Trends in Atomic Adsorption on Pt$_3$M(111) Transition Metal Bimetallic Surface Overlayers

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ABSTRACT: The general trends in adsorption behaviors of atomic H, N, O, and S on pure transition metal and bimetallic Pt–transition metal overlayers on Pt(111) are investigated from first principles. Consistent with d-band theory, the adsorbate binding energy on pure transition metal overlayers increases monotonically when the group number of the transition metal decreases. In contrast, bimetallic overlayers show a qualitatively different behavior for trends in adsorption. Using model Pt$_3$M(111) bimetallic surface overlayers, we find the binding of atomic N, O, and S to the Pt$_3$M overlayers increases first and then decreases when moving left in the periodic table. We correlate the different binding energy trends in terms of the change in adsorption geometry resulting from the competition between the adsorbate–metal interactions and formation of Pt$_3$M surface alloys. Charge transfer between the surface atoms and the adsorbates is much larger for early transition metals, leading to the different trends in adsorbate binding energies on Pt$_3$M overlayers with early transition metal M. We also find the surface segregation tendencies of solute metals M are influenced by the binding strength of the adsorbates to the alloy overlayers. O adsorbates qualitatively change the segregation tendency of early transition metals to segregate to the Pt(111) surface.

1. INTRODUCTION

In the pursuit of rational design of heterogeneous catalysts, bimetallic surface alloys take a prominent role owing to the possibility to tailor the surface reactivity by changing the composition and structure of the bimetallic surfaces. Efforts involving alloying of Pt catalysts have been particularly successful and led to the discovery of several promising Pt-based bimetallic materials with improved catalytic activity. For example, alloys of Pt and some early transition metals demonstrated a pronounced increase in catalytic activity for the oxygen reduction reaction (ORR); specifically, the activity of Pt$_3$M is enhanced by an order of magnitude over a pure Pt catalyst. Similarly, even though the pure Bi surface is easily poisoned in the hydrogen evolution reaction (HER), Pt–Bi surface alloys show improved catalytic performance for HER compared with pure Pt.

Considering the importance of adsorption in the cycle of heterogeneous catalysis, it is not surprising that the improvement in catalytic activity of bimetallic surfaces is often correlated with a change in the adsorption behavior. As suggested by Sabatier’s principle, the optimum rate of a catalytic reaction is achieved on surfaces where adsorbates bind neither too strongly nor too weakly. A more quantitative description of this general principle in heterogeneous catalysis is the Bronsted–Evans–Polanyi relation that the activation energy of the adsorbate dissociation changes linearly with the adsorption energy on a catalytic surface. A general understanding of the adsorption behavior on bimetallic surfaces would not only contribute to a better understanding of the catalysis process but also serve as a guide to screen and discover better bimetallic catalysts.

Chemisorption on solid surfaces involves strong interactions between the electrons of adsorbates and the surface atoms. On pure transition metal surfaces, the differences in chemical bonding between the adsorbate and the metal atoms are often described in terms of the interactions between the adsorbate and the metal d-band states. By describing such interactions as a perturbation on the transition metal d band, adsorbate binding energies can be correlated with a single descriptor of the surface. As a descriptor of adsorption properties, the d-band center has been applied to study a wide range of catalytic systems, including the atomic and molecular adsorbates on pure metals, bimetallic “sandwich” structures, and nanoparticles. The ligand and strain effects on the chemical properties of transition metal surfaces can also be explained partly from the d-band center model. The adsorption properties on binary surfaces show correlations with the d-band center in some systems, but the correlation is often
not as good as the adsorption on monometallic surfaces.\textsuperscript{3,26} There are also reports showing that the adsorption behavior on some surfaces cannot be explained from the simple d-band model.\textsuperscript{27–29} Clearly, for bimetallic surfaces, there are factors in addition to the d band that affect the adsorption on bimetallic surfaces.

In this paper, we study the behavior of atomic adsorbates (O, N, H, and S) on the bimetallic (Pt/transition metal) overlayers on Pt. The composition and structure of a bimetallic surface layer are dependent on many factors, and here we focus on understanding the effect of the surface solute metals on the adsorbates. Using density functional theory, we performed a systematic study of the atomic adsorption on Pt\textsubscript{3}M (M = transition metals) overlayers of Pt(111). We find the trends in binding energy on Pt\textsubscript{3}M are different from the monotonic trend of binding energy on pure transition metal overlayers. The existence of solute atoms in the overlayers leads to dramatic changes in the adsorption geometry and binding strength on some Pt\textsubscript{3}M overlayers.

2. METHODS

We perform first-principles total energy calculations for transition metal overlayers in the presence and absence of different atomic adsorbates (H, N, O, and S). These calculations are based on density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP)\textsuperscript{30,31} using the projector-augmented wave (PAW) method.\textsuperscript{32} The generalized gradient approximation (GGA) of Perdew and Wang\textsuperscript{33} is used to approximate the electronic exchange and correlation. For early transition metals, we use potentials that treat semi-core p or s states as valence. An energy cutoff of 520 eV is used for the plane wave basis set of the electronic wave functions. The Brillouin-zone integrations are sampled using Monkhorst-Pack k-point meshes corresponding to an $11 \times 11 \times 1$ grid for the $2 \times 2$ supercell used in the study. Spin polarization is included in all DFT calculations.

To study the effect of surface solute atom on the adsorption, the binding energies of different adsorbates on bimetallic Pt\textsubscript{3}M overlayers are calculated. The solute metals M are 3d (Ti--Cu), 4d (Zr--Ag), and 5d (Hf--Au) transition metals. We use a slab model with 7 atomic layers and a vacuum region of 10 Å in thickness for the surface calculations. The surface overlayer is a $2 \times 2$ structure of Pt\textsubscript{3}M (Figure 1b and 1c), and all other layers are pure Pt(111). The bottom three layers of the slab are fixed at the Pt bulk equilibrium positions with a lattice constant of 3.985 Å, and all other layers are fully relaxed. As a comparison, we also use the same set of parameters to study the adsorption on pure transition metal overlayers over a Pt(111) substrate (Figure 1a). We note that the lattice constant of bulk alloys would change with the alloy elements,\textsuperscript{34} which could introduce strain in the surface layer and affect the adsorption behavior.\textsuperscript{24} Because our study is intended merely to elucidate the trends of the electronic wave functions. The Brillouin-zone integrations correspond to an $11 \times 11 \times 1$ grid for the $2 \times 2$ supercell used in the study. Spin polarization is included in all DFT calculations.

The adsorbates considered in the paper are atomic H, N, O, and S. The dissociative binding energies of H, N, and O are calculated by eq 1

$$E_{\text{bind}}(A) = E_{A/\text{slab}} - \left( \frac{1}{2} E_{A(g)} - E_{\text{slab}} \right)$$

where the first term is the total energy of an adsorbate A (H, N, or O atom) on the given slab, the second term is the total energy of $A_2$ (H$_2$, N$_2$, or O$_2$) from DFT calculations for the gas phase, and the third term is the total energy of the slab in vacuum. The binding energies of S are referenced to H$_2$S as in eq 2

$$E_{\text{bind}}(S) = E_{S/\text{slab}} - \left( E_{H_2S(g)} - E_{H_2S(g)} \right) - E_{\text{slab}}$$

The binding energies of the adsorbates are calculated for the fcc sites of the (111) surface at a 1/4 ML adsorbate coverage (Figure 1). The fcc sites of the (111) surface are usually the most stable adsorption sites for Pt alloys at low adsorbate coverage.\textsuperscript{23}

In addition to the adsorption behavior on surface overlayers, we also study the surface segregation tendency of the solute transition metal atom in the presence and absence of the adsorbates. The segregation energy is calculated as the energy difference between the slabs where the solute atom M is in the surface and in the bulk. A negative segregation energy indicates the solute atom prefers to segregate to the surface, whereas a positive value shows the solute atom tends to stay in the bulk. We use a slab where the solute atom M situated in the fourth layer to model the structure that M is in the bulk. In all segregation energy calculations, the solute atom has a 1/4 ML surface (or fourth) layer coverage and the adsorbate coverage is also 1/4 ML.

3. RESULTS AND DISCUSSION

3.1. Adsorption on Pure Transition Metal Overlayers.

We first study the atomic adsorbates H, N, O, and S on a pure transition metal overlayer (i.e., a monolayer of the overlayer) over a Pt(111) substrate. The dissociative binding energies of these adsorbates on transition metal overlayers (Table S1, Supporting Information) are shown in Figure 2. It is obvious that all adsorbates bind to the surface more strongly for early
The adsorbate binding energy on pure transition metal overlayers gets stronger when the late transition metal M moves left in the periodic table. The change in binding energy with different surface atomic neighbors and one solute transition metal M nearest neighbor. Among the four adsorbates, the binding energy of H is only weakly dependent on Pt₃M solute atoms. However, for N, O, and S, the trend in binding energy on Pt₃M overlayers is clearly different from pure metal overlayers: when going left in a series of transition metals, the binding of these adsorbates to the Pt₃M surface increases first and then decreases for early transition metals. The most negative binding energy does not appear at the leftmost element of a series but in the middle of the transition metal series. This trend is especially pronounced for the oxygen adsorbates. There exists a sharp turning point at Mo and W for the oxygen binding energy on Pt₃M surfaces. Again, there are deviations for some 3d metals due to the magnetic properties of these elements.

If we only consider the results of Figure 3 for late transition metals M, the trend of adsorbate binding energy on Pt₃M overlayers is similar to that on pure transition metal overlayers. The adsorbate binding to the Pt₃M overlayers gets stronger when the late transition metal M moves left in the periodic table. The change in binding energy with different surface

transition metals than late transition metals. When going left in the periodic table, the adsorbate binding gets stronger monotonically on 4d and 5d metals. Because of the strong magnetic moments of some 3d elements (e.g., Fe, Mn, and Co) at surfaces, the adsorbate binding energies on these metals show some deviations from the monotonic trend. Among the four adsorbates, oxygen has the most negative binding energy and forms strong bonds with early transition metals. In contrast, hydrogen adsorbates do not interact with the surface as strongly as other adsorbates and the binding energy of hydrogen changes relatively little on different transition metals. The dissociative binding energies of all adsorbates are negative on early transition metal overlayers but change to positive for some late transition metals. A positive dissociative binding energy indicates no energetic preference for the gas molecule to dissociate on the surface and the atomic adsorption is not thermodynamically stable. Compared to the experimental observations of adsorption on polycrystalline transition metal surfaces,35 the calculated adsorption binding energy on pure transition metal overlayers shows similar monotonic trends but relatively smaller changes between early and late transition metals.

The adsorbate binding energy on pure transition metal monolayer is determined by the electron interactions between the adsorbate and the surface atoms.36,37 When an adsorbate atom moves closer to a transition metal surface, the adsorbate level interacts with the sp and d states of the surface transition metals. While the interactions with the broad sp band of transition metals give similar contributions to the adsorbate binding on different transition metal surfaces, the differences in binding energies can be largely described by the interactions with the more localized d states of transition metals. The effect of the interactions between the adsorbate states and the d states is similar to a two-level problem that creates bonding and antibonding orbitals.38 When the d-band center of the transition metal is higher in energy, the adsorbate binds to the surface more strongly because the antibonding (or bonding) states would be higher (or lower) relative to the Fermi energy and become empty (or occupied).39 The d-band center of the transition metal overlay is determined by two factors: the filling of the d band of the transition metal and the shifting of the d band due to the interactions with the subsurface Pt layers. The d-band center of the transition metal overlay moves higher in energy monotonically when going left in the periodic table because the reduction in d-band filling. Conversely, the d-band center of the surface atom is lowered by the strong interactions between the early transition metal monolayers and Pt subsurface layers. Of the two factors, the d-band filling of the surface transition metals determines the position of the d-band center primarily and leads to the monotonic trends in binding energy within the transition metal series.

3.2. Adsorption on Pt₃M(111) Bimetallic Transition Metal Overlayers. We next study the adsorption on Pt₃M(111) bimetallic overlayers. The model Pt₃M overlay has 1/4 ML transition metal solute atoms on top of a Pt(111) substrate (Figure 1). Compared to the flat pure transition metal monolayer, the relaxed structures show moderate fluctuations in the alloy overlay. On the basis of the results of adsorbate binding energy on pure transition metal surfaces, one might suspect the adsorbate binding on Pt₃M overlayers would follow a similar monotonic trend within a series of transition metals. However, our calculations reveal a qualitatively different trend for the adsorbate binding on Pt₃M(111). In Figure 3, we plot the binding energies of four atomic adsorbates (H, N, O, and S) on different Pt₃M overlayers with a Pt(111) substrate (Table S2, Supporting Information). We consider the adsorption on the same fcc site of the Pt₃M(111) surface that has two Pt nearest neighbors and one solute transition metal M nearest neighbor. Among the four adsorbates, the binding energy of H is only weakly dependent on Pt₃M solute atoms. However, for N, O, and S, the trend in binding energy on Pt₃M overlayers is clearly different from pure metal overlayers: when going left in a series of transition metals, the binding of these adsorbates to the Pt₃M surface increases first and then decreases for early transition metals. The most negative binding energy does not appear at the leftmost element of a series but in the middle of the transition metal series. This trend is especially pronounced for the oxygen adsorbates. There exists a sharp turning point at Mo and W for the oxygen binding energy on Pt₃M surfaces. Again, there are deviations for some 3d metals due to the magnetic properties of these elements.

If we only consider the results of Figure 3 for late transition metals M, the trend of adsorbate binding energy on Pt₃M overlayers is similar to that on pure transition metal overlayers. The adsorbate binding to the Pt₃M overlayers gets stronger when the late transition metal M moves left in the periodic table. The change in binding energy with different surface
solute atoms is consistent with the d-band model. We use a weighted d-band center\(^{38}\) that takes into account the different d-band coupling matrix element\(^{37}\) of the surface atoms to describe the d band of the Pt\(_3\)M overlayers. In Figure 4, the adsorbate binding energies on different Pt\(_3\)M surfaces are plotted with the weighted d-band center of the overlayer (Table S3, Supporting Information). The lines are the linear least-squares fitting of the binding energy for each adsorbate with respect to the weighted d-band center. According to the d-band model, an upward shifting in the d-band center of the surface atoms usually indicates stronger interactions with adsorbates and therefore a higher adsorbate binding energy. When going left in the periodic table, the weighted d-band center of these Pt\(_3\)M surfaces moves upward to the Fermi level, leading to an increase in the adsorbate binding energy. In addition, the adsorbate binding energies on late transition metal Pt\(_3\)M overlayers follow a characteristic linear relationship with the weighted d-band center of the surface, similar to the adsorption behavior on pure metals\(^{37}\) and pure metal overlayers.

The adsorbate binding on Pt\(_3\)M bimetallic surfaces shows a different trend for early transition metals M. Even though the weighted d-band center of the bimetallic surface continues to shift higher when M goes left in the early transition metal series, the adsorbate binding on the alloy overlayers does not get stronger. This trend is inconsistent with a simple d-band explanation, so we examine other contributions to the binding, namely, the atomic structure of the adsorbed state. In Figure 5, we plot the distance between the adsorbate and the surface atoms of the 4d Pt\(_3\)M overlayer. For O, N, and S, the distance between the adsorbate and the surface solute atom M exhibits a similar trend to the adsorbate binding energy on the Pt\(_3\)M surface. The shortest adsorbate−M distance appears at the element in the middle of the 4d series, which corresponds to the Pt\(_3\)M overlayer that has the strongest adsorbate binding. The adsorbate−Pt distance changes in the opposite direction from the adsorbate−M distance. Among the four adsorbates, O has the most dramatic change in adsorbate−M distance on the Pt\(_3\)M overlayers of different solute atoms. We show the relaxed geometry of O on Pt\(_3\)Zr, Pt\(_3\)Mo, and Pt\(_3\)Ag in Figure 6. The O adsorbate still occupies the initial fcc site on Pt\(_3\)Zr and Pt\(_3\)Ag overlayers, which are the first and last elements of the 4d transition metals. However, on the Pt\(_3\)Mo overlayer, the O adsorbate relaxes with no energetic barrier from the fcc site to the atop site of Mo. A similar trend in adsorption geometry is
also observed on 5d metal Pt-M overlayers, and the O adsorbate moves from the fcc site to the atop site of W on Pt3W overlayer.

The deviation from a monotonic trend in adsorbate binding energy on Pt3M bimetallic overlayers is closely related to the change in adsorption geometry on the overlayer, especially for the O adsorbates. In Figure 7, we compare the effects of adsorbate sites on the binding energy of O on 4d Pt3M overlayers. The black line shows the binding energy of a fully relaxed adsorbate on the alloy overlayers. Red line is the binding energy of O relaxed at the fcc sites of the surface. Green line is a bond number weighed sum of the O binding energy on pure metal overlayers.

where \( E_{\text{bind}}(M) \) is the binding energy of O on a pure transition metal M overlayer over Pt(111) and \( E_{\text{bind}}(Pt) \) is the binding energy of O on Pt(111). The modeled binding energy is shown as the green line in Figure 7. The modeled binding energy has the same monotonic trend as the binding energy of O relaxed at the fcc site of the Pt3M overlayers, indicating a similar degree of contributions of the nearest-neighbor surface atoms to the adsorbate binding at the fcc sites. When the adsorption site changes on the bimetallic overlayers, the adsorbates behave very differently on the Pt3M overlayers. The binding energy on Pt3Mo increases by almost 1 eV/adsorbate when O moves from the fcc sites to the atop sites on Mo. We also calculated the O binding energy at the atop site of other 4d early transition metals on the Pt3M overlayers. The atop site of Zr is not preferred for the O adsorbates, whose binding is 0.42 eV weaker at the atop site than the relaxed fcc sites. O binds stronger to the atop site of Nb than the relaxed fcc sites (0.35 eV increase in binding energy), but there is an energy barrier for the O to relax spontaneously from the fcc sites to the atop site. Even when considering the O adsorption on the atop site of Nb, the trend in binding energy on the Pt3M overlayers is still similar to Figure 3.

We have shown that the adsorption behavior on Pt-M bimetallic overlayers is very different from pure metal overlayers. We next examine the correlation between the adsorption behavior and formation of surface alloys between Pt and the solute transition metal M. We calculate the formation energy of Pt3M surface alloys using eq 4

\[
E_F(Pt_3M) = \frac{1}{3}E_{\text{bind}}(M/Pt) + \frac{2}{3}E_{\text{bind}}(Pt)
\]

where \( E(Pt_3M/Pt) \) is the total energy of a Pt3M layer on Pt(111) and \( E(M/Pt) \) is the total energy of a pure M layer on Pt(111). The quantity \( E_F(Pt_3M) \) is essentially the mixing energy of Pt−M mixing in the surface layer. To find the global ground state surface ordering of Pt and M, careful studies of the configuration space based on methods such as cluster expansion are needed. The calculated formation energies for 4d Pt3M surface alloys are shown in Figure 8. When going left in the period table, the formation energy of Pt3M surface alloys gets more negative, suggesting stronger bonds between Pt−M for early transition metals. From the perspective of bond order conservation, there exists a competition between the formation of adsorbate−M bonds and the Pt−M bonds in the Pt3M alloy overlayers with adsorbates. While the adsorbates tend to bind stronger to pure early transition metal overlayers, early
transition metals M also form strong Pt−M bonds in the alloy overlayer, making it difficult to form strong bonds between M and the adsorbates at the same time. The competition between the formation of these two types of bonds results in the strongest adsorbate binding on Pt3M surface where M is in the middle of the transition metal series.

To further understand the effects of alloy overlayers on the O adsorption, we perform Bader charge analysis41,42 to determine charge transfer between Pt, M, and O. Formation of Pt3M alloy overlayers results in a charge transfer between Pt and solute atoms. It is obvious from Figure 9 that the Pt atom gains negative charge from the solute 4d atoms. The amount of charge transfer is small for late transition metals but gets considerably larger in early transition metals. Because the simple d-band model does not apply well for systems with large charge transfer (e.g., ligand effect),29,43 this explains why the d-band model does not predict correctly the binding energy trend on early transition metal Pt3M overlayers. Similar to the trend of formation energy of Pt3M surface alloys, the degree of charge transfer is correlated to the bond strength between Pt and solute atom M. When surface metal atoms interact with the O adsorbates, additional charge transfer takes place to form chemical bonds between O and the surface atoms. The adsorbed O atom gains charge from surface atoms during the process (Figure 9). We show the change of Bader charge of the surface atoms with the adsorption of O atom in Figure 10. The change of Bader charge at the Pt site is relatively similar in Pt3M surfaces when O occupies the fcc sites, but the charge change at the solute atom shows different trends in early and late transition metals. For late transition metal M, the amount of charge transfer from M gradually increases when going left in the transition metal series, indicating increased interactions with the O adsorbates. However, the trend is reversed for early transition metals. Since early transition metals transfer a fair amount of charge to form surface alloys with Pt, they cannot transfer more charge to O without undermining the Pt−M bonds. Thus, there is a competition between Pt−M and M−O bonds. The reduced amount of charge transfer between O and M results in longer M−O distance (Figure 5) and weaker O binding (Figure 3). The change of stable adsorption site of O from the fcc site to the atop site of Mo is a special condition that facilitates Mo to form strong bonds with O while keeping the moderate Pt−Mo bonds.

Figure 9. Bader charge of the Pt site of Pt3M(111) in the presence and absence of O. Green line shows the Bader charge of adsorbed O. Red dots are the Bader charge of Pt and O when O is fixed at the fcc site on Pt3Mo(111).

Figure 10. Change of Bader charge with the O adsorbates for Pt and M in Pt3M(111). Red dots are the change of Bader charge when O is fixed at the fcc site on Pt3Mo(111).

3.3. Adsorption Induced Surface Segregation on Pt3M(111) Surface Alloys. We last briefly consider the stability of the Pt3M surface and surface segregation of solute atoms. The thermodynamic tendency of solute atoms to segregate to the alloy surfaces plays an important role in determining the composition and structure of alloy surfaces.44−48 The interaction of adsorbates with surface atoms could change and sometimes even reverse the segregation tendency of solute atoms to the surfaces.48−52 We calculate the segregation energy of 4d transition metals to the surface of Pt(111) in the presence and absence of adsorbates (Figure 11).

Table S4, Supporting Information, lists the segregation energy for all 3d, 4d, and 5d metals to the surface of Pt(111) in the presence of adsorbates. When going left in the transition metal series, Pt binds stronger with transition metal M. To maximize the energetically preferred Pt−M bonds, the solute atoms tend to stay in the bulk rather than to occupy the surface sites. Therefore, only the Ag atom has a negative segregation energy and an energetic preference to segregate to the surface of Pt in vacuum (similar to the results by Ruban et al.47). However, the presence of adsorbates can change this behavior. If the adsorbate binds to the solute atom M so strongly that the increased adsorbate−M binding overcomes the energy penalty for M to occupy a surface site, the solute atoms M can then segregate to the surface. The H adsorbate does not interact strongly with the solute atom M, and the segregation energy in the presence of H is almost exactly the same as the segregation...
energy in vacuum. However, the O adsorbate induces surface segregation for all 4d metals, and Mo has the strongest tendency to segregate to the surface with O. The segregation tendency with N and S adsorbates is dependent on the type of solute atom M.53

We would note that the surface segregation tendency is dependent on many factors, including the adsorbate coverage, surface structure, and bulk composition.54,55 A detailed evaluation of surface segregation requires knowledge of these conditions. Also, our discussion is based on thermodynamic considerations; metastable surface structures and compositions could exist due to kinetic barriers.

4. CONCLUSIONS
We studied the adsorption of atomic H, N, O, and S on pure transition metal and bimetallic Pt−transition metal overlayers from first principles. On pure transition metal overlayers over a Pt(111) substrate, the adsorbate binding energy increases monotonically with the surface transition metal when going left in the transition metal series. The monotonic trend in adsorbate binding energy is in agreement with the general prediction from d-band electronic structure considerations. The adsorption behavior shows a different trend on bimetallic Pt,M(111) overlayers. Different from a monotonic trend on pure metal overlayers, the binding of atomic N, O, and S to the Pt,M overlayers increases first and then decreases when going left in the periodic table. We find that this binding energy trend correlates with the change in adsorption geometry on the bimetallic overlayers. The O adsorbates can relax spontaneously from the fcc sites to the atop site of Mo and W on the bimetallic overlayers. We find that charge transfer between the surface atoms and the adsorbates is much larger for early transition metals than for late transition metals and contributes to the trend in adsorbate binding energies on Pt,M overlayers with early transition metals M. We also examined the surface segregation behavior of metal M in Pt in the absence and presence of adsorbates. While it is not energetically preferred for most transition metals to segregate to the clean Pt(111) surface (in vacuum), the tendency can be qualitatively reserved by O adsorbates. The strong solute−O binding overcomes the energetic penalty of surface segregation (in the absence of adsorbates), making it energetically favorable to bring these solutes to the surface.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information contains DFT binding energies of different atomic adsorbates (H, N, O and S) on pure transition metal M overlayers and Pt,M alloy overlayers on a Pt(111) substrate, weighted d band centers for late transition metal Pt,M overlayers, and segregation energies of solute atom M to the surface of Pt(111) in the presence of the above atomic adsorbates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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