

# Ligand and ensemble effects in adsorption on alloy surfaces

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Density functional theory is used to study the adsorption of carbon monoxide, oxygen and nitrogen on various Au/Pd(111) bimetallic alloy surfaces. By varying the Au content in the surface we are able to make a clear separation into geometrical (or ensemble) effects and electronic (or ligand) effects determining the adsorption properties.

## 1. Introduction

Alloying is used extensively to alter the chemical properties of metal surfaces, and alloys often have catalytic properties that are substantially different from those of the constituents.<sup>1–7</sup> In order to rationalize the various experimental observations, alloying effects in heterogeneous catalysis are often divided into ligand effects and ensemble effects.<sup>8</sup> Ligand effects loosely describe changes in the chemical properties of the atoms in the surface due to alloying,<sup>9</sup> while ensemble effects refer to changes in the catalytic properties of an ensemble of atoms in the surface when the chemical composition of the ensemble changes.<sup>10</sup> Studies have indicated that the influence of alloying on surface adsorption properties can be well described either in terms of the ligand effect or/and of the ensemble effect.<sup>11–14</sup>

It is usually difficult to distinguish clearly between ligand and ensemble effects. There are several reasons for this. For real high surface area catalysts, there is first the problem that whereas the bulk composition of the alloy catalyst particles is usually known, the surface composition is not. Studying adsorption and reactions on well defined single crystal surfaces alleviates this problem, see for instance the study of the Cu<sub>3</sub>Pt(111) alloy.<sup>9,15</sup> Still one cannot in general vary the composition of the surface without both affecting the distribution of the ensembles and changing the electronic structure of the individual constituent atoms in the surface.<sup>16–18</sup>

In the present paper we use extensive density functional calculations to separate the two effects. We consider the adsorption of molecular CO, and atomic O and N on bimetallic Au/Pd(111) surface alloys on top of a Pd(111) substrate. By considering 18 different adsorption structures for a number of surface compositions we can systematically separate ensemble and ligand effects. We show that the ligand effects can be accounted for by changes in the d-band centers of the surface metal atoms. The ensemble effect is shown to be well described by a simple linear interpolation model in which the adsorption energy at a mixed site is the appropriate average of the properties of the constituents.

In the following we first discuss the method of calculation. We then consider in some detail CO adsorption on different Au/Pd(111) surfaces and introduce our analysis of ligand and ensemble effects. Finally we show that similar results can be found for other adsorbates, and show results for N and O

adsorption on different Au/Pd(111) surfaces. We also show that our analysis can be used generally to discuss variations in adsorption properties and reaction barriers due to alloying.

## 2. Calculation details

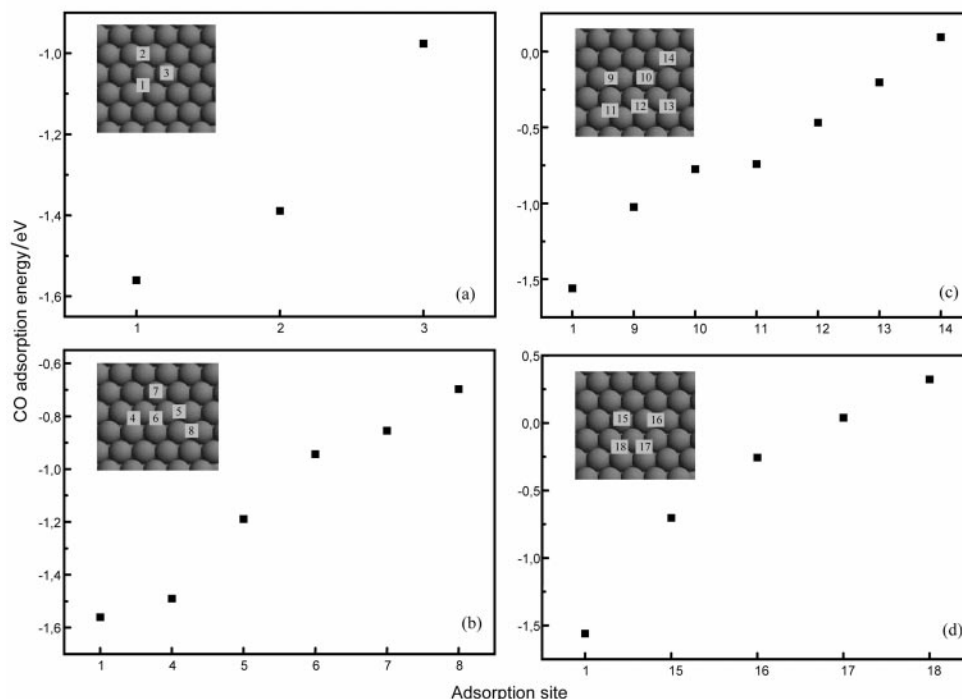
In the present theoretical work, we have used density functional theory (DFT) to calculate the energy for CO, O and N adsorption on various Au/Pd(111) bimetallic surfaces. The Kohn–Sham one-electron equations are solved on the basis of plane wave with kinetic energies below 25 Ry and ultra-soft pseudopotentials are used to describe the ionic cores.<sup>19</sup> The exchange-correlation energy and potential are described by the RPBE functional.<sup>20</sup> The self-consistent electron density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states at small  $K_B T = 0.1$  eV, and Pulay mixing of the resulting electronic density.<sup>21</sup>

We describe the surface using a three-layer slab with a  $2 \times 2$  unit cell, as shown in the insert in Fig. 1. We gradually substitute Au for Pd on the surface at lattice positions, as illustrated from (a) to (d). 18 different sites have been investigated on various Au/Pd(111) surfaces. Each position is indicated by a number in the inset of Fig. 1. One adsorbate is included in each  $2 \times 2$  supercell making the coverage  $\frac{1}{4}$  in all cases.

For all cases in the present study, the lower layers are pure Pd. In all cases the adsorbate has been allowed to relax while the positions of all the metal atoms are fixed at the lattice position of the substrate. We have checked that inclusion of substrate relaxations changes the adsorption energy by less than 0.1 eV. We have also checked that including more Pd layers and increasing the number of  $k$ -points change the adsorption energy by less than 0.03 eV. These effects are much smaller than the effects of changing the surface composition, which is the object of the present study.

## 3. CO adsorption

The adsorption of CO on the Pd(111) surface has been extensively studied by both experimental<sup>22–26</sup> and theoretical approaches.<sup>20,27–30</sup> It is therefore a good system to use for validation of the theoretical approach. CO adsorption on hollow site 1, bridge site 2 and atop site 3 have all been



**Fig. 1** Correlation between adsorption site and adsorption energy for CO adsorption on Au/Pd(111). The numbers listed along the horizontal axes indicate the different adsorption sites, as shown in the insert figures. Dark balls represent Pd. Light balls represent Au.

checked, as shown in Fig. 1(a). It can be seen that adsorption on a hollow site is more favorable than bridge and atop adsorption, in good agreements with other studies.<sup>22–31</sup> Experimentally, the adsorption energy has been estimated to be between 1.47 and 1.54 eV<sup>32,33</sup> for hollow adsorption and 0.98 eV for atop adsorption,<sup>32</sup> which is consistent with our calculation. The adsorption energy shown in Fig. 1 is the same as in similar DFT calculations<sup>29–31</sup> for the adsorption at top, bridge and hollow sites.

The adsorption on AuPd pseudomorphic overlayers on Pd(111) surfaces has been explored. Pd alloy is a simple system since it presents a continuous solid solution without miscibility gap over the whole range of concentrations, and there is little surface segregation.<sup>34</sup> CO adsorption on bimetallic Au/Pd(111) surfaces has also been studied experimentally.<sup>35–37</sup> For the Au/Pd(111) surface alloy obtained by annealing Au monolayer-covered Pd(111) substrates, the adsorption with vibrational frequency at 46/258 meV has been observed by high-resolution electron energy loss spectroscopy (HREELS), and is indicated as the CO adsorption on Pd atoms adjacent to one or more Au surface atoms. In the present work, we then consider CO adsorption on three kinds of Au/Pd(111) alloy surfaces, Au<sub>1</sub>Pd<sub>3</sub>/Pd(111) (Fig. 1(b)), Au<sub>2</sub>Pd<sub>2</sub>/Pd(111) (Fig. 1(c)), and Au<sub>3</sub>Pd<sub>1</sub>/Pd(111) (Fig. 1(d)).

It is clear from Fig. 1 that the CO adsorption energy depends greatly on the adsorption geometry. We can see that the CO on all these alloys prefers to bind to Pd sites. This means that it changes from hollow site 4 to ontop site 15 with increasing Au content on the surface. This result is consistent with the experimental observations.<sup>35–37</sup>

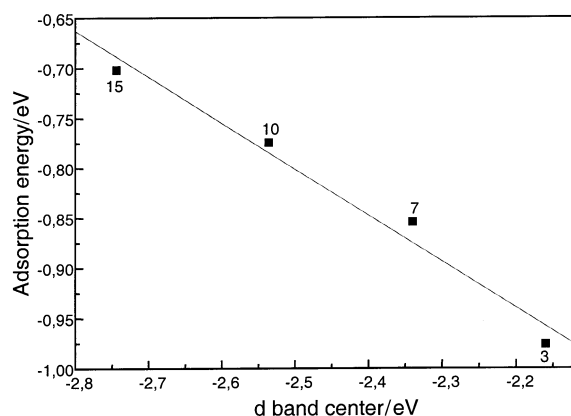
We will now show that the large variation in adsorption energies in Fig. 1 can be rationalized in a model, which is local in the sense that we relate the adsorption energy to the properties of the atoms to which the CO bonds directly.

We relate the adsorption energy to two properties of the adsorption site. The first is the composition of the site. For adsorption in a threefold site with a varying ratio of Au and Pd atoms, there are clearly large differences. This effect, which is related to the nature of the ensemble of metal atoms to which the adsorbate binds, we will refer to as the *ensemble*

*effect*. But even if the adsorption site has the same composition, the adsorption energy can still vary (*cf.* site 1 and 4) because the atom(s) to which the adsorbate bonds have different surroundings. This effect, which is related to the nature of the ligands of the active site, we refer to as the *ligand effect*.

### 3.1 The ligand effect

We first focus on the ligand effect. We can do that most easily by considering CO atop adsorption on Pd(111) (site 3) and various Au/Pd(111) surfaces (site 7, 10, 15). In all cases CO bonds to the same metal atom, so there is no ensemble effect. The difference between the different adsorption sites is the coordination shell around the Pd atom to which CO bonds. In Fig. 2 we plot the adsorption energy as a function of the center of mass of the density of one-electron metal states (in the absence of the CO) projected onto the atomic d orbitals of the Pd atom. This property of the electronic spectrum of the adsorption site clearly correlates very well with the adsorption energy, as would be expected from the detailed analysis of



**Fig. 2** Adsorption energy of CO on atop sites of Pd as a function of the d-band center of Pd for the clean metal surfaces, d-band centers are relative to the Fermi energy. The numbers in the figure correspond to the numbers of the adsorption sites shown in Fig. 1.

Mavrikakis *et al.*<sup>38</sup> The ligand effect is therefore related to the electronic structure of the adsorption site, and a good measure of the reactivity is the metal d band center. Here the rule is that the Pd d states decrease in energy as the number of Au neighbors increases (due to a local compression induced by the large Au atoms), and low-lying d states interact more weakly with CO and other adsorbates than higher-lying ones.

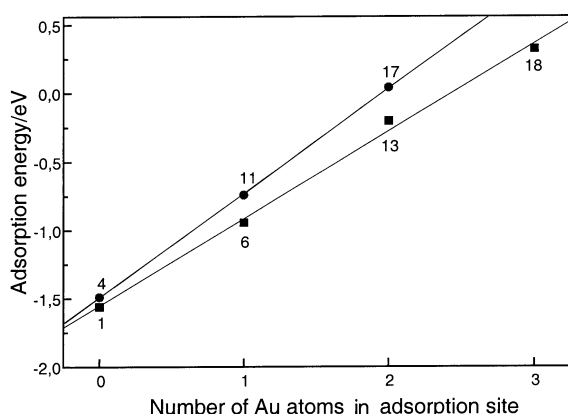
In fact, we also find that the Au d band center on bare surfaces also shifts away from the Fermi energy with the increase in Au neighbors. For this reason we find that the bonding ability of Au on Au/Pd(111) surfaces also decreases with Au alloying.

### 3.2 The ensemble effect

Turning now to the ensemble effect, we notice that there is no simple set of results where we vary the ratio of Pd and Au atoms in an adsorption site without changing the ligands around the adsorption site at the same time. We therefore need a method for separating the two effects quantitatively. We propose the following.

We first consider a variety of adsorption sites with both ligand and ensemble effect. The squares in Fig. 3 show the variation in the CO adsorption energy on hollow sites with different composition. From “1” to “18”, the composition of the hollow site changes gradually from pure Pd to pure Au. We can see that the interaction between CO and the surfaces decreases linearly with the increasing number of Au atoms in the adsorption site. It is obvious that the corresponding change in adsorption energy must be ascribed to both ligand and ensemble effects, and we call it the “total effect”. In the following, we will separate the two effects from the total effect.

The next step is to figure out the ligand effect. Now consider additional configurations which have the same number of Au atoms in the adsorption site, but where the ligands around the adsorption site are different. Such a set of configurations is included as circles in Fig. 3. In comparison with site 1, the composition of site 4 is the same as that of site 1; the difference is that every Pd in site 4 has two Au neighbors, as shown in Fig. 1(b), while there are no Au neighbors for Pd in site 1, as shown in Fig. 1(a). Setting the ligand effect on pure Pd surfaces to zero, the energy difference between adsorption at 4 and 1 corresponds to the ligand effect on Pd induced by two Au neighbors. Here, we assume the ligand effect for the same kind of adsorption site on the same surface to be identical, while the energy difference between the adsorption at the sites with different constituents is ascribed to the ensemble effect of alloying. Thus, for the case of  $\text{Au}_1\text{Pd}_3/\text{Pd}(111)$ , the

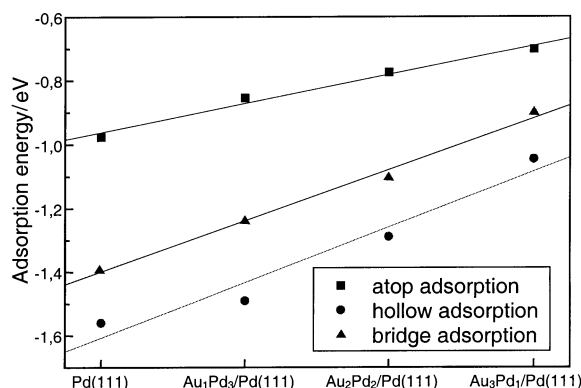


**Fig. 3** Correlation between the energy of CO adsorption on hollow sites of Au/Pd(111) surfaces and the composition of the adsorption sites. The number along the horizontal axes corresponds to the number of Au atoms on hollow sites. The number beside each symbol is the corresponding number of adsorption site, shown as inset in Fig. 1.

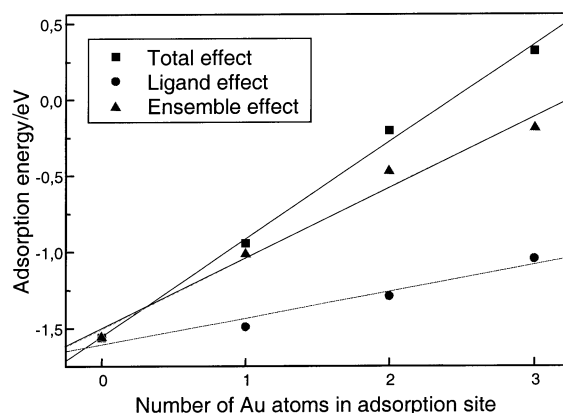
ligand effect at site 4 is the same as that at site 6. Since the contribution of the ligand effect is relative to the case of pure Pd(111), the ligand effect estimated from the energy difference between site 4 and site 1 is considered to represent the ligand effect of the alloy surface, and the energy difference between site 4 and site 6 corresponds to that induced by the ensemble effect. Similarly, we can also estimate the contributions of the ligand effect to the adsorption energy at sites 13 and 18 from the energy differences between 11 and 6, and 17 and 13, respectively.

Now, we have obtained the contribution of ligand effects on three kinds of alloy surfaces to CO adsorption energy for hollow adsorption. Using the same method, we also obtain the ligand effect for bridge adsorption. The results are shown in Fig. 4. It can be seen that the ligand effect for the different kind of adsorption sites is similar, in general, and the influence for adsorption at bridge and hollow sites is a little stronger than for atop adsorption. The reason is that the overlap between the CO  $2\pi^*$  state and the metal d state is larger for the bridge and hollow sites than for atop sites, leading to a stronger coupling.<sup>31</sup>

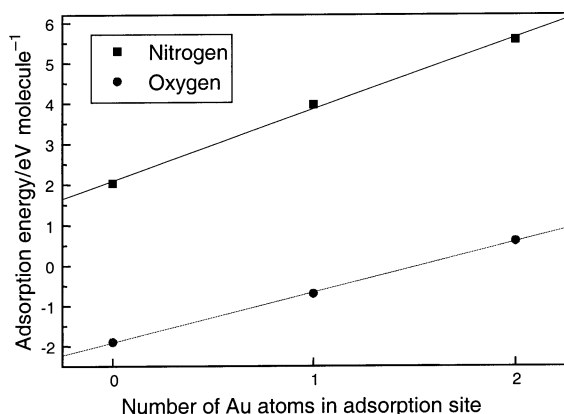
The final step for this process is to separate the ensemble effect from the total effect. If we also set the ensemble effect for pure Pd surface to zero, we can obtain the similar variety in adsorption energy due to the ensemble effect by subtracting the ligand effect from the total effect, as the triangles in Fig. 5. Clearly, the contribution of the ligand effect to the adsorption



**Fig. 4** Influence of ligand effect on the different adsorption sites on Au/Pd(111) alloy surfaces. The squares, triangles and circles correspond to the contribution of the ligand effect for CO adsorption on an atop, bridge and hollow sites, respectively, on the different surfaces shown along the horizontal axes.



**Fig. 5** Separation of the ligand and ensemble effects from the total effect for the case of CO adsorption on hollow sites of Au/Pd(111). The number along the horizontal axes corresponds to the number of Au atoms at the hollow site. The squares, circles and triangles correspond to total effect, ligand effect and ensemble effect, respectively.



**Fig. 6** Correlation between the energy of nitrogen and oxygen adsorption on hollow sites of Au/Pd(111) surfaces and the composition of the adsorption sites. The number along the horizontal axes corresponds to the number of Au atoms at the hollow site. Squares and circles represent nitrogen and oxygen adsorption, respectively.

energy is considerably less than that of the ensemble effect. In addition, the adsorption energy due to the ligand, ensemble, and therefore the total effect, varies linearly with the ratio of the two components.

The conclusion is that at a mixed adsorption site the adsorption energy can be estimated as follows. The largest effect is the ensemble effect, while the ligand effect is also sizable. To a first approximation the adsorption energy can be obtained as a linear interpolation between the adsorption energies and the constituents.

#### 4. N and O adsorption

Nitrogen and oxygen adsorption on an Au/Pd(111) alloy surface is also studied in our work to demonstrate the linear relationship between the adsorption energies and the composition of the adsorption site. The results are shown in Fig. 6.

Fig. 6 shows the energy of nitrogen and oxygen adsorption at hollow sites of different composition. Just as in Fig. 4 and 5, “0” represents a hollow site with three Pd atoms and 0 Au atom, “1” corresponds to the hollow site with two Pd atoms and one Au atom, “2” to the site with one Pd atom and two Au atoms. It is clearly seen that the effect of alloying on both nitrogen and oxygen adsorption displays a similar linear relationship to that for CO adsorption. With increasing Au content, the binding strength between the adsorbate and metal is weakened linearly.

#### 5. Analysis of the ensemble effect

In this section we consider in more detail the reason for the linear correlation between the adsorption energy and the ratio of Pd to Au atoms at the adsorption site. The starting point of the discussion is a qualitative picture of the electronic structure of adsorption systems. We follow here the picture developed in ref. 31. It has been shown here that a useful way of understanding adsorption is to include the interaction between the adsorbate states and the electronic states of the metal surface in two steps. First, we consider the interaction with the metal sp states and then include the coupling to the d states. The sp-bands of all the transition metals are half filled in the metallic state, and the bands are broad. The interaction between adsorbate states and the metal sp-bands can be strong, but it will not vary strongly from one metal to the next. The interaction with the d-bands, on the other hand, will depend strongly on the kind of metal, since the d-bands are narrow and their width and position relative to the Fermi level varies strongly from one metal to the next. We can write

the total interaction energy,  $E_{\text{hyb}}$ , in terms of the sp and d contributions as:

$$E_{\text{hyb}} = E_{\text{sp-hyb}} + E_{\text{d-hyb}} \quad (1)$$

For atomic O and N adsorption, the adsorbate states of interest are the 2p valence states, whereas for molecular CO adsorption the most important states to consider are the  $2\pi^*$  and  $5\sigma$  states.

Even if the coupling to the metal d states determines the trends in adsorption energies from one metal to the next,  $E_{\text{d-hyb}}$  is usually quite small, and can often be estimated using second-order perturbation theory.<sup>31</sup> If we characterize the adsorbate state by its one-electron energy  $\varepsilon_a$ , the d states by their fractional filling,  $f_d$ , and average one-electron energy,  $\varepsilon_d$ , and the interaction by the coupling matrix element  $V_{\text{ad}}$  we can write the interaction energy as:<sup>31,38</sup>

$$E_{\text{d-hyb}} = C_1(f_d) \frac{V_{\text{ad}}^2}{|\varepsilon_a - \varepsilon_d|} + C_2(f_d) \alpha V_{\text{ad}}^2 \quad (3)$$

Here  $C_{1,2}(f_d)$  are functions of the filling of the metal d band. The first term is the (attractive) interaction due to the formation of bonding and anti-bonding states, and depends on the filling of the d bands, because this determines the filling of the bonding and anti-bonding states formed due to the adsorbate-metal d interaction. The second term is repulsive and stems from the energy cost of orthogonalizing the adsorbate and metal d states to each other. One immediate consequence of eqn. (3) is that if we consider situations where an adsorbate interacts with the same kind of metal atoms (so that  $V_{\text{ad}}$  is the same) changes in the surroundings of these metal atoms will enter through changes in the position of the metal d bands, and the associated change in the adsorption energy,  $\delta E_{\text{d-hyb}}$ , can be written as:

$$\delta E_{\text{d-hyb}} \approx \frac{\partial E_{\text{d-hyb}}}{\partial \varepsilon_d} \delta \varepsilon_d = C_1(f_d) \frac{V_{\text{ad}}^2}{(\varepsilon_a - \varepsilon_d)^2} \delta \varepsilon_d = \gamma \delta \varepsilon_d \quad (4)$$

This is the reason for the linear relation in Fig. 2 between  $\varepsilon_d$  and the atop adsorption energy of CO. In this case CO always adsorbs in the atom site over a Pd atom, and the sole role of the Au atoms in the surface is to shift the d states of the Pd.

Let us now move to the case of adsorption in a hollow site composed by three metal atoms termed “1”, “2” and “3”. Imagine including the coupling to the d electrons of the three metals one by one. The interaction between adsorbate and d state of metal 1 can be expressed according to eqn. (3) as

$$E_{\text{d1-hyb}} = C_1(f_{d1}) \frac{V_{\text{ad1}}^2}{|\varepsilon_a - \varepsilon_{d1}|} + C_2(f_{d1}) \alpha V_{\text{ad1}}^2 \quad (5)$$

For coupling with metal 2, the interaction is

$$E_{\text{d2-hyb}} = C_1(f_{d2}) \frac{V_{\text{ad2}}^2}{|\varepsilon_a - \varepsilon_{d2}|} + C_2(f_{d2}) \alpha V_{\text{ad2}}^2 \quad (6)$$

Here in principle we should include the effect of the first coupling on the state  $|a\rangle$ , but since the effect is only first order in the small parameter,  $|V_{\text{ad1}}|/|\varepsilon_a - \varepsilon_{d1}|$ , such effects will be third order and can be neglected. It means that, to second order, the contributions from the three metal atoms are additive:

$$\varepsilon E_{\text{d-hyb}} = \sum_{i=1}^3 \delta E_{\text{di-hyb}} \quad (7)$$

This means that, to second order, the ligand effect is linear in the number of neighbors of a certain kind and seen in the DFT calculations.

#### 6. Conclusion

DFT-GGA periodic slab calculations are used to analyze the adsorption of CO, nitrogen and oxygen on Pd(111) and



various Au/Pd(111) bimetallic surfaces. The results indicate that the CO adsorbed on Au/Pd(111) alloy surfaces prefers to occupy the Pd adsorption sites surrounded by Au atoms, which is in good agreement with experimental observations.

In addition, both the ensemble and the ligand effect have been used to explain the degradation of surface adsorption by Au alloying. From the viewpoint of the ensemble effect, the interaction between adsorbates and Au/Pd(111) bimetallic surfaces is weakened by the presence of Au at the adsorption site, which shows that the "mixed" sites are less favorable than "unmixed" Pd sites, and this effect becomes more obvious as alloying proceeds. From the viewpoint of the ligand effect, the decreasing adsorption behavior on the Au/Pd(111) bimetallic surface is well explained by the changes in the electronic structure near the Fermi level of the surface metal atom. The change in the surface electronic structure is manifested as a shifting of the d band center away from the Fermi level, which leads to the weaker interaction between the adsorbates and the metals.

Finally, a method is proposed to separate the ensemble and ligand effect on the basis of DFT calculation. It provides a clear quantitative description of the two effects induced by alloying. For adsorption on alloy surfaces, the largest effect is the ensemble effect. To a first approximation the adsorption energy can be obtained as a linear correlation between the adsorption energies and the constituents.

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