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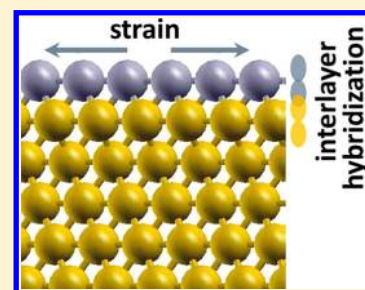
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S Supporting Information

ABSTRACT: The focus of this work is on the Pt/MS structures (MS = Au, Ir, Ru, or Pt substrate), as promising electrocatalysts and a prototype for more general systems: (active element monolayer)/(metal substrate) (AE/MS). We evaluate from first principles the effects of AE monolayer strain and the interlayer AE–MS electronic state hybridization on surface reactivity and reveal rationale for the interlayer hybridization to dominate over the strain effect in determining the AE/MS surface reactivity. We find, however, that, if AE is weakly bound to MS, the surface electronic structure does not suffice to characterize the surface reactivity, because of involvement of other factors related to lattice response to adsorption of a reaction intermediate. Guided by our findings, we trace surface reactivity to a newly introduced hybridization parameter that reflects important features of the electronic structure of the AE/MS surface, which are not taken into account in the original *d*-band center model.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



The design of cost-effective and stable materials with desired surface reactivity is a goal of great importance for many applications. One of the most challenging problems in this area is reduction of cost and increase in activity of electrocatalysts for the proton exchange membrane fuel cells (PEMFCs) and direct methanol (ethanol) fuel cells DMFC (DEFC). The best catalysts on both electrodes of these fuel cells so far contain a significant amount of scarce and expensive platinum and other Pt-group elements. Furthermore, the activity of the Pt-based catalysts for the oxygen reduction reaction (ORR) on the cathodes is relatively low. As to anode catalysts, they suffer from poisoning by CO, which comes with hydrogen produced from natural gas in the case of PEMFC, and as a product of methanol (ethanol) decomposition in the case of DMFC (DEFC). An enormous effort has been made to solve these problems by replacement (or, at least, reduction of load) of Pt in the electrocatalysts and by optimizing the catalyst surface reactivity. For example, a Pt monolayer supported on Au(111) substrate has been reported to be more active toward methanol and ethanol electro-oxidation than Pt(111).¹ Pt submonolayers on Ru nanoparticles,^{2,3} as well as Pt–M mixed monolayers (M = Au or Pt-group metals) on Ir(111)⁴ are found to be more tolerant to the CO poisoning than commonly used anode catalysts: Pt or Pt–Ru alloys. Some reduction of Pt load in ORR electrocatalysts has been achieved in core–shell nanoparticle designs.^{5–8} Trimetal Pt-free sandwich-like structures have also been proposed as efficient ORR catalysts.⁹

Although in some of these works and dozens of others not cited here success has been achieved through “trial and error” search, it becomes clear that significant progress in this area can be made only based on rational design approaches. Fortunately, the basis for rational design is taking shape (e.g., ref 9). Indeed, there are robust models that link the activity of electrocatalysts

to the binding energies of reaction intermediates to a catalyst surface (e.g., ref 10). Furthermore, the strength of the adsorbate bonding is traced to the local density of the electronic states (LDOS) of surface atoms that is depicted in the widely used *d*-band center model.¹¹ It is also known in general how the LDOS of a surface site depends on its surroundings (e.g., ref 9). This picture provides only general guidelines to the rational design of efficient catalysts. However, a lack of understanding of important details of the relationship among the surface composition/morphology, its electronic structure, and reactivity is still hindering reliable predictions of new materials. The goal of this work is to make important steps toward this understanding.

Most of the promising systems discussed above comprise an active element (AE) monolayer deposited on a metal substrate (MS). A common feature of these systems is that AE atoms are in contact with other elements. Since, in general, there is a lattice mismatch between the AE and MS bulk structures, and since, in cases of interest, the AE atoms retain the pattern of the MS surface, the AE–AE bond lengths in AE/MS differ from those in native AE surface. This is defined as a strain effect of the substrate on the AE environment. The other effect comes from the fact that the AE and MS elements are different, and thus the hybridization of the AE–MS electronic states in AE/MS differs from that in the native AE surface. We will call it the “interlayer hybridization effect”.

The strain effect originates from the difference in in-plane overlapping of the AE wave functions in AE/MS and elemental AE surfaces.¹² For example, if the AE layer in AE/MS is

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expanded as compared to the native AE surface, the AE–AE overlapping is reduced. This causes narrowing of the AE d -band and its shift toward E_F that makes the AE/MS surface more reactive. The interlayer hybridization also influences the reactivity of the AE/MS surface through a shift/reshaping of the AE d -band. For example, if reactivity of the native AE surface is low due to the deep location of its d -band and if the d -band of the MS element has a high density around E_F , the AE–MS hybridization in the AE/MS structure shifts the local AE d -band toward E_F , and in this way enhances its reactivity (see ref 9). Although the relative role of both effects in the formation of the electronic structure of the AE/MS surfaces has not been clarified, most authors (see refs 1, 13, and 14) focus on the strain effect. Meanwhile, other works^{9,15} evidence that interlayer hybridization is important.

To unveil and rationalize the relative role of the above effects, we calculate and analyze the electronic structure of the Pt/MS system, where MS = Ru, Ir, Pt, or Au using a density functional theory (DFT)-based computational method (computational details are given in the Supporting Information). In our analysis, we choose the binding energy of OH as a descriptor of surface reactivity, because it appears to be the key intermediate for various reactions, such as ORR on cathodes and CO removal from anodes of fuel cells, as well as oxygen evolution in photocatalytic splitting of water.

To evaluate the strain and interlayer hybridization effects in Pt/Ru(0001), we compare and contrast the projected LDOS of the surface Pt atoms in Pt/Ru(0001), Pt(111) with lattice parameter contracted to the a -parameter of *hcp* Ru, and Pt(111) with its equilibrium lattice parameter (all equilibrium lattice parameters used in this work were obtained from DFT calculations). The projected LDOS for Pt d - xy - and d - xz -states are plotted in Figure 1. Note that in our coordinate frame, all surfaces are oriented in the xy -plane. As seen from panel “a” in the figure, the d - xy -states response to the bond contraction as expected: the sub-band is shifted toward lower energies. The d -

xz -states of Pt, however, hardly change upon the contraction (see panel “b”).

The difference in the strain effect on the d - xy - and d - xz -states is naturally explained by the fact that the in-plane-oriented d - xy -states are sensitive to the change in lattice parameter due to their geometry. In addition, lattice contraction is usually accompanied by increase in the first–second layer separation that compensates the contraction effect on overlapping of the surface atom d - xz -states with the second layer electronic states.

What is very important here is that surface reactivity is determined by the z -oriented states, because they are involved in the hybridization with the adsorbate electronic states. However, the z -oriented states hardly react on the contraction. We thus should not expect a noticeable decrease in the Pt(111) reactivity upon the lattice contraction even though the d -band center moves toward lower energies due to the in-plane state contribution.

Next, we compare the d - xy - and d - xz -states of surface Pt atoms in the contracted Pt(111) and Pt/Ru(0001) (see panels “c” and “d” in Figure 1). Importantly, both structures have the same in-plane Pt–Pt bond lengths, therefore, all differences in the projected LDOS should be totally attributed to the interlayer hybridization. One can see that, in this case, the difference in the d - xy LDOS is not quite pronounced, whereas the d - xz -sub-band is significantly shifted toward lower energies as compared to that of the contracted Pt. This shift should cause a decrease in surface reactivity. We thus can expect the Pt/Ru surface reactivity to be lower than that of Pt(111) that purely results from interlayer hybridization of the z -oriented d -states of Pt.

We have performed a similar analysis for Pt(111), Pt/Au(111), and Pt(111) with the lattice parameter expanded to that of Au and came to similar conclusions: the lattice expansion of Pt causes a noticeable narrowing of the d - xy -sub-band, while the d - xz -sub-band hardly responds to the expansion. On the other hand, the Pt d - xz -sub-band in Pt/Au is found to be much narrower than that in Pt with both equilibrium and expanded lattice parameters. This narrowing is caused by the interlayer hybridization of Pt and Au d -states, which is weak because of energetic separation of the d -bands of Au and Pt (the Au d -band is located at lower energies). The projected LDOS of Pt in Pt/Au and Pt(111) (with equilibrium and expanded lattice parameters) can be found in the Supporting Information (Figure S1).

To trace our results to surface reactivity, we list in Table 1 the binding energies of OH ($E_B(\text{OH})$) calculated for the above-considered surfaces, as well as d -band centers and centers of the d - xy - and d - xz -sub-bands (centers of gravity in the energy scale). Pt(111) is used as a reference for all numbers. We find that, as suggested by the analysis of the projected Pt LDOS,

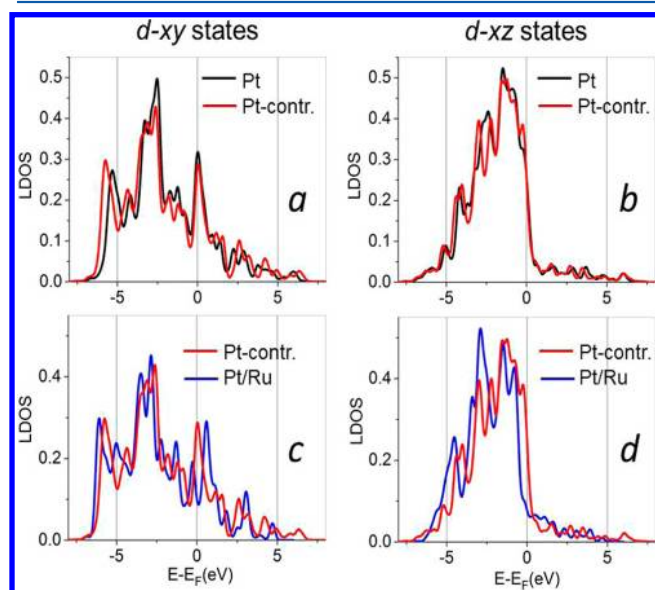


Figure 1. Projected LDOS of surface Pt atoms calculated for Pt(111) with the equilibrium lattice parameter (Pt), Pt(111) with the in-plane bond lengths equal to those of Ru(0001) (Pt-contr.), and Pt monolayer on Ru(0001) (Pt/Ru).

Table 1. Centers of Gravity of the Pt Total and Projected LDOS and OH Binding Energies Calculated for the AE/S Structures

	$\Delta E(d\text{-tot})$, eV	$\Delta E(d\text{-}xy)$, eV	$\Delta E(d\text{-}xz)$, eV	$\Delta E_B(\text{OH})$, eV
Pt(111)	0	0	0	0
Pt-contr.	−0.12	−0.24	−0.05	−0.01
Pt/Ru(1000)	−0.37	−0.35	−0.37	−0.27
Pt-expand.	0.26	0.50	0.11	0.06
Pt/Au(111)	0.58	0.69	0.49	0.04

$E_B(\text{OH})$ is significantly lower for Pt/Ru(0001) than for Pt(111) due to the interlayer hybridization.

Considering Pt(111) (with contracted, equilibrium, and expanded lattice parameters) and Pt/Ru, one can see that the correlation between $E_B(\text{OH})$ and the center of the d - xz -subbands is much clearer than that between $E_B(\text{OH})$ and the center of the total d -band. It reflects the fact that the z -oriented states are those that are involved in the binding of adsorbates, while the total d -band also includes the in-plane oriented d -states that do not participate much in chemical bonding. Therefore, we propose to trace surface reactivity to the z -oriented d -states rather than to the entire d -band. Currently, a majority of available DFT-based computational codes provide projected LDOS as output, and it is easy to sum the densities of d - xz -, d - yz - and d - z^2 -states of surface atoms and associate surface reactivity with this sum.

We also propose here further improvement of the d -band center model, which naturally comes from analysis of its basis.¹¹ The d -band center model originates from the second order perturbation theory approximation for the energy of hybridization between a narrow d -band of the surface and electronic states of adsorbate (see eq 1 of ref 11). Since differences of energies of occupied and nonoccupied states of surface and adsorbate are in the denominators of eq 1 of ref 11, the equation reflects the fact that the hybridization energy is higher if the density of the surface d -states is higher around E_F . However, the d -band center (E_{dbc}) does not always characterize the amount of d -states around E_F . Indeed, E_{dbc} as a center of gravity, has an increased contribution from the peripheral parts of LDOS:

$$E_{\text{dbc}} = \int N(E)E \, dE / \int N(E) \, dE \quad (1)$$

Here $N(E)$ denotes LDOS. If a d -band is narrow and relatively symmetric (as it is for elemental Pt or Pd), there is still a correlation between E_{dbc} and LDOS around E_F . However, this correlation may be washed out in the AE/MS structures, where interlayer hybridization causes peripheral peaks in AE LDOS. To fix this disadvantage, we propose other quantity—hybridization parameter—that can better correlate with surface reactivity:

$$\text{HP} = \int \frac{cN(E)}{|E| + c} \, dE / \int N(E) \, dE \quad (2)$$

where c is a constant. Comparing the above equation and eq 1 in ref 11, one can see that our expression for HP holds key features of the hybridization energy derived in ref 11, and at the same time, it is much simpler than eq 1 in ref 11. The details of derivation of this equation are provided in the Supporting Information. We have calculated HP for the systems under consideration using the sum of the densities of d - xz -, d - yz -, and d - z^2 -states as $N(E)$ and $c = 0.2$ eV in eq 2. The results clearly show that HP characterizes surface reactivity much better than the d -band center (see Figure 2). It is worth mentioning that variation of the constant c within a wide range (0.2–1 eV) does not change the $E_B(\text{OH})$ –HP correlation qualitatively. The comparison of the results obtained for $c = 0.2$ eV, 0.5 eV, and 1.0 eV is shown in the Supporting Information (Figure S2).

Coming back to Table 1, one can notice that the correlation between the surface LDOS and $E_B(\text{OH})$ gets totally destroyed if we add Pt/Au(111) to the consideration: although all considered Pt d -band and sub-band centers of Pt/Au(111) are located much closer to E_F than those of Pt(111), $E_B(\text{OH})$ of

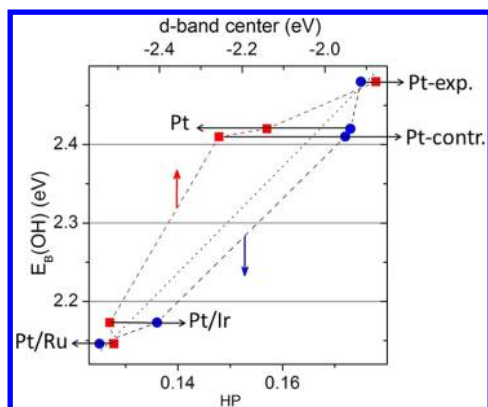


Figure 2. Calculated $E_B(\text{OH})$ plotted versus the d -band center energies (red squares) and the hybridization parameter (blue circles) for Pt/(Ru(0001), Pt/Ir(111), Pt with in-plane bond lengths equal to those of Ru(0001) (Pt-contr.), Pt(111) with equilibrium lattice parameter, and Pt(111) with in-plane bond lengths equal to those of Au(111) (Pt-exp.).

Pt/Au(111) is only slightly higher than that of Pt(111). This finding suggests that $E_B(\text{OH})$ on Pt/Au depends also on a factor other than the LDOS of a clean surface, and we find this factor to be related to the surface structural response to OH adsorption. It is important to mention now that, according to our calculations, for all clean Pt/MS surfaces under consideration, including Pt/Au, the Pt monolayer retains the substrate periodicity (Pt atoms take face-centered cubic (fcc)-hollow sites). For Pt/Ru(0001), Pt/Ir(111), and Pt(111), adsorption of OH does not disturb this pattern (see left panel of Figure 3). In contrast to those, however, Pt/Au(111)

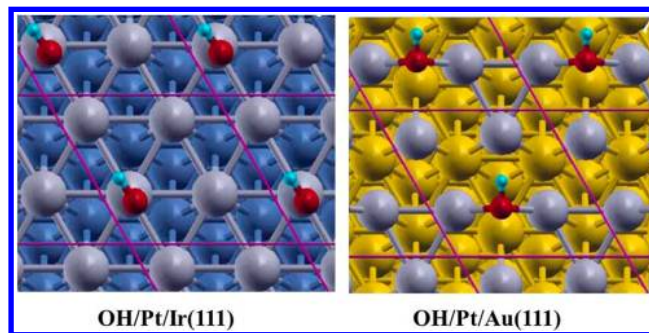


Figure 3. Geometric structure of the Pt/Ir(111) and Pt/Au(111) surfaces adsorbed with OH. Blue, yellow, gray, red, and small bright blue balls represent Ir, Au, Pt, O, and H atoms, respectively. The purple lines mark the supercell boundaries.

undergoes surface reconstruction upon OH adsorption, as shown in the right panel of Figure 3. This reconstruction changes the surface electronic structure and costs extra energy, which leads to a break in the correlation between $E_B(\text{OH})$ and LDOS of clean surfaces.

Surface reconstruction upon adsorption is a well-known phenomenon that occurs when an adsorbate significantly changes the potential energy surface of the system.¹⁶ However, the question is, why does Pt/Au reconstruct upon OH adsorption, while the other considered structures do not? To answer this question, we compare strength of Pt bonds to various substrates. Our calculations show that Pt binds much weaker to Au than to other substrates under consideration: the formation energy of the Pt layer $E_{\text{form}}(\text{Pt})$ on Au(111) is found

to be 0.464 eV/atom less than that on Pt(111). For comparison, $E_{\text{form}}(\text{Pt})$ is higher on Ir(111) and Ru(0001) than on Pt(111) by 0.367 eV/atom and 0.632 eV/atom, respectively. Since Pt–Pt bonds are stronger than Pt–Au bonds and the Pt–Pt bonds are expanded in Pt/Au(111), Pt atoms tend to reconstruct, in order to make Pt–Pt bonds shorter, and a perturbation, such as OH adsorption, induces this reconstruction. It is worth mentioning that to ensure that clean Pt/Au(111) does not undergo the reconstruction, we relaxed its structure starting with various perturbed configurations. In particular, we started with the reconstructed Pt/Au structure shown in Figure 3, but with removed OH. We found that in the course of relaxation, Pt atoms move back to fcc sites of Au(111) restoring the nonreconstructed surface geometry.

In summary, using the results of our first-principles calculations performed for Pt monolayer–substrate structures, we show that the AE–MS interlayer hybridization is the main factor controlling surface reactivity, whereas contribution of the well-known strain effect to the reactivity is not significant. We find that the LDOS of the AE/MS surface is not always sufficient to characterize the surface reactivity: if the AE monolayer is weakly bound to the substrate (e.g., like in Pt/Au), possible surface reconstructions destroy the correlation between LDOS and the reactivity. We also introduce the hybridization parameter (eq 2) that is more closely related to the reactivity of the AE/MS surfaces than the widely used d -band center energies.

■ ASSOCIATED CONTENT

■ Supporting Information

Computational details; projected local densities of Pt electronic states in the Pt and Pt/Au; rationale for the hybridization parameter expression. 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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