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Another way of looking at bonding on bimetallic surfaces: the role of spin polarization of surface metal d states

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Online at stacks.iop.org/JPhysCM/21/492201**Abstract**

The nature of electronic and chemical properties of an unstrained Pt monolayer on a 3d transition metal substrate, M (M = Cr, Mn, Fe), is studied using spin-polarized density functional theory calculations. High spin polarization of Pt d states is noted, verifying the magnetization induced on Pt, which is observed to be responsible for redirecting the analysis of bond formation on a metal surface towards a different perspective. While the shift in the Pt d band center (the average energy of the Pt d band, commonly used to predict the reactivity of surfaces) does give the expected trend in adsorbate (oxygen) chemisorption energy across the bimetallic surfaces in this work, our results show that for spin-polarized Pt d states, the variation in strength of adsorption with respect to the Fermi level density of states is more predictive of Pt chemisorption properties. Hence, this study introduces a scheme for analyzing trends in reactivity of bimetallic surfaces where adsorption energies are used as reactivity parameters and where spin polarization effects cannot be neglected.

1. Introduction

The theoretical approach towards heterogeneous catalysis and electrocatalysis often involves the investigation of the overall rate of reaction as a function of a certain ‘reactivity parameter’ and the use of such a relationship for systematic and rational design of optimal catalysts. The ‘reactivity parameter’ is usually taken to be the enthalpy of adsorption of key intermediates [1, 2]. The rational approach to catalysis has then proceeded towards making a connection between this ‘reactivity parameter’ and a more fundamental property of metals or alloys, which can be deduced roughly from the periodic table or more reliably from electronic structure calculations [3] or from the characterization of single-crystal surfaces [4]. A simple but extensively used reactivity concept, the d band model, was proposed [5], in which the reactivity of a metal surface is governed by the coupling of the adsorbate

states with the metal d states. The basic idea of the d band model emanates from the use of molecular states *renormalized* to stronger binding energies as a result of their interaction with metal s, p states, which is essentially the same across transition and noble metals. The d band model then accounts for both the molecular states and the perturbations on the metal surface. This perturbation is accounted for in the d band model through the coupling matrix element (V of the order of an eV) connecting molecular orbitals and metal d states, supporting the importance of the availability of states in a window of several eV around the Fermi level (E_F). In particular, the model identifies three surface parameters that affect surface reactivity: (1) the center of the d band (ϵ_d); (2) the local filling of surface d states; (3) the coupling matrix element (V). Across similar systems, parameters (2) and (3) are assumed to slightly differ so that the surface reactivity is correlated only with the position of the ϵ_d . Furthermore, the simplicity of the scheme is exhibited by the estimation of ϵ_d as the average energy of the entire d band which can be readily obtained

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from first-principles calculations [6] or through photoemission spectroscopy [7].

Bimetallic surfaces have exhibited interesting catalytic properties which inspired numerous researches, but pose a major challenge of one not knowing *a priori* how the electronic and chemical properties will be modified relative to the parent metals. A reliable predictor of the change in catalytic properties is imperative. In the past few years, the d band center has been used specifically for Pt 3d transition metal–Pt sandwich structures [8] and for wide range of Pt and Pd overlayer structures [9, 10]. It is found that strain due to lattice mismatch and ligand effects (metal–metal interaction) can either broaden or narrow the metal surface d band, which in turn changes the surface d bandwidth. If the d band filling is constant, ε_d is bound to shift up or down relative to E_F to conserve the d band filling [8]. A linear correlation between the shift in ε_d and the binding energy of simple adsorbates (H, O, CO) was commonly observed. The use of ε_d to predict chemisorption properties of such systems, however, requires numerous simplifications and assumptions. For instance, in the formation of bimetallic surfaces, it is important to assume that no significant charge transfer occurs between interacting metals so that the d band filling of the overlayer system remains constant. More importantly, spin polarization effects are generally not incorporated due to the complexity involved in the calculations and on the basis of the notion that spin polarization does not have a bearing on the modification of the Pt chemisorption property as observed in the oxygen adsorption energetics on Pt–Ni systems [11]. However, aside from the fact that Ni–Pt systems have very weak metal–metal interaction [9], the systems are well strained. Our own calculation of lattice parameters of Ni (3.52 Å) and Pt (3.99 Å) gives a lattice mismatch of about 12%. Therefore, it is obvious that the modification of the Pt surface reactivity is purely due to geometric effects and not the Pt–Ni electronic interaction or the ferromagnetic character of Ni. Therefore, we initiated an investigation on the changes of the Pt chemisorption property due to its interaction with 3d metals of the first transition series, M (M = Cr, Mn, Fe), which are known to have magnetic behavior. This study incorporates the true nature of the substrate and its effect on the electronic and chemical properties of the surface. Interestingly, the results redirect analyses on bonding on metal surfaces towards a different reactivity concept.

2. Computational details

The choice of 3d transition metals rests on a very small lattice mismatch with Pt in a (001) facet, with the result that a pseudomorphic Pt monolayer is neither stretched nor contracted. This preserves the optimized Pt–M bond lengths and ensures Pt–M interaction as the origin of modification of electronic and chemical properties. Furthermore, the Pt/M structures (sometimes called bimetallic surfaces in this study) are the closest experimentally viable structures. The binding energy of atomic oxygen was used to probe the changes in the Pt chemisorption property due to its wide application in industrial catalytic processes. The total energies of all the

systems are calculated using *ab initio* investigation based on spin-polarized density functional theory (DFT) [12] employing the projector augmented wave (PAW) method [13] in treating the electron–core interactions and a plane-wave basis set as implemented in the Vienna *ab initio* Simulation Program (VASP) [14, 15]. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [16] was used for the exchange–correlation functional, which is known to correctly predict the magnetic ground states of the systems in this work. Brillouin-zone integrations were performed on a grid of $(11 \times 11 \times 11)$ and $(4 \times 4 \times 1)$ Monkhorst–Pack \mathbf{k} points for bulk and surface calculations, respectively. The substrates are modeled by slab of five (bcc Cr(001), bcc Mn(001) and bcc Fe(001)) layers in a (2×2) unit cell. Each slab is separated by ~ 12.0 Å of vacuum. The top three layers which include the Pt monolayer and the top two layers of the substrate are allowed to relax to within a force tolerance of $0.005 \text{ eV \AA}^{-1}$ using the conjugate gradient algorithm. The kinetic energy cut-off is increased until the total energy is converged. For adsorbate/bimetallic systems, a 400 eV kinetic energy cut-off was sufficient to converge the total energies to within 5 meV/atom.

3. Results and discussion

The calculated equilibrium lattice constants for bulk Cr (2.854 Å), Mn (2.832 Å for a_{\parallel} and $c/a = 1.06$), Fe (2.834 Å) and fcc Pt (3.980 Å) are in excellent agreement with experimental results (Cr (2.88 Å) [17], Mn (2.85 for a_{\parallel} and $c/a = 1.05$) [18], Fe (2.86 Å) [19] and Pt (3.92 Å) [20]). For the magnetic ground state configurations, all the possible NM (non-magnetic), FM (ferromagnetic) and AF (antiferromagnetic) orderings of all substrates are considered and we found that Mn and Fe are in AF and FM states, respectively, which is in good agreement with experiments [18, 21, 22]. Cr is experimentally observed to exhibit a peculiar AF spin-density wave (SDW) [23] and our spin-polarized DFT calculation yields AF as the magnetic ground state. This closely related AF state is considered in this work. The Pt monolayer is in a Pt(100)-(1 × 1) structure and follows the lattice parameter of the substrates. Figure 1 depicts the optimized structure of Pt/M. d and a give the Pt–M interlayer distance and lattice parameter, respectively. The magnitudes are shown in table 1.

We note that d and l for all bimetallic systems are contracted with respect to that of the pure Pt system. This indicates strong Pt–M binding, which can be verified through a calculation of the Pt desorption energy, E_{des} , defined as the energy needed for the formation of one Pt atom vacancy, as given in the following expression:

$$E_{\text{des}} = E_{\text{Pt/slab}} - [E_{\text{Pt}^*/\text{slab}} + E_{\text{Pt}}] \quad (1)$$

where $E_{\text{Pt/slab}}$ is the total energy of the Pt/M system, E_{Pt} is the total energy of an isolated Pt atom and $E_{\text{Pt}^*/\text{slab}}$ is the total energy of the Pt/slab system with one surface atom vacancy. Table 1 shows the calculated E_{des} . We note an enhanced Pt binding on all the substrates. Given the *stronger metal–metal*

Table 1. Optimized atomic structure data for Pt monolayers on Cr, Mn and Fe substrates and for the pure Pt system. The lattice mismatch is expressed in per cent (with respect to the calculated lattice parameter of the substrates). The Pt binding is given by the desorption energy in eV for the formation of one Pt atom vacancy.

Pt/M system	Lattice constant (Å)	Lattice mismatch (%)	Pt–M interlayer distance, d (Å)	Pt–M bond length, l (Å)	Pt–M binding, E_{des} (eV)
Pt	3.980	—	1.93	2.77	6.59
Pt/Cr	2.854	1.21	1.59	2.56	6.67
Pt/Mn	2.823	0.11	1.61	2.56	6.63
Pt/Fe	2.834	0.49	1.63	2.59	6.77

Table 2. Electronic structure calculation data for Pt and for Pt/M (M = Mn, Cr, Fe).

Pt/M system	Pt magnetic moment (μ_B)	Work function, Φ (eV)	d band center relative to E_F (eV)	Integrated occupied d electron states ($\times 10^2$)
Pt	0	5.65	−1.80	4.96
Pt/Mn	0.22	4.56	−2.19	5.12
Pt/Cr	0.10	4.53	−2.44	5.76
Pt/Fe	0.42	4.28	−2.42	5.77

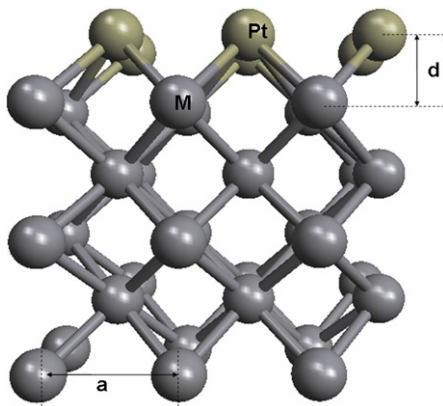


Figure 1. Geometry of the Pt monolayer on the M(001) substrate (M = Cr, Mn, Fe). d and a give the Pt–M interlayer distance and the lattice parameter, respectively.

(This figure is in colour only in the electronic version)

interaction in the bimetallic surfaces and the *very small lattice mismatch* between the interacting metals, we are then assured of a strong electronic Pt–M interaction (ligand effects) as the origin of the changes in the Pt surface reactivity.

For the Pt/M electronic structure, the induced magnetic moment on Pt in Bohr magnetons (μ_B) and the work function (Φ) in eV of the Pt surface are shown in table 2. The work function for all the bimetallic surfaces decreases as compared to that for pure Pt whose value is in agreement with the experiment [24]. This change in work function can be related to the degree of d state occupancy (table 2). The decrease in work function varies in the order Pt > PtMn > Pt/Cr > Pt/Fe in accordance with the increase in total occupied d states: Pt < PtMn < Pt/Cr < Pt/Fe. This correlation is expected but nevertheless necessary in checking the relative changes in the electronic structure among the systems and in ascertaining the *degree* of Pt d band filling. We recall that the Pt d band filling is significant in properly accounting for the shift of ε_d . This

will be discussed in detail later on. Next, figure 2 shows the local density of d states projected on a Pt atom in an energy range where the states near and at E_F can be clearly depicted. First, the states are spin split in energy. This explains the induced magnetic moment on Pt. ε_d was also calculated and the values are given in table 2. The Pt–M interaction drops the d band center from E_F relative to pure Pt; hence, we expect the binding of an adsorbate on the bimetallic surface to be weaker than on the pure metal. In general, all the parameters that have been used to describe the electronic and magnetic properties of the bimetallic surfaces in this study show a large ‘jump’ in magnitude from pure Pt to the bimetallic surfaces, but within the Pt monolayer on substrates, we note relatively close values.

To probe the change in the bond formation on the Pt surface, and hence, in the Pt surface reactivity, we used the chemisorption energy of atomic oxygen which is given by the following expression:

$$E_b = E_{total} - [E_{slab} + E_{gas-phase\ adsorbate}] \quad (2)$$

where E_b is the chemisorption energy, E_{total} is the total energy of the adsorbate/Pt/M system, E_{slab} is the total energy of the bare Pt/M system and $E_{gas-phase\ adsorbate}$ is the total energy of the free O atom. We found that among the high symmetry sites for O atom chemisorption, the bridge is the most stable, followed by the hollow and then the top. These results are in agreement with previous spin-polarized DFT calculations [25, 26]. Given the knowledge of the shift in ε_d as discussed previously, we predict that the order of decrease in the binding energy of O should be Pt > Pt/Mn > Pt/Fe > Pt/Cr. This is clearly shown in the plot of binding energies versus the Pt surface ε_d position (figure 3). We note that the variation of oxygen binding from Pt(001) to Pt/Cr is not linear. This implies that ε_d is not entirely predictive of Pt chemisorption properties of these systems. Previously, we noted the differences in the extent of spin polarization of the d band at E_F among the systems and so we were able to point out the possible role of the Fermi level local density of states (LDOS – E_F) as well.

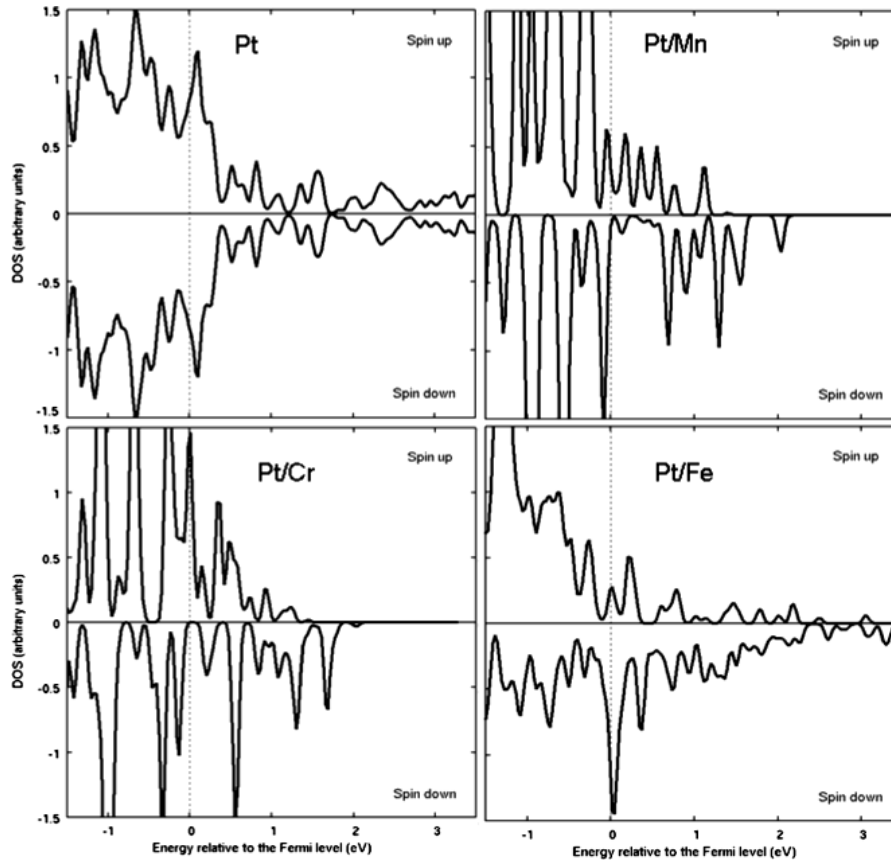


Figure 2. Total d states projected on a Pt atom in the energy range that encompasses the states in the immediate vicinity of the E_F .

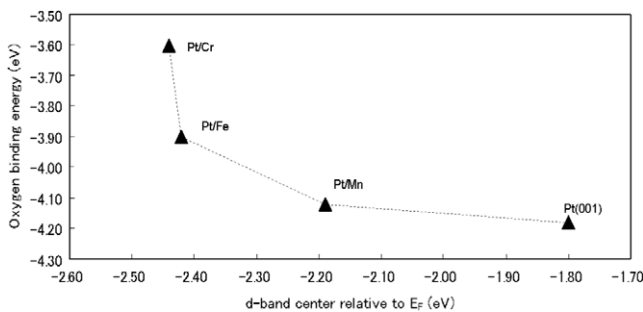


Figure 3. The variation of oxygen binding energy with the shift in d band center position relative to E_F . The dashed line is a guide for the eye.

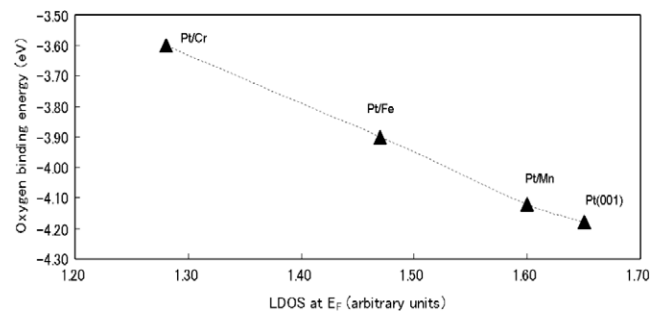


Figure 4. The linear correlation between oxygen binding energy and the total density of d states at E_F (LDOS $- E_F$). The dashed line is a guide for the eye.

In figure 4, we show the variation of the strength of oxygen adsorption with LDOS $- E_F$. A linear correlation is derived, contrary to the case for the same plot obtained using ϵ_d for Pt. The LDOS $- E_F$ parameter could then provide a much more reliable indicator of the modification of Pt bimetallic surface chemisorption properties.

In the following, we show how the ϵ_d falls short in accounting for the changes in chemisorption properties of Pt. First, we may think that the coupling matrix element (V) across the systems changed. However, we considered the same Pt 5d and O 2p interaction and noted the relatively close magnitudes of work functions of bare Pt monolayers, so

the coupling between Pt 5d and O 2p states barely changes across the bimetallic surfaces. Next, as we have shown before (last column of table 2), the d band filling changes across the systems, which can be attributed to the charge transfer to Pt as a result of strong hetero-metal bond formation. This may already be considered as one of the reasons why ϵ_d is not predictive of Pt chemisorption properties of these systems. As we recall, ϵ_d requires the d band filling to be constant, so that it can shift in accordance to the changes in the bandwidth. Now, assuming that the density of states curve of Pt remains unchanged across the bimetallic surfaces, the increase in the d band filling (no matter how small) should raise the E_F and consequently

modify the Fermi level local density of states (LDOS – E_F). This is verified by the observed upshift of E_F in the non-magnetic (NM) configurations of all bimetallic surfaces with respect to that of the pure Pt. Therefore, even in the case where spin polarization is not accounted for, LDOS – E_F can still change due to the increase in d band filling and in effect contribute to the modification of the electronic structure of Pt. Therefore, both the changes in the d band filling and those in the spin polarization of the d states of the bimetallic surfaces are believed to significantly alter LDOS – E_F ; however, for systems with highly spin-polarized d states at E_F (e.g. Pt/Cr and Pt/Fe (figure 2)), the role of spin polarization in effecting change in LDOS – E_F is seen to be more pronounced. For instance, in the case of Pt/Cr, the estimated LDOS – E_F in its non-magnetic (NM) configuration is reduced to half due to spin polarization close to 100% at E_F .

The formation of bonding on the surface is now viewed with the accommodation of the role of LDOS – E_F . LDOS – E_F is a measure of number of electron states that can be excited from occupied to unoccupied states at lowest energy cost and, hence, indicative of the ability of the surface to respond to an external perturbation, such as the presence of a ‘reactant’ above the surface [27], through a population of its unoccupied states. In this work, the strength of the binding depends on the substantial population of the unoccupied O 2p states which are known to be a little above E_F . To verify this, we calculated the change in the work function ($\Delta\Phi$) of the Pt surface upon O adsorption. If charges are transferred to an adsorbate, a negative dipole (pointing towards surface) arises, which reinforces the original surface dipole due to electron ‘spill-out’, causing the surface work function to increase. The more enhanced the charge transfer to the adsorbate is, the greater the increase in work function must be. The illustration of such a mechanism is shown in figure 5 (inset). On the basis of our calculations, we see that the surface work function at the most stable adsorbate–metal surface distance also changes in the same order as the adsorbate binding energy: Pt > Pt/Mn > Pt/Fe > Pt/Cr. Moreover, the plot of O binding energy versus change in surface work function, as shown in figure 5, also gives a linear correlation. However, a closer look at Pt/Mn shows a little shift to the left in comparison to that of figure 4. This means that Pt/Mn may have lesser available electronic states at E_F than what had been predicted with our estimated LDOS at E_F . Nevertheless, the linear trend is still preserved. Finally, the new scheme for adsorption on spin-polarized and strongly bonded systems can be applied to Pt–Fe alloys to reconcile the theoretically predicted moderate increase in reactivity based on the shift of Pt ϵ_d [3] with a very large measured enhancement factor for oxidation–reduction–reaction (ORR) activity discovered by Toda *et al* [28, 29].

4. Conclusion

In summary, in heterogeneous catalysis and electrocatalysis, we often seek for a reliable predictor of metal surface reactivity which can be derived from a linear correlation between a fundamental property of the surface and a ‘reactivity

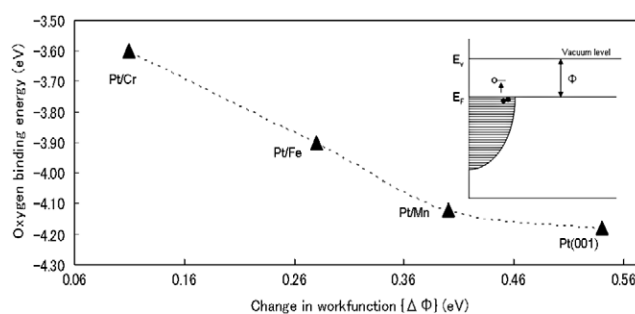


Figure 5. The variation of the oxygen binding energy with the change in surface work function. The mechanism of the transfer of charges to the unoccupied state of the adsorbate (empty circle) is shown in the inset.

parameter’. In this study, we have shown that such is achieved by the variation in the chemisorption energy of an adsorbate with the local density of d states at the Fermi level (LDOS – E_F) for highly spin-polarized and strongly bonded bimetallic surfaces. Such a parameter emanates from the varying degree of spin polarization of d states close to E_F and changes in the Pt d band filling. We expect the same trend to work for other simple adsorbates (e.g. H, H₂, and CO). In this scheme, the use of free molecular states in an unperturbed surface should remain valid. These findings further suggest reformulation of reactivity models for bimetallic systems. Just as there are catalysts that are novel in their own right (e.g. near surface alloys that yield a unique combination of low H binding energy and low H₂ activation [30] and that of Pt/Pt/Fe for the case of O₂ [31, 32]), so there are specific factors that affect the bond formation on surfaces which deserve further attention.

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