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Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3*d* transition metals

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The modification of the electronic and chemical properties of Pt(111) surfaces by subsurface 3*d* transition metals was studied using density-functional theory. In each case investigated, the Pt surface *d*-band was broadened and lowered in energy by interactions with the subsurface 3*d* metals, resulting in weaker dissociative adsorption energies of hydrogen and oxygen on these surfaces. The magnitude of the decrease in adsorption energy was largest for the early 3*d* transition metals and smallest for the late 3*d* transition metals. In some cases, dissociative adsorption was calculated to be endothermic. The surfaces investigated in this study had no lateral strain in them, demonstrating that strain is not a necessary factor in the modification of bimetallic surface properties. The implications of these findings are discussed in the context of catalyst design, particularly for fuel cell electrocatalysts. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1737365]

I. INTRODUCTION

Pt-group metals are among the most widely used catalysts. They are also, however, among the most expensive metals. Thus, there is a particular interest in modifying the chemical properties of less expensive metals to mimic the Pt-group metals, or alternatively, modifying the properties of Pt to achieve higher activity or selectivity in a catalytic reaction so that less metal would be required. For example, in hydrogen fuel cell applications one needs an anode electrocatalyst that is both CO-tolerant and efficient at splitting hydrogen. Likewise, the cathode electrocatalyst must be efficient at splitting oxygen, but not poisoned by the O-containing products. Bimetallic catalysts represent one approach to meeting these criteria, as the adsorption properties of molecules can be tuned by the composition and structure of the bimetallic surface.[1] However, it is still difficult to know *a priori* how the chemical and electronic properties of a particular bimetallic surface will be modified relative to the parent metals. These properties depend explicitly on the geometric structure and chemical composition of the surfaces considered.

The adsorption properties of many atoms and small molecules on transition metals have been shown by Hammer and Nørskov to depend primarily on the electronic structure of the surface,[2,3] which in turn is determined its geometric structure and chemical composition. In that work it was shown that the interactions between adsorbates and transition metal surfaces could be considered via a two level orbital mixing picture. The adsorbate orbitals are first broadened by interactions with the broad *s*-electron band, and then split by strong interactions with the sharper *d*-band. These authors further demonstrated that modification of the surface electronic structure can result in a predictable modification of the surface chemical properties, for example the adsorption properties of small molecules. Specifically, a correlation between the average energy of the *d*-band and the adsorption energy of many atoms and small molecules was established.

There are two critical factors that contribute to the modification of the electronic properties of a metal in a bimetallic surface. First, the surface bond lengths are typically different than those of the parent metals. This gives rise to strain effects that modify the electronic structure of the metal through changes in orbital overlap.[4] According to these arguments, when the surface atoms are subjected to tensile strain, the *d*-orbital overlap is decreased, resulting in a sharpening of the *d*-band and an upshift in its average energy (the *d*-band center). For simple adsorbates such as H, O, and CO, this results in a stronger adsorption energy when compared to those of the parent metal surface. On the other hand, when the surface atoms are under compressive strain, the *d*-orbital overlaps are increased, resulting in a broadening of the *d*-band and a lowering of its average energy. Correspondingly, the adsorption energies of simple adsorbates are expected to decrease compared to those of the parent metal surface.

The second factor that contributes to the modification of surface properties in bimetallic systems is the electronic interaction between the two metals. This effect, also termed the ligand effect,[5,6] arises because the presence of other metals

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around a metal atom changes its electronic environment, giving rise to modifications of its electronic structure and consequently, its chemical properties. A critical question is which of these two effects, strain or the ligand effect, is more important? More specifically, under what conditions does strain dominate the modification of behavior of bimetallic surface properties, and under what conditions does the ligand effect dominate? The purpose of the present paper is to identify conditions where the ligand effect can have a dominant role in the modification of the chemical properties of a bimetallic surface. In this respect, it is complementary to the previous work that identified the importance of strain in the modification of the electronic and chemical properties of bimetallic surfaces[4] and seeks to further our understanding of how to design these surfaces. There are also other important phenomena that can affect the properties of bimetallic surfaces, such as ensemble effects,[5] and bifunctional catalysis, in which the two metals function independently. These phenomena were not considered in this work.

Ruban *et al.* studied the changes in the electronic structure of epitaxial monolayers of one metal on another metal for the late transition metals.[7] In that work, the changes in electronic structure were largely attributed to the strain induced by epitaxy. However, it is difficult to separate the effect of strain from that of the ligand effect in this scenario, because they both exist simultaneously. On the other hand, the fact that these authors were able to account for the changes so well using strain alone suggests that the ligand effect may be weak in these systems.

The cleanest way to single out the ligand effect is by using an epitaxial subsurface layer in an otherwise unperturbed surface, so that the surface lattice constant is not changed. In this scenario, the subsurface atoms will be strained, as they must adopt the lattice constant of the surface, but the surface will not be laterally strained. Therefore, any changes in the electronic or chemical properties of the surface may be considered as primarily due to the interactions with the subsurface metal atoms (the ligand effect) and not to surface strain. Thus, in this study we examine Pt(111) slabs, where the second layer of metal atoms has been replaced by one of the 3*d* transition metals.

Some explanation of why this is a reasonable and relevant model is needed. Pt segregates to the surface in many Pt-bimetallic mixtures, and a Pt-rich surface is expected in all of the cases in the present study [for close-packed fcc (111) surfaces].[8] Additionally, there are several reported cases of Pt alloys where the first layer is Pt-rich, and the second layer is enriched in the other metal, most notably Ni–Pt(111) alloys.[9] Kitchin *et al.* recently reported experimental investigations of the effects of subsurface Ni on the chemical properties of Pt(111) single crystals.[10] In that study, thin films of Ni on Pt(111) were prepared by physical vapor deposition of Ni onto the surface, followed by subsequent annealing to drive the Ni atoms into subsurface positions. This particular structure was found to have a weaker hydrogen adsorption energy than either pure Ni(111) or Pt(111) surfaces. Several other investigations of Pt–3*d* alloys in fuel cell applications have suggested that the alloy films used in these studies were covered by a Pt skin.[11–13] Thus, our model

is an idealization of Pt-rich Pt–3*d* alloy surfaces intended to illustrate the electronic interactions between the surface atoms and subsurface atoms in the absence of strain.

We did not consider the possibility that the formation of a bulk alloy could change the lattice constant of the slab, but the effect of this could be estimated from the principles of strain[4] and is discussed later. We also did not consider the stability of these structures with respect to reconstructions or in the presence of adsorbates. Oxygen is reported to induce Ni segregation in Ni–Pt alloys,[14] and the oxidation of Pt₃Ti surfaces at low oxygen pressures is also reported.[15] Toda *et al.* have reported, however, that in many of the Pt–3*d* systems they have investigated that the alloy particles are covered by a thin skin of Pt, even under hot H_3PO_4 reaction conditions and in the electrocatalytic reduction of O_2.[11] Clearly, there are nontrivial issues to be understood on the effects of surface segregation under reaction conditions, but this topic is beyond the scope of this paper.

II. CALCULATION DETAILS

The Pt(111) surfaces were modeled by a 2×2 unit cell with four layers of metal atoms periodically repeated with 4–6 equivalent layers of vacuum (>10 Å) separating the slabs to represent the Pt(111) surface. The four atoms in the second layer of the slab were substituted with one of the 3*d* transition metals between (and including) Ti and Ni. The first and second layers were allowed to relax to their lowest energy configuration, whereas the third and fourth layers were frozen at the bulk Pt–Pt distance (2.84 Å, as determined by DFT for the RPBE exchange/correlation functional used in this work). The electronic structure was calculated with the DACAPO-2.7 code,[16] which uses plane waves as the basis set, and ultra-soft Vanderbilt pseudopotentials (created with the PW91 exchange/correlation functional) to represent the core electrons. The mismatch between the exchange/correlation functional used to create the pseudopotentials and the exchange/correlation functional used in the calculations is not expected to affect the results.[17] In all of the calculations, a $4\times4\times1$ Monkhorst–Pack *k*-point set was used. For the H adsorption calculations a plane wave cut-off energy of 350 eV was used, and for the O adsorption calculations a 450 eV plane wave energy cutoff was used. The calculated adsorption energies on Pt changed by less than 0.05 eV with higher cutoff energies. Maximum symmetry constraints were applied in all cases. In previous work on Ni–Pt systems, it was found that including spin polarization in the calculations did not affect the trends in adsorption energies observed.[10] Therefore, spin polarization was not included in any of the calculations in this work. A dipole correction scheme was used to ensure the slabs were electronically decoupled. The *d*-band density of states was determined by projection of the plane waves onto spherical harmonic orbitals, with the cutoff radius at infinity. The *d*-band center was calculated as the first moment of the projected *d*-band density of states on the surface atoms referenced to the Fermi level, and the mean squared *d*-band width was calculated as the second moment.

The structure of the surface *d*-electron bands is a critical factor in the adsorption properties of many simple

TABLE I. Electronic and geometric structure calculation results.

Second layer identity	d-band center (eV)	Mean-squared d-band width (eV^2)	d-band filling (electrons/atom)	Layer separation (Å)
Ti	−3.16	13.03	9.35	2.14
V	−3.18	13.21	9.32	2.10
Cr	−3.12	12.84	9.30	2.04
Mn	−3.00	12.14	9.29	2.01
Fe	−2.84	11.10	9.29	2.05
Co	−2.74	10.47	9.30	2.04
Ni	−2.60	9.70	9.31	2.04
Pt	−2.44	9.11	9.26	2.34

adsorbates.[3] In correlating adsorption properties with the d-band structure, it is convenient to use a single, characteristic value that is representative of the d-band. The density of states at the Fermi level, ρ_F, has been used in many studies because the electrons at the Fermi level are the most energetically available electrons for chemical reaction. The value of ρ_F, however, is only a single point in the distribution of states, and may reflect little of the d-band structure. Furthermore, there has been only limited success in understanding trends in catalysis using ρ_F (Ref. 18, Chap. 2). In some cases, however, there is a general correlation between ρ_F and the d-band properties, as will be shown later. Another choice of parameter for correlation has been the number of d-holes, or unoccupied d-states. The reasoning is that these empty orbitals are required to interact with the occupied states in adsorbates. It will become apparent below why this parameter is unsuitable to explain the variations in dissociative adsorption energies of H_2 and O_2 for the systems examined in this work.

Hammer and Nørskov have shown that the interactions between adsorbates and transition metal surfaces involve the entire d-band.[3] Therefore, a more logical choice of parameters is one that depends in a functional way on the entire d-band, such as its average energy. The first moment of the d-band is the average energy of the band, also called the d-band center. An alternative choice would be the mean-squared band width, or the second moment. As we will show later, however, these two moments are highly correlated in these systems.

III. RESULTS AND DISCUSSION

A. Electronic structure

The results of our electronic structure calculations are listed in Table I and are shown graphically in Fig. 1. In each bimetallic case, the surface Pt d-band is lower in energy and broader in width than the pure Pt slab. The magnitude of the shift in the surface d-band center relative to pure Pt(111)
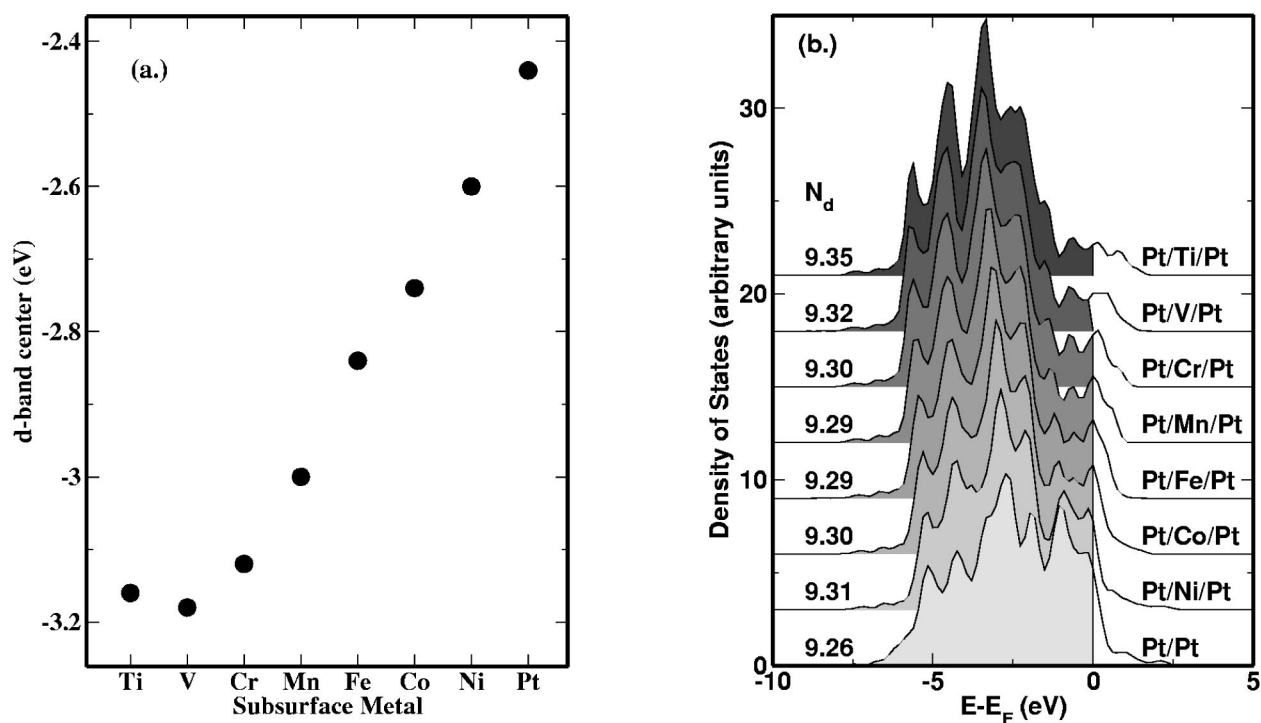

FIG. 1. (a) Variations in the surface d-band center of Pt(111) slabs containing subsurface 3d metals. (b) Calculated surface d-band DOS for subsurface-3d-metal-containing Pt slabs. The number of d-electrons/surface atom is shown for each band.
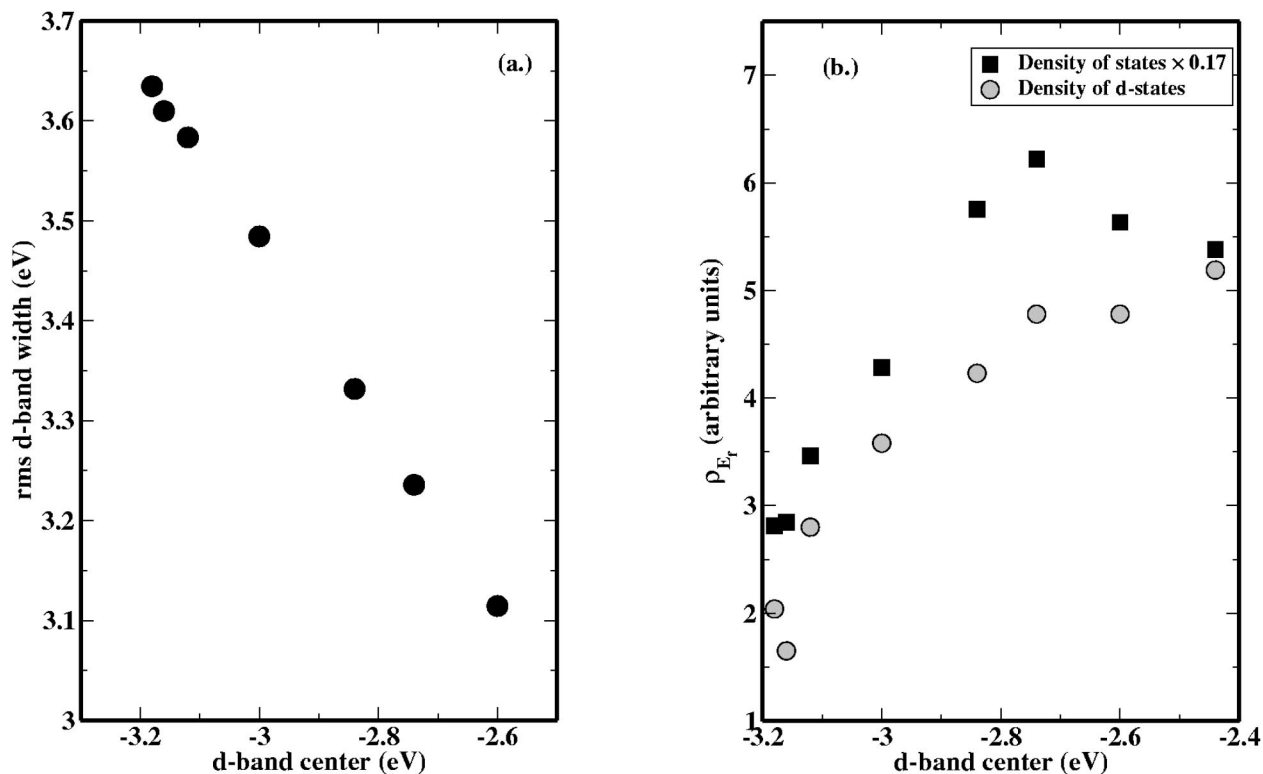
FIG. 2. (a) Correlation between the first and second moments of the d-band density of states. (b) Correlation between the density of states at the Fermi level and the d-band center for the total density of states and d-band density of states.

generally increases as the subsurface metal moves to the left in the periodic table, consistent with the trend in the magnitude of the matrix element[7] for these metals. This suggests why strain was capable of explaining the trends shown by Ruban *et al.*,[7] the ligand effect is weakest between the late transition metals, and most likely to be dominated by strain for these bimetallic combinations. Interactions between early transition metals and late transition metals are seen to be the strongest, and these combinations were not considered in that work.

The number of d-electrons per surface Pt atom was calculated by integrating the projected surface d-band density of states up to the Fermi level. In each case, we calculated $\sim 9.3d$-electrons/Pt atom [also shown in Table I and Fig. 1(b)]. Thus, the d-band filling does not appear to change substantially by the formation of the bimetallic structure. Correspondingly, the number of unoccupied d-states does not change either. Thus, correlations between the number of d-holes and chemical properties of these systems are not expected.

Conservation of the d-band filling is significant, because it means that if the band widens, it must move down in energy in order to maintain the constant d-band occupancy. Conversely, if the band becomes narrower, it must move up in energy to conserve the d-band filling. Thus, the band width and band center are related. This can be shown analytically, by assuming a simple, rectangular form of the d-band. By assuming that the d-band filling is a constant (as observed in our DFT calculations) and using the constraint that the total number of states is conserved, one can easily show that the second moment of the band, the mean squared

band width ($\bar{W}$), is proportional to the square of the first moment of the band, the d-band center (ϵ_d),

$$\bar{W} = \frac{1}{3}\left(\frac{1}{0.5-f_d}\,\epsilon_d\right)^2 (1-3f_d+3f_d^2), \qquad (1)$$

where f_d is the fractional filling of the d-band, and is a constant. The calculated surface d-band density of states are not rectangular in shape [see Fig. 1(b)], but the same constraints apply to them and this functional relationship still holds true, as shown in Fig. 2(a), where $\sqrt{\bar{W}}$ is seen to vary linearly with ϵ_d with a negative slope as predicted by Eq. (1) for $f_d = 0.93$.

Since the height of the rectangle must decrease as the bands broaden to maintain a constant total number of states (constant area), the rectangular band model predicts that the density of states at the Fermi level should decrease as the band gets wider. Figure 2(b) shows that the density of states at the Fermi level generally decreases with decreasing energy of the d-band center, for both the d-band and the total density of states, as predicted by the rectangular band model. Careful inspection of Fig. 1(b) reveals that the decrease in the density of states at the Fermi level arises from the combination of a state crossing the Fermi level and the diminution of that state. Therefore, unlike the d-band center, which is a function of all the states in the d-band, the density of states at the Fermi level may depend sensitively on the behavior of a localized state near the Fermi level. However, bonding interactions between the d-band and an adsorbate depend on the nature of the entire d-band, not just the behavior of a single
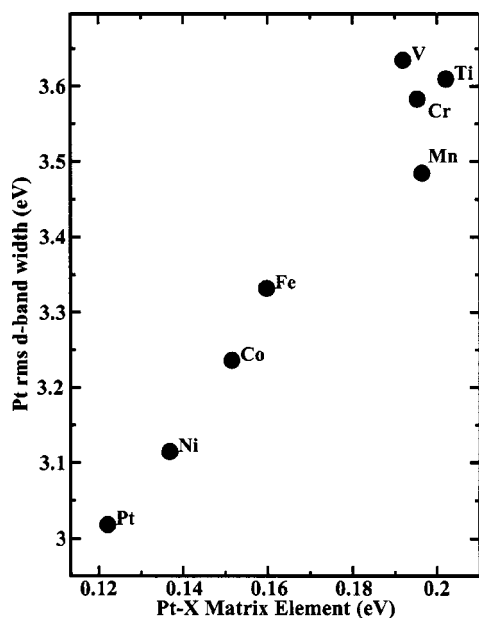
FIG. 3. Relationship between the surface *d*-band width of Pt with subsurface metal X and the matrix element between Pt–X.

FIG. 4. Trends in dissociative adsorption energies for H_2 and O_2 on Pt(111) slabs containing subsurface 3*d* metals.

state. Consequently, the density of states at the Fermi level is not generally expected to be a useful indicator of chemical reactivity.

The electronic properties of the surface Pt atoms in these calculations are modified without the introduction of lateral surface strain. The modification is due primarily to the electronic interactions between the Pt surface atoms and the second layer 3*d* metal atoms. Within a tight-binding formalism, the *d*-band width is proportional to the matrix elements between the *d*-orbitals.[19] For an alloy consisting of metal 1 and metal 2, these can be estimated by

$$V_{ddm}^{(1,2)} = \eta_{ddm} \frac{\hbar^2 (r_d^{(1)} r_d^{(2)})^{3/2}}{m d^5} \qquad (2)$$

where η_{ddm} is a constant, set to unity for convenience, $\hbar^2/m = 7.62\,\mathrm{eV\,\AA^2}$. $r_d^{(i)}$ is a length characteristic of metal *i*, and can be found in the Solid State Table in Ref. 19. Finally, *d* is the distance separating the metals, the interlayer separation found in Table I. These matrix elements are related to the strength of the interaction (bonding) between the two metals; in this work that is the strength of the interaction between the surface Pt atoms and the subsurface 3*d* metal. The proportionality between the Pt–X matrix element and the root mean-squared (rms) width of the surface Pt with subsurface metal X is shown in Fig. 3. Clearly the surface *d*-band width is proportional to the matrix element between the surface Pt and subsurface metal, suggesting that the change in band width is due to strong bonding between the Pt and subsurface 3*d* metal. As discussed earlier, the band then moves down in energy to conserve the number of *d*-states.

Finally, we consider the effect that the lattice constant could change due to formation of a Pt–3*d* alloy. The nearest neighbor distances for all the 3*d* transition metals except Ti are smaller than that of Pt. In the context of Vegard's law,
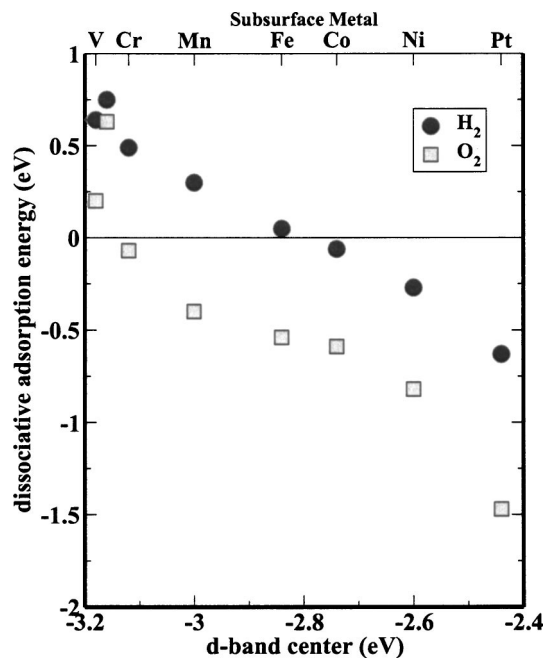
which predicts a linear variation in alloy lattice constant with composition, this means that the lattice constant of the alloy will be smaller than that of Pt. According to the strain arguments discussed earlier, this indicates that the *d*-band will likely be even wider and lower in energy than shown here in this work. Thus, assuming that the alloys would still have an fcc-like structure, the estimates above could be viewed as an upper bound on the alloy results. The real alloys are certain to be much more complicated than these simple models though. Some of the 3*d* metals have bcc crystal structures, others have hcp structures, and the variations in lattice constant with composition are usually not linear.[20] A change in the alloy crystal structure would have a corresponding change in electronic and chemical properties, but this is beyond the scope of this paper.

B. H_2 and O_2 dissociative adsorption energies

In addition to characterizing the electronic structure of these slabs, we have also calculated the dissociative adsorption energies for H_2 and O_2 on each slab. The energetics of dissociative adsorption of these molecules and their subsequent surface reactions play an important role at the surfaces of fuel cell electrocatalysts.[21] If oxygen binds too strongly to the cathode, for example, it could poison the surface and reduce its activity. On the other hand, if it binds too weakly, the coverage of O adatoms may be too low for significant reaction to take place or dissociation could become activated. Dissociative adsorption energies were calculated as $2E_{\mathrm{slab,ads}} - 2E_{\mathrm{slab}} - E_{\mathrm{molecule}}$, where $E_{\mathrm{slab,ads}}$ is the energy of a slab with an O or H atom on it at 0.25 monolayer coverage in the threefold, fcc site. E_{slab} is the energy of a clean slab; and E_{molecule} is the energy of an H_2 or O_2 molecule in the gas phase. Zero-point energies were not included in any of the calculations. As with the clean slabs, the top two layers and

the adsorbate were allowed to relax to the lowest energy configuration. The third and fourth layers were fixed at the bulk lattice parameter previously mentioned, 2.84 Å. The results are summarized in Fig. 4. There is a nearly linear trend in the adsorption energies versus the surface d-band center; the adsorption energy decreases as the d-band center becomes more negative. The dissociative adsorption for both H_2 and O_2 becomes endothermic when the surface d-band center shifts to sufficiently negative values. It is now obvious why the density of states at the Fermi level has sometimes been successfully used in correlations with chemical properties; in some cases, there is a strong correlation between the d-band center and the density of states at the Fermi level [see Fig. 2(b)]. However, it is also apparent in Fig. 2(b) that the correlation is not monotonic, and thus may be nontrivial to use. Therefore, the d-band center with the more intuitive adsorption model of Hammer and Nørskov is a more useful indicator of chemical reactivity.

These results have important implications for catalyst design, particularly for proton exchange membrane (PEM) fuel cell electrocatalysts. On the PEM fuel cell anode, one desires a catalyst that is both CO tolerant and active at dissociating H_2. The CO tolerance of a surface can be enhanced by modifying it in such a way that CO binds more weakly to it, thus reducing its coverage. One method for reducing the CO adsorption energy on a surface is to lower its d-band center, by alloying with another metal, for example, Ref. 22. The present work shows, however, that if the surface d-band center is lowered too much, then dissociative adsorption of H_2 becomes energetically unfavorable. Thus, the bimetallic surface may be very CO-tolerant, but unsuitable for use as a fuel cell anode catalyst.

For the cathode, a similar balance must be made. One needs a catalyst that can dissociate O_2, but not bind the resulting O adatoms too tightly. Enhanced electrocatalytic activity in the reduction of oxygen was shown on several Pt–$3d$ alloy surfaces, particularly Pt–Fe and Pt–Ni, compared to that of pure Pt.[11] In that work, Toda et al. suggest that adsorption of O_2 is the rate-determining step, and that alloying results in an enhanced metal–oxygen interaction that leads to an increased coverage of O_2^-, which subsequently dissociates. However, it has been shown that reducing the dissociative adsorption energy of oxygen results in an increase in the oxygen dissociation barrier.[23] Therefore, it seems likely that the dissociation barrier for O_2 on the Pt–$3d$ surfaces in this study would be higher than that on pure Pt(111). On the other hand, a more weakly bound O adatom may be more reactive than a more strongly bound O adatom, resulting in a rate enhancement. Finally, the adsorption energies of both H_2 and O_2 decrease on these bimetallic surfaces due to the downshift in energy of the surface d-band center. Marković et al. report that the enhancements in the oxygen reduction reaction on Pt_3Co and Pt_3Ni surfaces can be explained by a reduction in the surface coverage of OH_{ads} species.[24] The adsorption energy of many atomic adsorbates and small molecules decreases as the surface d-band center decreases in energy.[23] It is probable that the adsorption energies of surface species such as OH_{ads} will decrease as well, which could result in a lower coverage of these species on

the surface and more available active sites for oxygen dissociation.

IV. CONCLUSIONS

In the present study we have shown how subsurface $3d$ transition metal atoms modify the electronic and chemical properties of a Pt surface by the ligand effect in the absence of lateral strain. In each case, the Pt surface d-band was broadened by the interactions with the subsurface $3d$ metal, with the magnitude of the effect increasing as the subsurface $3d$ metal changed from Ni to Ti. The number of d-electrons remained constant in each case, and consequently the average energy of the band (the d-band center) decreased to maintain a constant d-band filling, in accordance with a rectangular band model. A simple model relating the d-band width to the matrix element between the surface Pt and subsurface $3d$ metal was introduced to explain the change in width. The decrease in the average energy of the surface d-band caused a corresponding decrease in the dissociative adsorption energies of H_2 and O_2, in some cases making dissociative adsorption endothermic. These results show the importance of the ligand effect in the chemical properties of bimetallic surfaces containing both early and late transition metals. This work further demonstrates that adsorption properties of molecules on transition metal surfaces can be tuned by changes in the surface d-band structure, either by strain-induced shifts or through the ligand effect.

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