PHYSICAL REVIEW B **74**, 153414 (2006)

Adsorption trends for water, hydroxyl, oxygen, and hydrogen on transition-metal and platinum-skin surfaces

G. S. Karlberg
Department of Applied Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden

(Received 9 August 2006; published 25 October 2006)

Using density-functional theory calculations the adsorption energies for water, hydroxyl, oxygen and hydrogen on Ru, Rh, Pd, Ag, Ir, Pt, and Au surfaces have been investigated. By replacing the topmost layer of all surfaces with a layer of platinum atoms, a simple model for so-called platinum skins was constructed. Apart from providing a close connection to the area of fuel cells the comparison with platinum-skin surfaces also helps to elucidate clear trends regarding adsorption on clean surfaces. The correlation between these trends and experimental trends in the literature is discussed.

DOI: 10.1103/PhysRevB.74.153414 PACS number(s): 82.65.+r, 82.45.Jn

Interaction between water and metal surfaces is important in many areas ranging from catalysis and corrosion to biophysics and energy production. Despite considerable efforts, many issues regarding this interaction are still unsolved.[1,2] Nonetheless, our motivation to understand water-metal systems is increasing, among others, due to the interest in replacing our fossil fuel economy with an economy based on renewable energy resources. This in turn has put focus on fuel cells and the energy rich and clean catalytic reaction when water is formed from hydrogen and oxygen.

With the comprehensive goal to be able to make cheaper and more efficient fuel cells this reaction is being studied from several points of view, including electrochemical experiments,[3] surface physics experiments in ultrahigh vacuum,[1,2] and electron-structure calculations.[4–11] The revelation, in electrochemical experiments,[12–14] that alloys with small amounts of platinum, so-called platinum skins, gave a higher efficiency than pure platinum have inspired several investigations. Various explanations have also been put forward in the literature.[5–10] However, what is lacking to a great extent is a transfer of experience between the field of surface physics and the field of electrochemistry.

The aim of this Brief Report is to provide a link between experiences from surface physics and electrochemistry. This is done by comparing calculations of adsorption and interaction energies for water, hydroxyl, oxygen, and hydrogen on pure transition-metal surfaces with the corresponding calculations when the surfaces were covered with a monolayer of platinum. In this study platinum skins are modeled by simply replacing the topmost layer of the metal substrate with a layer of platinum atoms. Clearly, many aspects, such as the segregation energy, are left out in such a model. However, due to its simplicity the model easily rationalizes the trends in adsorption and interaction energies. Among others, by comparing the platinum-skin surfaces with the pure surfaces valuable insights about the adsorption characteristics can be obtained.

In this study the density-functional theory calculations are performed using the Vienna *ab initio* simulation package VASP.[15–17] For the exchange-correlation functional the Perdew-Wang 91 version of the generalized-gradient approximation is employed.[18] The electron-ion interaction is described using the projector-augmented-wave (PAW) method,[19,20] with plane waves up to an energy of 400 eV. All calculations are performed using periodic supercells with five metal layers and more than 13 Å of vacuum. Two different surface unit cells have been used: $(\sqrt{3}\times\sqrt{3})R30°$ and 2×2, both with $6\times6\times1$ k-point meshes. The adsorbates were attached to one side of the slab, and a dipole correction scheme was used throughout the study. Whereas the spin character of, for instance, the hydroxyl molecule is important in gas phase and solutions,[21,22] on the metal surfaces of this study the no-spin character was found. Hence, the calculations were preformed without spin polarization. In all calculations the adsorbates and the three topmost layers of metal atoms were allowed to relax. Concerning the stable site for low-coverage adsorption all high-symmetry sites were tested. In the case of hydroxyl, both tilted and upright adsorption geometries were tried out. The following lattice constants were used for Ru, Rh, Pd, Ag, Ir, Pt, and Au, respectively: 3.82, 3.85, 3.96, 4.16, 3.88, 3.98, and 4.18 Å. These same lattice constants were used also when the topmost layer was replaced by platinum. The interaction energy is defined according to

$$E_{int} = E_{ads} - \sum E_{ads}^{LC}, \tag{1}$$

where E_{ads} is the adsorption energy for the overlayer structure, and $\sum E_{ads}^{LC}$ is the sum of the adsorption energies of the individual molecules in the overlayer at a low coverage (LC), here, 1/3 of a monolayer (ML) coverage.

The adsorption energies for water, hydroxyl, oxygen, and hydrogen were calculated for both pure and platinum-skin alloyed surfaces of Ru, Rh, Ir, Pd, Pt, Ag, and Au. A coverage corresponding to 1/4 ML was used for O and H and 1/3 of a ML for water and hydroxyl. Since the interaction among water and hydroxyl molecules on the surface is of particular interest, this adsorbate-adsorbate interaction energy is calculated for all surfaces in this study. This is done by comparing the adsorption energies of the structures shown in Fig. 1 with the adsorption energies of equal amounts of water and hydroxyl at 1/3 of a ML coverage. Whereas all adsorption energies and adsorbate-adsorbate interaction energies are presented in Fig. 2, for the sake of clarity the low-coverage results and the interaction results are discussed separately.

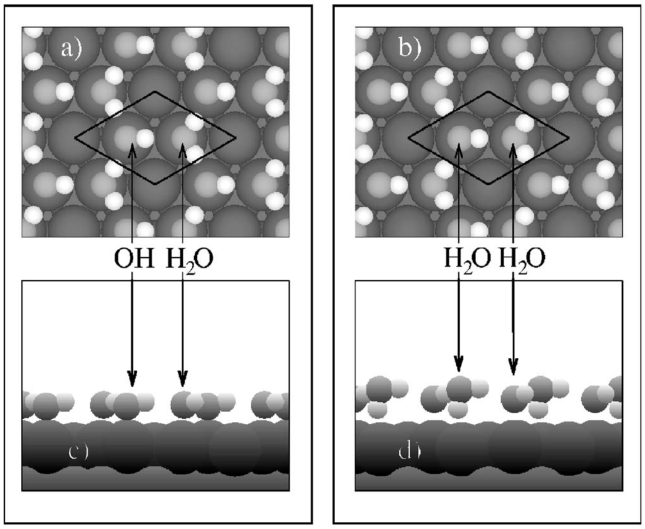

FIG. 1. The structures used to calculate hydroxyl-water [(a) and (c)] and water-water [(b) and (d)] interaction as seen from above and from the side. The black rhomb indicates the supercell used for the calculations. The hydroxyl-water mixed structures contain 1/3 of a monolayer of water and 1/3 of a monolayer hydroxyl. The pure water structures contain 2/3 of a monolayer water.

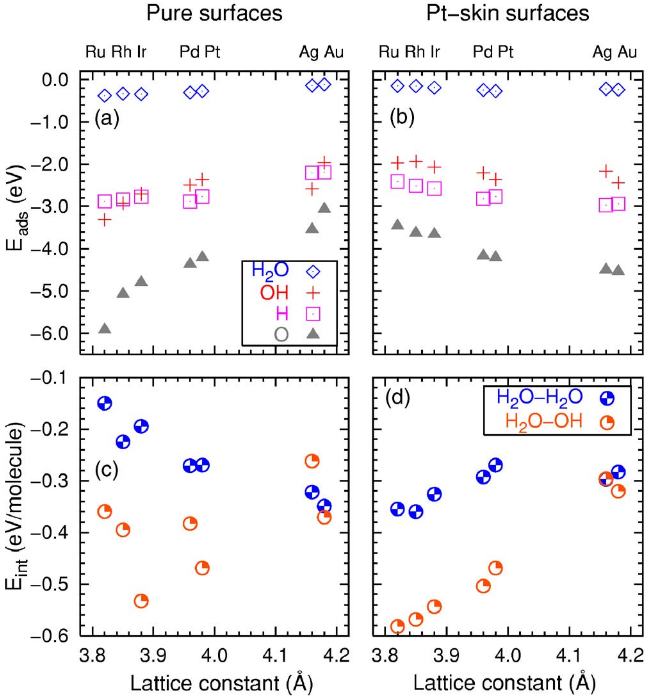

FIG. 2. (Color online) Adsorption energies for H_2O, OH, H, and O on (a) Ru, Rh, Ir, Pd, Pt, Ag, and Au, and (b) the same adsorption energies when the topmost layer of metal atoms is replaced by a layer of platinum. The coverage is 1/4 of a monolayer for H and O and 1/3 of a monolayer for OH and H_2O. Furthermore, the adsorbate-adsorbate interaction energies for the two adsorbate overlayers shown in Fig. 1 are given both for (c) the pure metals and (d) for the platinum-skin alloys.

TABLE I. Adsorption site preferences for OH and H on Ru, Rh, Ir, Pd, Pt, Ag, and Au, and the same surfaces where the topmost layer of atoms has been replaced by a layer of platinum. In general, the OH molecule adsorbs with the molecular axis upright in fcc sites, whereas the axis is tilted upon bridge-site adsorption.

	Ru	Rh	Ir	Pd	Pt	Ag	Au
OH (pure)	fcc	bri	bri	bri	bri	fcc	fcc
OH (Pt skin)	bri	bri	bri	bri	bri	fcc	fcc
H (pure)	fcc	fcc	top	fcc	top	fcc	fcc
H (Pt skin)	top	top	top	fcc	top	fcc	fcc

The low-coverage adsorption on the pure-metal surfaces is shown in panel (a) of Fig. 2. As expected, of all adsorbates oxygen forms the strongest bond and water the weakest on all surfaces in the study. Hydroxyl and hydrogen, on the other hand, prove to have quite similar low-coverage adsorption energies overall. In particular, the hydrogen adsorption energy is fairly constant on the noble and transition metals, respectively. Concerning which site is the most stable water and O display clear preferences regardless of the metal; the top site for water, and the fcc site for O. An exception is provided by Ru where O adsorbs in the hcp site. On the other hand, Ru is a hcp metal and hence the Ru(0001) surface is used. For hydroxyl and hydrogen the stable site alters between fcc, bridge and fcc, top sites, respectively (Table I).

The zero-order effect of putting a layer of platinum on the surfaces of this study is that the adsorption characteristics become more platinumlike. This can be observed both from the low-coverage adsorption energies on the platinum skins shown in panel (b) of Fig. 2, and from the site preferences shown in Table I. This conclusion is strengthened by the observation that to the next level of accuracy the adsorption energy varies linearly with lattice constant, increasing to the right of platinum and decreasing to the left. Such a trend was obtained by Mavrikakis *et al.*[23] for O and CO adsorption on Ru when the lattice constant of Ru was varied. According to Mavrikakis and co-workers the change in binding energy can be understood by considering the effect of the strain or compression on the *d*-band states of the transition metal in question. From this they find a linear dependence on the lattice constant. Hence, the linear trend underpins the conclusion that the topmost layer determines the adsorption characteristics. The deviation from a linear dependence between the adsorption energy and the lattice constant can thus be seen as a measure of the influence of the next-uppermost layers in the alloys.

On pure surfaces the H_2O-H_2O interaction increases almost linearly with an increasing lattice constant [panel (c) in Fig. 2]. This effect is unexpected since the smaller lattice constants are the ones most similar to ice, and hence ought to give the strongest hydrogen bonds. Still, according to the present calculations, the water-surface interaction suffices to reverse the trend expected from pure ice. For the H_2O-OH interaction, on the other hand, the trend on pure metals indeed is an increase in the hydrogen-bond strength with a decreasing lattice constant. A dependence on the underlying surface can be observed also in this case since there is a clear difference between the 4*d* and 5*d* transition metals [panel (c) Fig. 2]. The corresponding results for platinum-skin alloys provides further support for the importance of the underlying surface for the adsorbate-adsorbate interaction strength. For the H_2O-OH interaction adding a layer of platinum makes all surfaces fall on the line of the 5*d* transition metals, hence removing the difference between the 5*d* and 4*d* substrates. For the H_2O-H_2O interaction adding a platinum layer reverses the trend compared to pure surfaces. Note that in the latter case the H_2O-H_2O interaction shows a dependence on the layer beneath platinum since there the noble-metal platinum skins deviate from the linear trend for the transition-metal platinum skins.

In summary, both the adsorption energy and the adsorbate-adsorbate interaction energy are to a large extent determined by the topmost layer of the underlying surface. In fact, even for the loosely bound water molecule changing the substrate greatly affects the adsorbate-adsorbate interaction.

Having obtained the total energies for the adsorption of water, hydroxyl, oxygen, and hydrogen on various surfaces, an interesting question to study is the energy balance for water and hydroxyl dissociation. In addition to clean surfaces, also O precovered surfaces are of interest since water dissociation on O precovered surfaces is of great importance in catalysis, corrosion, and electrochemistry. The following energy differences are formed:

$$\Delta E_1 = 2E(\mathrm{OH}) - E(\mathrm{H_2O}) - E(\mathrm{O}), \tag{2}$$

$$\Delta E_2 = E(\mathrm{OH}) - E(\mathrm{O}) - E(\mathrm{H}), \tag{3}$$

$$\Delta E_3 = E(\mathrm{H_2O}) - E(\mathrm{OH}) - E(\mathrm{H}), \tag{4}$$

where $E(M)$ corresponds to the total energy for molecule or atom M adsorbed on a given surface at low coverage. The first equation corresponds to water dissociation on an O precovered surface, and the latter equations to hydroxyl and water dissociation on clean surfaces. To estimate the importance of a water-related adsorbate-adsorbate interaction the above differences are calculated both including and excluding the high-coverage interaction shown in parts (c) and (d) of Fig. 2. The effect of high coverage is included by adding the mean H_2O-H_2O and H_2O-OH interaction energy per molecule obtained for the relevant surface to the total energy terms of H_2O and OH, respectively. Hence, in this way the energy differences (2–4) above are obtained both for high- and low-coverage situations. The results are shown in Fig. 3 and will be discussed below.

On O precovered pure transition-metal surfaces the balance for water dissociation is approximately the same for all surfaces in this study. This indicates a covariation of the adsorption energies of 2OH and O+H_2O. Moreover, on most surfaces the balance for water dissociation is determined by the presence of water itself [panel (a) of Fig. 3]. This means that water is needed in the hydroxyl overlayer in order to stabilize the layer. Once the water is removed the hydroxyl becomes thermodynamically unstable, and will recombine to form water and O if the recombination barrier is low. Recently, it was found that a low OH recombination barrier in combination with facile proton transfer is what enables water desorption from mixed water-hydroxyl overlayers on platinum already around 200 K.[24] Comparable desorption temperatures for mixed water-hydroxyl overlayers are found also on Ru and Pd.[2] This suggests that similar processes may also be active on these surfaces. For Ag, on the other hand, OH recombination-induced water desorption does not occur until around 300 K.[2] The latter, however, is consistent with the low-coverage stability of OH on Ag, shown in panel (a) of Fig. 3. Furthermore, the preference for upright fcc site adsorption for OH, Table I, provides further explanations for the slow OH recombination.

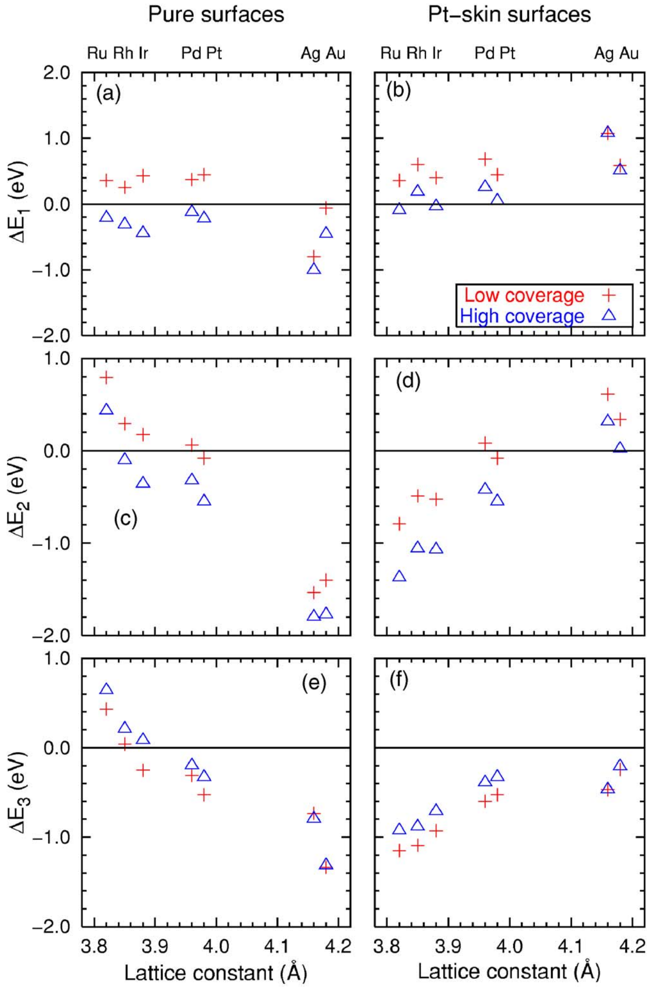

FIG. 3. (Color online) The energy balance for water dissociation on (a) oxygen-covered and (e) clean surfaces of Ru, Rh, Ir, Pd, Pt, Ag, and Au, and [(b) and (f)] the same surfaces where the topmost layer of atoms has been replaced by a layer of platinum. In addition the corresponding energy balance for hydroxyl has been calculated for (c) the pure and (d) platinum-skin alloyed surfaces.

Concerning the dissociation of water and hydroxyl, no covariation in the adsorption energies exists between the molecules and their constituents. Hence, inclining trends are obtained. What dominates these trends in the case of hydroxyl dissociation is the increasing adsorption energy for O compared to hydroxyl. For the case of water dissociation the trend is dominated by the increase in adsorption energy for (OH+H) compared to water. As can be seen, hydroxyl is stable in the presence of water on all surfaces in this study except for Ru. In addition, intact water layers are more stable than partially dissociated water layers on Ag, Au, Pt, and Pd. To more accurately evaluate the stability of pure-water layers both the zero-point energy and the adsorbate-adsorbate interaction related to hydrogen need to be taken into account. The latter effect was included in a recent study by Michaelides and co-workers.[11]

Since the adsorption-energy trends for pure-metal surfaces were reversed when forming a platinum-skin alloy, also the trends with respect to dissociation would be expected to be reversed. This is also the case as can be seen from Fig. 3. Once again the cancellation of the adsorption trends for 2OH and O results in a flat trend for water dissociation on the oxygen-covered platinum skins. On oxygen-free platinum-skin surfaces OH is stable except for the platinum skins formed on noble metals. Concerning pure-water layers platinum skins prevent dissociation on all surfaces.

In summary, adsorption trends for water, hydroxyl, atomic oxygen, and atomic hydrogen adsorbed on Ru, Rh, Pd, Ag, Ir, Pt, and Au have been studied. By replacing the topmost layers of these surfaces with a layer of platinum a simple model of so-called platinum-skins have been constructed. Apart from providing a close connection to the area of fuel cells the comparison with platinum-skin surfaces also helps to elucidate clear trends regarding adsorption on clean surfaces. Among others it is found that the adsorption energy is mainly affected by the topmost layer of the substrate surface. This dependence on the topmost layer of the substrate is valid also for the adsorbate-adsorbate interaction. Regarding the dissociation of water on an oxygen-covered surface, this study provides strong evidence that similar mechanisms may be active on Pd(111) and Ru(111) surfaces, as has been observed on the intensely studied Pt(111) surface.

Financial support from VR and SSF/ATOMICS is gratefully acknowledged. I thank Göran Wahnström, Alexander Bogicevic, and Lars G.M. Pettersson for valuable discussions.

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