have performed first-principles electronic structure calculations of the CO adsorption on the Pt/Au system. In addition to pseudomorphic Pt overlayers, we have also addressed PtAu surface alloys on a Au(111) substrate. We find that pseudomorphic Pt overlayers on Au are more reactive than pure Pt substrates which is in fact very similar to the Pd/Au system. In the case of the adsorption at the ontop site of the overlayer system, the binding energy for two Pt monolayers is larger than that for one monolayer by 0.38 eV. In contrast, there is no such remarkable difference in the case of the adsorption on the fcc-hollow site, although the binding energy is largest for the two-monolayer thick Pt overlayer on Au. This difference in the binding energy comes from a significant second-layer effect for CO adsorption at the ontop site of the Pt/Au(111) overlayers which is much larger than the one for the fcc-hollow site.

We have clarified that this second-layer effect for the ontop-site adsorption essentially comes from highly-directional chemical bonding of C and Pt atoms in the direction perpendicular to the surface, where bonding orbitals have significant overlap with the second-layer atoms. In the case of monolayer PtAu surface alloys on Au(111), the binding energy becomes remarkably larger as the number of Pt atom in the topmost layer increases when the CO molecule can bind to more than one Pt atom. At the Pt ontop site, the CO binding energy is almost independent of the composition of the PtAu surface alloy.

This paper is structured as follows. After this introduction we describe the computational method used to address CO adsorption on bimetallic PtAu surfaces. In the following section, we first focus on the pseudomorphic overlayer systems and then address the surface alloys before the paper ends with some conclusions.

II. COMPUTATIONAL METHOD

Total energy calculations were performed on the basis of density functional theory [30, 31] within the generalized gradient approximation [32]. The projector augmented wave method [33, 34] is used to describe the core electrons as implemented in the VASP code [35, 36]. The cutoff energy of the plane wave basis sets for the wave function is set to be 420 eV. The Pt/Au bimetallic surfaces were modeled by periodic slabs consisting of six monolayers that are separated by a vacuum with a thickness corresponding to approximately five Au layers. The three bottom layers of the slabs have been kept fixed at their corresponding bulk positions, while all other atoms have been fully relaxed. Both 1×1 and $\sqrt{3} \times \sqrt{3}$ surface unit cells have been used. The total energies have been determined by summing over a Monkhorst-Pack **k**-point mesh of 15×15 and 8×8 for the 1×1 and $\sqrt{3} \times \sqrt{3}$ surface unit cells, respectively. It has been carefully checked that all results are well-converged with respect to these numerical parameters.

The CO adsorption energies have been evaluated according to

$$E_{\mathrm{ads}} = E_{\mathrm{surf+CO}} - (E_{\mathrm{surf}} + E_{\mathrm{CO}}) \,,$$

where $E_{\mathrm{surf+CO}}$ is the total energy of the bimetallic slab with the CO adsorbate, while E_{surf} is the energy of the corresponding clean slab and E_{CO} of the free CO molecule. It should be noted that stable adsorption leads to a negative adsorption energy, while the term "binding energy" refers to the absolute value of the adsorption energy for stable adsorption. The CO adsorption energies have been determined within a $\sqrt{3} \times \sqrt{3}$ surface unit cell corresponding to a coverage $\Theta_{\mathrm{CO}} = 1/3$ of CO molecules.

As far as the theoretical description of CO on Pt(111) is concerned, there exists the so-called CO-Pt puzzle: although experiments show that the most favorable adsorption site for CO on Pt(111) is the ontop site, DFT calculations predict the fcc-hollow site to be most stable [15]. Recent calculations indicate that the underestimation of energy gaps in present density functionals leads to an overestimation of the interaction of the $2\pi^*$ level of CO with Pt(111) thus favoring the wrong site [37]. Here we are not concerned with the correct site preference, but we are rather interested in chemical trends as a function of the number of pseudomorphic Pt overlayers and the composition of the surface alloys. These trends should be independent of the correct site assignment.

Furthermore, possible effects of an electrolyte and any external electric field are entirely neglected in our simulations. However, we have just recently shown that the presence of water on an metallic electrode hardly changes the chemisorption energies in specific adsorption because of the weak water-electrode interaction [27, 28]. This together with the fact that theoretical predictions for the reactivity of bimetallic overlayer systems obtained at the solid-vacuum interface have recently been fully confirmed in an experimental electrochemical study [29] indicates that the results presented here should also be relevant for the electrochemical solid-liquid interface.

III. RESULTS AND DISCUSSION

As a first step, we have analyzed the electronic structure of PtAu bimetallic electrodes by calculating the d-band center. This quantity can often be a convenient guidance to estimate the tendency for the reactivity of transition metal surfaces [12, 23] in the spirit of the frontier orbital concept [38]. The determination of the d-band center for Pt is problematic since the d-band at bulk and surface Pt atoms is not fully occupied and there are spurious components in the calculated local density of states (LDOS) above the Fermi energy obtained by projection

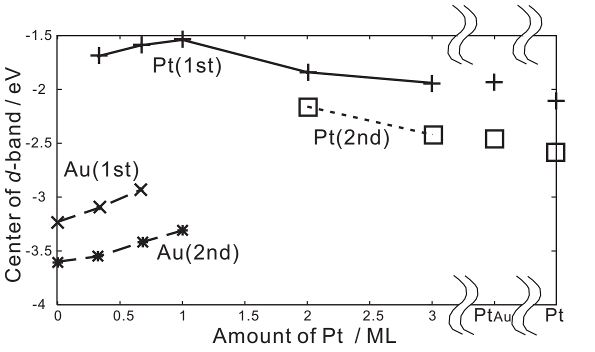

FIG. 1: Center of the local d-band of the topmost-layer atoms and the second-layer atoms estimated as the centroid for the energy of the d-electrons taking account of an energy range from the bottom of the d-band to 2 eV above the Fermi energy. The points in the figure represent the d-band centers for the bare Au(111) surface, one-monolayer surface alloys ($Pt_{0.33}Au_{0.67}$ and $Pt_{0.67}Au_{0.33}$) on Au(111), pseudomorphic Pt/Au(111) overlayers, Pt(111) with the lateral lattice constant of Au (Pt_{Au}) and relaxed Pt(111) from the left to the right of the horizontal axis.

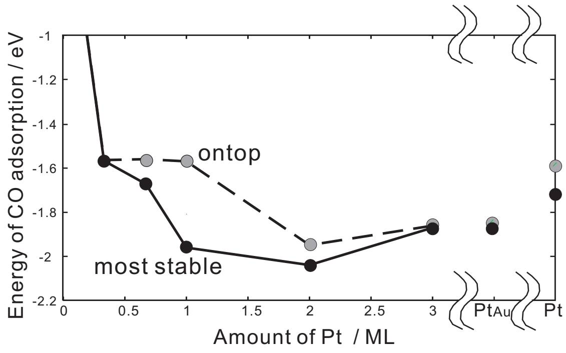

FIG. 2: Adsorption energy for CO on Pt surface alloys and pseudomorphic overlayers on the Au(111) surface. The most stable adsorption sites are the fcc-hollow site for the pseudomorphic overlayers and the pure Pt(111) substrates, the Pt-Pt bridge site for $Pt_{0.67}Au_{0.33}$, and the Pt ontop site for $Pt_{0.33}Au_{0.67}$.

onto the atomic orbitals. These spurious components can influence the determination of the d-band center. In order to avoid this influence, we estimated the centroid for the energy of the d-electrons by taking account of an energy range from the bottom of the d-band to 2 eV above the Fermi energy.

Figure 1 shows the center of the local d-band of the topmost-layer atoms and the second-layer atoms. Two one-layer surface alloys consisting of Pt and Au, i.e. $Pt_{0.33}Au_{0.67}$ and $Pt_{0.67}Au_{0.33}$, on the Au(111) surface are considered as well as pseudomorphic Pt overlayers with one, two and three Pt layers, a Pt(111) substrate with the lateral lattice constant of Au (Pt_{Au}), i.e., an expanded Pt substrate, relaxed Pt(111) and the bare Au(111) surface. Since the d-bands of Au atoms are fully occupied, the d-band centers at Au atoms are significantly lower than those at Pt atoms.

For the surface alloys, the d-band center of the first-layer Pt atoms decreases as the Pt concentration decreases, while the one of Au atoms increases as the Au concentration decreases. It means that the originally reactive Pt becomes less reactive and the originally unreactive Au becomes more reactive in a surface alloy geometry. Thus the present result indicates that these surface alloys should have intermediate properties between Pt and Au surfaces because of the Pt-Au interaction. In contrast, for the pseudomorphic Pt overlayers the d-band center of the first-layer Pt atoms becomes higher as the number of the monolayers decreases and the Pt-Au interaction increases. This is due to the localization of the d-electrons within the Pt overlayers causing a narrowing of the width of the d-band which then leads to upward shift of the d-band center to keep charge neutrality. Furthermore, an additional upward shift of the Pt d-band due to the lateral expansion by 5% (Pt$\rightarrow$ Pt_{Au}) is visible. Figure 1 also shows that the electronic structure at the first layer of a three-monolayer thick pseudomorphic Pt film on Au(111) is very similar to laterally expanded Pt(111), i.e., there is almost no interaction between Au and the topmost Pt layer any more. As far as the overlayers are concerned, the results are very similar to those already reported for the Pd/Au-system [25, 26].

Next, we have analyzed CO adsorption on these surfaces. Figure 2 shows calculated adsorption energies on the Pt pseudomorphic overlayers, pure Pt(111) substrates and the PtAu surface alloys. To identify the most stable adsorption site, we located the CO molecule at the ontop site, the fcc-hollow site, the hcp-hollow site, and the bridge site comparing the total energies. Full structure relaxation was performed for each adsorption site described above. The obtained most stable adsorption sites are the fcc-hollow site for the pseudomorphic overlayers and the pure Pt(111) substrates, the Pt-Pt bridge site for $Pt_{0.67}Au_{0.33}$, and the Pt ontop site for $Pt_{0.33}Au_{0.67}$. Recall that for the pure Pt(111) surface, this leads to the wrong CO adsorption site assignment with respect to the experiment [15]. In the case of the bare Au(111) surface, the calculated adsorption energy is -0.22 eV for both the ontop site and the fcc-hollow site, which means CO hardly adsorbs on the Au(111) surface because of the inertness of Au.

In general, we find that the CO interaction with the Pt/Au(111) overlayer systems is stronger than with the pure Pt(111) surface, in agreement with a previous study [13]. We additionally calculated CO adsorption energies on the bare Pt surface and the Pt surface with the Au lateral lattice constant corresponding to a very thick pseudomorphic overlayer in order to differentiate between geometric and electronic effects. The difference in the binding energy between these two surfaces comes from the lattice expansion effects induced by the Au substrate. In the case of the ontop site, the strain effects are larger than for the three-fold hollow site yielding almost degenerate binding energies for both sites at the expanded surface in contrast to the relaxed surface. On the other hand, the stabilizing effect of the additional Pt-Au interaction by going from a three-monolayer thick to a two-monolayer thick Pt film is much stronger for the three-fold hollow site. Moreover, as in the Pd/Au system [25, 26] there is a non-monotonic trend in the adsorption energies as a function of the number of overlayers with the maximum binding energies for two overlayers, in spite of the fact that the calculated d-band center implies more stable adsorption on one Pt monolayer. This indicates that the stability in the case of two Pt overlayers comes from the interaction between the CO molecule and the second layer Pt atoms that have a much higher d-band center than Au.

The most striking feature seen in Fig. 2 is that, in the case of ontop site adsorption, the CO adsorption on two pseudomorphic Pt overlayers is much more stable than on one Pt monolayer by 0.38 eV. In contrast, in the case of the adsorption on the fcc-hollow site, the difference in the binding energy between the two Pt monolayers and the one monolayer is much more modest. As a result, the binding energy in the case of one Pt monolayer for the most stable fcc-hollow site is significantly larger by 0.39 eV than for the ontop site. This value is much larger than the calculated difference in the binding energy for the ontop site and the fcc-hollow site of the Pt(111) surface, 0.14 eV. Thus, although DFT calculations fail to identify the most stable site for the CO adsorption on the bare Pt(111) surface [15], the fcc-hollow site in the case of one Pt monolayer on Au(111) might be more stable than the ontop site, but experimental data are not available so far.

In order to clarify the origin of the different behavior of the adsorption sites as a function of the number of overlayers, we calculated the electron charge density distribution for these four cases, i.e. the cases of the adsorption at the ontop and fcc-hollow sites on the one- and two-monolayer thick Pt overlayers on Au(111). In particular, we have analyzed the so-called charge density difference by determining the difference in the electron density distribution between the CO/Pt/Au(111) system and the sum of the clean bimetallic surface and the free CO molecule at the same positions. Thus the adsorption induced rearrangement and rehybridization of the electronic structure can be illustrated.

Isosurfaces of the charge density difference distribution for CO adsorbed on the two-monolayer thick Pt overlayer on Au(111) are presented in Fig. 3. In (a), the isosurface corresponding to 20% charge increase in the electron density distribution due to the CO adsorption at the ontop site is shown. It can be clearly seen that the chemical bonding between CO and the Pt overlayer is highly directional in the direction perpendicular to the surface involving mainly the Pt d_{z^2}-orbital, as will be demonstrated below. The increase in the electron density is mainly located on the CO molecule and the Pt atom directly below the CO molecule. Furthermore, there are additional symmetric changes in the underlying three second-layer atoms. These characteristics are the same

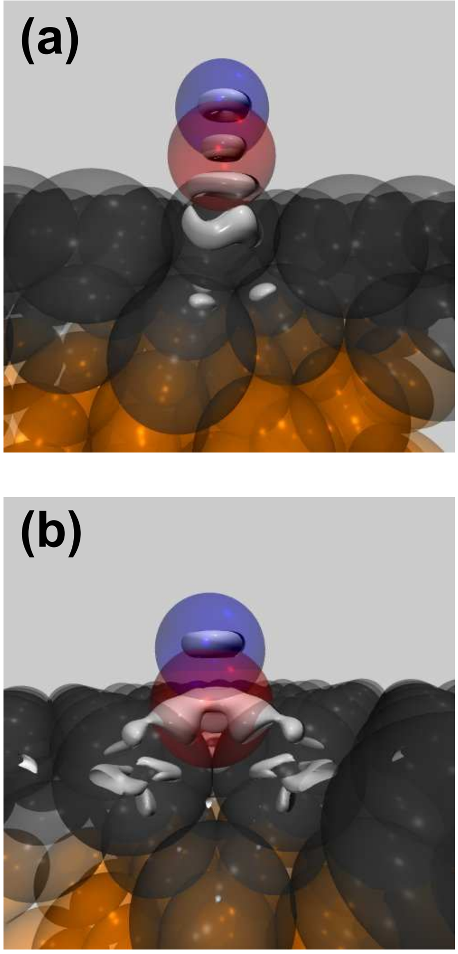

FIG. 3: Isosurfaces of the charge density difference distribution for CO adsorbed on (a) the ontop site and (b) the fcc-hollow site of the two-monolayer thick Pt overlayer on Au(111). The isosurfaces are shown at 20% increase in the electron density.

for the case of one Pt monolayer on the Au surface that is not shown in the figure. The electron redistribution in the second layer indicates that the strength of the chemical bonding is significantly dependent on the particular species of the second-layer atoms. This explains why the binding energy for two monolayers is remarkably larger than that for one monolayer as shown in Fig. 2: Since Pt is much more reactive than Au, the interaction with the second Pt layer enhances the binding energy.

In contrast, as seen in Fig. 3 (b), the adsorption-induced rearrangement of the electron density for CO adsorption at the fcc-hollow site is almost entirely localized in the first-layer, the electron density in the second layer hardly changes at all. In this case, a significant electron redistribution occurs within a extended region of the three Pt atoms adjacent to the fcc-hollow site. Due to this spread of bonding electrons in the direction parallel to the surface, they do not reach into the second layer. This means that, compared to the case of the ontop-site

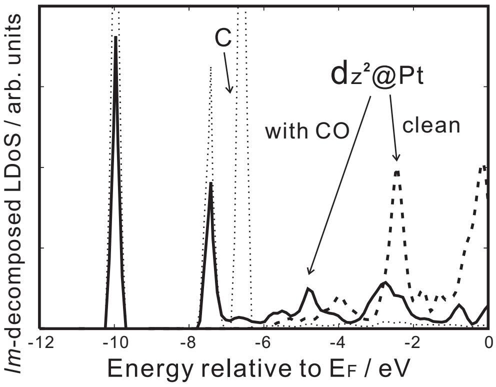

FIG. 4: Partial LDOS projected onto the Pt d_{z^2}-orbital at the ontop site of two Pt overlayers on the Au(111) surface. The LDOS of the electrons at the C atom of the adsorbed CO is also shown for comparison (thin dashed line).

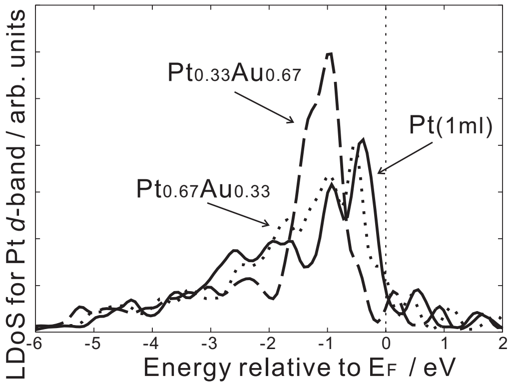

FIG. 5: Calculated d-band LDOS of Pt atoms in the clean pseudomorphic Pt overlayer, and the clean $Pt_{0.33}Au_{0.67}$ and $Pt_{0.67}Au_{0.33}$ surface alloys on Au(111).

adsorption, the influence of the second layer is rather small resulting in the modest change in the adsorption energy.

We have also analyzed the redistribution of the Pt d-electrons by determining the partial LDOS decomposed into angular- and azimuthal-momentum (lm) components. In Fig. 4, the LDOS projected onto the Pt d_{z^2}-orbital at the ontop site of the two Pt monolayers on the Au(111) surface is plotted together with the LDOS of the electrons at the C atom of the adsorbed CO molecule for comparison. In the case of CO adsorption, very sharp peaks at -10.0 eV and -7.4 eV are clearly seen in the Pt d_{z^2}-LDOS , while the clean surface exhibits peaks at much higher energies (-2.4 eV and -0.1 eV). The comparison with the LDOS of the C atom demonstrates that the peaks at -10.0 eV and -7.4 eV correspond to the interaction bonding between the CO molecule and the Pt atom at the ontop site. Since the d_{z^2}-orbital is highly directional in the direction perpendicular to the surface, the present result clearly confirms that the chemical bonds between CO and Pt have an elongated form in the direction perpendicular to the surface making the second layer effects important. As for the peak at -6.6 eV in the LDOS of the C atom, these electrons mainly belong to a CO bonding orbital, while they also partially contribute to the bonding with the d_{yz} and d_{zx} components of Pt d-electrons, however, with a much smaller amplitude than for the case of the peaks at -10.0 eV and -7.4 eV.

Turning to the surface alloys, we first note that the calculated adsorption energies shown in Fig. 2 for the ontop adsorption are almost the same for $Pt_{0.33}Au_{0.67}$, $Pt_{0.67}Au_{0.33}$, and one Pt monolayer on Au(111). As discussed above, the electron distribution contributing to the binding at the ontop site is highly directional in the direction perpendicular to the surface. Therefore, these binding orbitals are hardly affected by the surrounding topmost-layer atoms resulting in almost the same adsorption energies regardless of whether neighboring atoms in the first layer are Pt or Au. This also means that the slight decrease in the position of the Pt d-band center for increasing Au content in the surface alloy is not reflected in the adsorption energies.

In the case of the most stable adsorption on the surface alloys, the larger the number of Pt atoms in the first layer, the stronger the binding, as can be seen in Fig. 2, where the adsorption site changes as “Pt ontop”→“Pt bridge”→“Pt fcc-hollow”. This means that the change in the adsorption site is driven by the tendency of CO to maximize the interaction of with the Pt atoms by increasing the coordination number. Thus, the binding energy is mainly determined by the number of Pt atoms that are available to interact with the CO molecule in these three cases which could be regarded as an ensemble effect [2].

In order to understand the change in the binding energies in further detail, we have analyzed the electronic structure of these three surfaces. Figure 5 shows the calculated d-band LDOS at the Pt surface atoms for clean substrates. Note that there are Pt atoms only in the topmost layer of these three surfaces. It can clearly be seen that the d-band LDOS for the case of the $Pt_{0.33}Au_{0.67}$ surface alloy is significantly narrower than the ones for one Pt monolayer and for the $Pt_{0.67}Au_{0.33}$ surface alloy, which means that the Pt d-electrons in the $Pt_{0.33}Au_{0.67}$ surface alloy are well localized. This localization effect comes from the fact that the Pt atom has no neighboring Pt atoms in the case of the $Pt_{0.33}Au_{0.67}$ surface alloy, where in fact the Pt atom is essentially equivalent to a single Pt atom buried into the topmost layer of Au(111) surface. In addition, the calculated d-band center for $Pt_{0.33}Au_{0.67}$ shown in Fig. 1 is lower than for the other two surfaces in spite of the narrowing of the d-band. These results indicate that the charge neutrality for d-electrons is violated for the $Pt_{0.33}Au_{0.67}$ alloy surface. Therefore, we calculated the number of d-electrons in each case. We have found that the $Pt_{0.33}Au_{0.67}$ surface alloy has 0.13 (0.07) d-electrons more than the Pt monolayer (the $Pt_{0.67}Au_{0.33}$ surface alloy), respectively, which means that there is relatively strong hybridization between Pt and Au making Pt inert. The gradual increase in the population of the Pt d-electrons is consistent with the downward shift of the d-band centers in Fig. 1. Although localization effects can often increase the reactivity by narrowing the d-band and shifting the d-band center to a higher energy, the Pt-Au hybridization counterbalances this effect making this surface not more reactive than the pseudomorphic Pt overlayer.

IV. CONCLUSIONS

In conclusion, we performed total energy calculations based on density functional theory of the adsorption properties of CO on pseudomorphic Pt overlayers and PtAu surface alloys on the Au(111) surface. The Pt overlayers are expanded by about 5% due to the lattice mismatch. In general, the Pt/Au overlayers show larger binding energies than the clean Pt(111) surface. The CO adsorption energies show a non-monotonic behavior as a function of the number of Pt overlayers with the maximum binding energy for the two-monolayer thick Pt overlayer. In the case of the adsorption at the ontop site of the overlayer surfaces, the binding energy for two Pt monolayers is larger than that for one monolayer by 0.38 eV. In contrast, there is no such remarkable difference in the case of the adsorption on the fcc-hollow site. Our calculations demonstrate that a second-layer effect is responsible for this behavior which for the ontop-site adsorption essentially comes from the highly-directional chemical bonding between C and Pt atoms in the direction perpendicular to the surface, where bonding orbitals have significant overlap with the second-layer atoms. In the case of monolayer surface alloys, the binding energy becomes remarkably larger as the number of Pt atom in the topmost layer increases due to the possibility of higher coordination of the CO molecule with the Pt atoms while at the ontop site the binding strength is almost independent of the composition of the surface alloy due to a counterbalance of localization and hybridization effects.

Acknowledgments

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