Hydrogen Evolution Reaction on Palladium Multilayers Deposited on Au(111): A Theoretical Approach

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Ⓢ *Supporting Information*

ABSTRACT: We have investigated the electrocatalytic proper-
ties of multilayers of Pd epitaxially deposited on Au(111). In
contrast to the numerous previous works in this area, we have
focused on the kinetics of the electrochemical step for
hydrogen adsorption (Volmer reaction) and determined its
energies of activation. We have used a combination of density
functional theory calculations and our own theory of
electrocatalysis, which allows us to investigate the systems in
an electrochemical environment. Contrary to our previous
work with a submonolayer of Pd in Au(111), the activation
barrier for the hydrogen adsorption process from proton is very
low or almost zero for all bimetallic systems investigated. It is
about 0.2 eV for pure Pd(111). In the case of two layers of Pd

on Au(111) containing absorbed hydrogen in the subsurface, the adsorption free energy is less negative and the barrier lower
than for the other investigated systems. This is in agreement with experimental data that shows a larger activity for hydrogen
oxidation with hydride Pd systems.
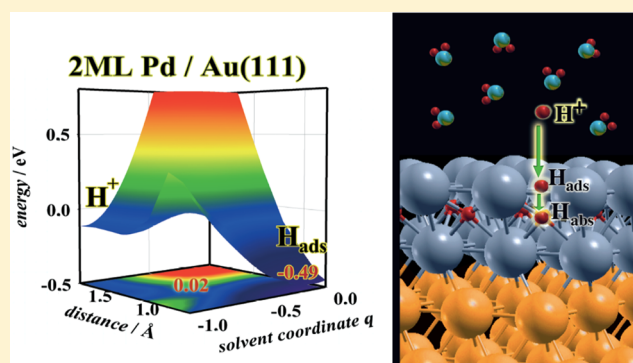
■ INTRODUCTION

Palladium, either in its pure form or as part of bimetallic
systems, has been widely investigated as electrode material.
Most studies have focused on the interaction between Pd and
hydrogen. During the last decades, interest in these systems
peaked several times, such as in the 1970s, due to the discovery
of superconducting properties of PdH_x, or at the end of the
1980s, when the possibility of cold fusion was announced. The
latter turned out to be one of the major fiascos in science.
Anyway, these facts demonstrate the passions that this system
can awaken, and, independent of how serious the motivations
were, it is a widely investigated system.

The Au/Pd bimetallic system, on which we shall focus on in
this work, has also been addressed in connexion with the
synergetic catalytic effects of both metals. A simple search via
the Internet shows about 388 000 scores, revealing its
importance for fundamental science and technological
applications.

Studies have been carried out in both surface science and
electrochemical environment, involving experimental as well as
theoretical approaches. In a recent publication,[1] we have given a
detailed list of previous works. Therefore, we shall mention
here only the relevant literature for the discussion of our
present results.

In the previous publication mentioned above,[1] we have
considered an ideal system consisting of a complete monolayer

of Pd underneath the surface of Au(111). According to
thermodynamic data such as the bulk phase diagram of Pd—Au
alloys,[2] the relative surface energy of Au and Pd (1.50 and 2.05
J/m^2, respectively[3]), and our own calculations of the formation
energy,[1] Pd underlayers are more stable than Pd overlayers.
Both experimental and theoretical results obtained with Pd—Au
alloys in vacuum indicate in many cases segregation of Au,
resulting in (nearly) pure Au in the topmost layers.[4,5] However,
we have to distinguish between stable and metastable systems.
Also studies of the *inverse* system in vacuum, that is, of the
formation of alloys by adsorbing Au on a Pd(111) single
crystal,[6] show that Au grows in a layer-by-layer fashion on
Pd(111) at 300 K and starts to diffuse into the bulk only after
annealing to above 600 K.

In an electrochemical environment, where the electrode is in
contact with an electrolyte, the situation could be very different.
While pseudomorphical growth of Pd on Au(hkl) has been
observed by Monte Carlo simulation, no underpotential
deposition (UPD) has been predicted by these studies.[7]
Therefore, UPD of Pd on Au should not be expected.
However, experimental evidence has been found in a large
number of studies (see, for example, refs 8—11). In addition, we

have to consider that, in an electrochemical environment, the presence of anions and other complexing species can play an important role in the stabilization of these overlayers. Effectively, epitaxial layer-by-layer growth occurs both when Pd is directly electrodeposited on Au, and also when surface-limited redox replacement (SLRR) is used.[12] In these cases, no signs of significant surface alloying have been found with in situ electrochemical scanning tunneling microscopy (EC-STM).[9,10]

Recently, based on density functional theory (DFT) calculations of thermodynamic properties, it has been suggested[13] that hydrogen adsorption on Pd–Au alloys can induce the segregation of Pd to the surface of the catalyst. However, considering that hydrogen is a small atom in comparison to Pd (its mass is two orders of magnitude lower), this exchange process is hardly probable. Effectively, the height of the barriers for the latter process given by these authors is also very high ($\approx$2 eV!!). Nevertheless, it is interesting that the barrier for Au atoms to go from the second to the first layer is also high; thus, the deposition of Pd on Au in an electrochemical environment can generate metastable Pd overlayers. It has also been suggested[14] that adsorbed oxygen can trigger the segregation of Pd to the surface. Since oxygen is heavier than hydrogen, this process could occur more easily. It is well-known that during the surface oxidation of metal electrodes the place exchange with oxygenated species takes place.[15] In any case, the presence of vacancies or defects should probably be necessary to facilitate such processes. Therefore, a full range of surface Au/Pd (stable or metastable) compositions can be achieved according to the experimental boundary conditions. It is an important issue, since certain ensembles of Au and Pd atoms act to promote the formation of desirable products and inhibit undesirable side reactions. One case that recently has gain attention is the formation of Pd monomers (see, for example, ref 16).

One particular property of Pd is that it can absorb large quantity of hydrogen. However, due to its high specific mass, it is no longer considered as a practical candidate material for hydrogen storage. Nonetheless, it can be used as a model to study fundamental properties of hydrogen storage materials, and to better understand mechanisms and kinetics of hydrogen adsorption and entry into metals.

For many decades, diverse mechanisms have been proposed for the adsorption–absorption processes on Pd.[17–21] An often used strategy to separate adsorption and absorption processes has been the use of multilayers of Pd on Au (thin Pd films deposited onto Au substrates). Detailed analysis of the possible reaction mechanisms using diverse electrochemical techniques[6,22,23] has demonstrated the complexity of this system.

Pd hydrides show a quite complicated phase diagram with two main forms, α- and β-PdH$_x$.[24] DFT calculations for the (111) surfaces of Pd and Pd hydride[25] show that, at a surface covered by a full monolayer of hydrogen, H binds less strongly to Pd hydride than to Pd. The activation barrier for desorption at H coverage of one monolayer is slightly lower on Pd hydride. Experimental results obtained in the gas phase[26,27] show that Pd–Au absorbs much more hydrogen than Pd, and that dissolution directly competes with surface oxidation of hydrogen. Because of the expanded lattice of Pd–Au alloys in comparison to pure Pd, they dissolve H$_2$ more exothermically than Pd and, consequently, their dilute phase solubilities are greater at a given hydrogen pressure in these alloys than in Pd.[27]

Electrochemical studies of the Pd–Au system have already been carried out in the 1950s.[28] More recently, the development of new techniques for the characterization at the nanoscale and powerful computational methods has allowed a detailed correlation between structural, electronic and catalytic properties. Examination of the behavior of diverse nanostructures such as Pd–Au core–shell nanoparticles (for example, refs 29 and 30, and references therein) and Pd nanoclusters (for example, refs 10 and 30, and references therein) on Au and carbon electrodes becomes feasible.

The electronic structure of Pd and its hydride has been investigated in the past,[31–34] as well as for Pd covered by adsorbed hydrogen.[34–36] Also the energetics for the adsorption and absorption on Pd(111) is well documented.[34–38]

In this contribution, we focus on the Volmer step of hydrogen evolution reaction on Pd–Au systems. We compare the electrocatalytic properties of Pd(111) with nML Pd/Au(111) for one ($n = 1$) and two ($n = 2$) pseudomorphic layers of Pd. Also the effect on the electrochemical adsorption of a monolayer of hydrogen absorbed in 2ML Pd/Au(111) is analyzed. We discuss the effect of the electronic properties on the activity in the framework of the electrocatalysis theory developed in our group.[39,40] In contrast to several previous investigations using DFT, we have paid special attention into the kinetics of electrochemical processes; that is, we calculated barriers for electron transfer to a proton interacting with the electrode material in a solvent environment. In a future work, we shall analyze in detail the absorption process in these systems.

■ RESULTS AND DISCUSSION

Electronic Changes on the Bimetallic Systems. The first attempts to explain the effect of alloying on the electronic properties have been based on a simple approach, the rigid band model.[41] Later, another theoretical analysis[42,43] involving the position of the center of the d-band became very popular with experimentalists because its simplicity allows comparing different systems and correlating their catalytic activity. However, there are some dark shadows in these analyses that require a better theoretical framework. Our theory of electrocatalysis allows shedding some more light onto the behavior of these systems in an electrochemical environment, taking explicitly into account electron transfer, electronic structure, and solvent effects.

In a previous work,[44] we have investigated the electrocatalytic activity of one monolayer of Pd on different substrates in connexion with their electronic properties. We have demonstrated that both strain and chemical effects are important and that Pd on Au substrate is the most promising system in agreement with experimental results.[9,10,16] Later, combining experiments and theory, we have focused on the ensemble effect investigating in detail different nanostructures of Pd on Au(111), including clusters, rows, monomers, and one complete monolayer of Pd.[45] Now, we shall show the effect of successive Pd layers on Au(111).

Au and Pd have quite different positions of their bands, making the catalytic properties of these metals very distinctive. While the d-band of the Pd(111) surface extends above the Fermi level, that of the Au(111) surface is negatively shifted by about 1.5 eV. Also, their lattice constants are very different: 3.89 and 4.07 Å for Pd and Au, respectively (see computational details in the Supporting Information). Therefore, combined systems of these elements show both strain and chemical
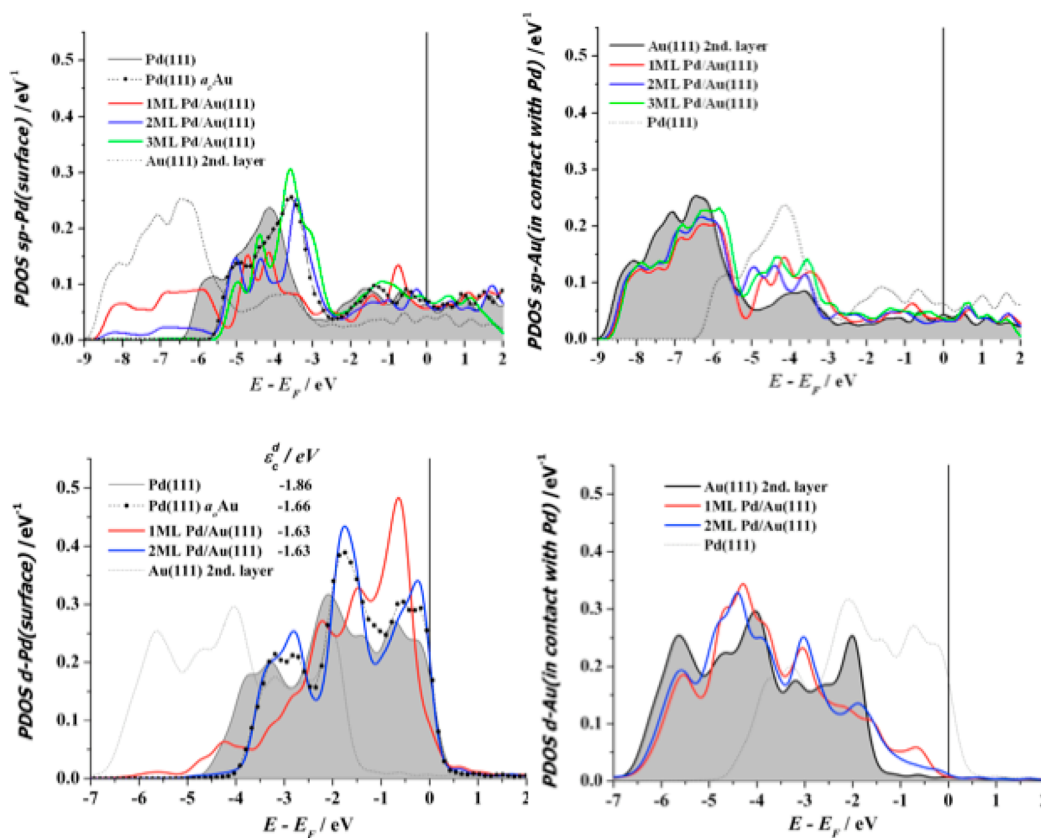
Figure 1. Projected density of states (PDOS) onto the sp- and d-bands of Pd and Au for the bimetallic systems investigated in this work. The corresponding electronic states for the monometallic systems also are shown for comparison. Additionally, the PDOS for an artificial system of Pd(111) with the lattice constant of Au(111) are shown.

effects. They are not easy to separate, and its combination together with the ensemble effect have been recognized as responsible for the enhancement or inhibition of the catalytic properties (see, for example, refs 43−49).

Figure 1 displays the electronic density of states projected onto the sp- and d-band of Pd and Au for the bimetallic systems investigated in this work. Additionally, the electronic structure of an artificial system consisting of a Pd(111) slab calculated using the lattice constant of Au (4.07 Å) is shown to disentangle geometrical from chemical effects. The latter system reflects the effects of the lateral expansion of Pd without the interference of the ligand effects of Au. In this case, both sp- and d-bands retain the main features of Pd(111), but they become thinner and shift to higher energies, as expected from strain effects (lateral expansion). The center of the d-band shifts from −1.86 eV for Pd(111) to −1.66 eV for the artificial system, in agreement with previous studies.[42,45] The real system (1ML Pd/Au(111)) shows a similar d-band center (−1.63 eV), but the distribution of the electronic states is much different. A high peak appears at about −0.5 eV below the Fermi level. Moreover, these features are similar to those of Pd underneath the surface of Au(111) investigated in the previous work.[1]

When only one monolayer of Pd is deposited on Au(111), the chemical effects are by far the strongest. In order to yield the highest overlap, a redistribution of electronic states takes place. Their features substantially change in comparison with Pd(111), and even in comparison with the artificial system. The sp-states of Pd shift to lower energies, and new states appear in the region between −9 and −6 eV below E_F, while the sp-states of the Au layer in contact with Pd decrease in this energy range

and increase between −5 and −3 eV below E_F. Starting from three monolayers or more of Pd, only strain effects on the sp-bands can be observed (compare with the sp-band of the artificial system).

The redistribution of the d-states is much more complicated than that of sp-states. Probably, rehybridizations including interactions between sp- and d-states of both components take place, and simultaneously a stronger localization occurs, due to geometric effects. However, almost all bimetallic systems show d-band center positions similar to the artificial system. When the number of Pd monolayers deposited on Au increases, the chemical effects, appreciable in the structure of the d-band, are attenuated for the surface layer of Pd. Practically only geometric effects are observed starting from two monolayers of Pd, as becomes evident if we compare their d-electronic states with those of the artificial system of Pd(111) calculated with the lattice constant of Au. Since d-bands are less extended in space than sp-bands, chemical effects fall off more rapidly for the former.

Volmer Reaction. The dissociation reaction of the hydrogen molecule as well as the following hydrogen adsorption and absorption can be very well characterized through DFT calculations alone. These processes have been widely investigated on Pd (see, for example, refs 25, 34, 36−38, and 50−53).

Figure 2 shows the adsorption energy for hydrogen at 0.25 coverage on the most favorable site, fcc of pseudomorphic nML Pd/Au(111), in comparison with the adsorption on Pd(111) and the artificial system Pd(111)@ with the lattice constant of Au(111). Although the variation in energy between the various
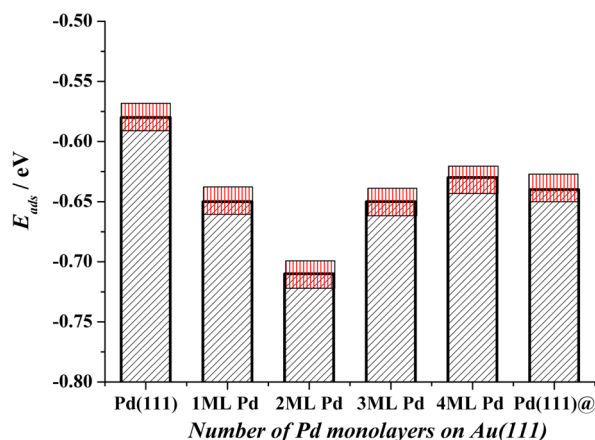
Figure 2. Adsorption energy of hydrogen on thin monolayers of Pd on Au(111) at the fcc sites. Results for Pd(111) and the artificial system Pd(111)@ with the lattice constant of Au(111) are also shown for comparison. The red region at the top of the bars indicates the uncertainty in the calculations.

systems spreads in a range of 0.15 eV, and DFT calculations are hardly more precise than 50 meV, a certain compensation of errors can be expected for the differences between similar systems. The red shaded region at the top of the bars indicates an estimate of the uncertainty in these calculations. The adsorption is stronger on the bimetallic systems than on Pd(111). The 2ML Pd/Au(111) seems to be the most active system. After 4ML Pd, only the strain effect is responsible for the activity. These results describing the thermodynamics of the adsorption process are in agreement with those of Roudgar and Groß.[49]

In our previous works,[44,45] we have investigated the catalytic properties of a monolayer of Pd on Au(111) for the global hydrogen evolution reaction ($2H^+ + 2e^- \rightarrow H_2$) using the first version of our electrocatalysis theory.[46] Now, we shall focus on the catalytic activity of the Pd−Au systems for hydrogen adsorption in an electrochemical environment for the first step of the HER, the Volmer reaction ($H^+ + e^- \rightarrow H_{ads}$), which cannot be treated only by DFT. We investigate the kinetics of the adsorption at coverage of 1/4 on the most favorable site (fcc) for the most strongly adsorbed species. We do not consider the weakly adsorbed species (on top). It is claimed that the latter is the species which most frequently participates in the hydrogen evolution reaction,[21] and the strongly adsorbed hydrogen simply is a spectator.[54]

We followed the same procedure as in our previous paper concerning gold electrodes modified by an underlayer of palladium,[1] applying the improved version of our model.[40] To follow all the details of the electrocatalysis theory used within this work could be quite difficult. Therefore, we repeat the procedures for the more relevant calculations and provide a detailed description in the Supporting Information.

Briefly, we calculated with DFT the energy and the density of electronic states (H-PDOS = ρ_H) of a single H atom as a function of the distance (z) to the electrode surface for the absence of solvent.

In the theory of electrocatalysis,[40] the density of states of the hydrogen orbital is given by[40]

$$\text{H-PDOS}(z, q, \varepsilon) = \rho_H(z, q, \varepsilon)$$
$$= \frac{1}{\pi} \times \frac{\Delta(z, \varepsilon)}{[\varepsilon - (\varepsilon_H(z) + \Lambda(z, \varepsilon) - 2\lambda(z)q)]^2 + \Delta(z, \varepsilon)^2}$$
$$(1)$$

Here $\varepsilon = E - E_F$ is the energy coordinate, ε_H is the position of the center of ρ_H (when the H atom is far away from the surface, it is the energy level of the orbital 1s). $\lambda(z)$ is the energy of reorganization of the solvent, q is the solvent coordinate, and $\Delta(z,\varepsilon)$ and $\Lambda(z,\varepsilon)$ are the chemisorption. The chemisorption functions account for the interaction of the 1s orbital with the electronic states of the metal. They have contributions from both sp- and d-bands.

We fit the density of states obtained from DFT at various distances with eq 1 for the case that the solvent coordinate q is equal to zero, since DFT calculations are for the absence of solvent. In this step, we obtained the chemisorption functions and the position of the 1s orbital when the H atom approaches the surface: $\Delta_{sp,d}(z,\varepsilon)$, $\Lambda_{sp,d}(z,\varepsilon)$, and $\varepsilon_H(z)$. In a second step, we calculate the density of states using eq 1 in the presence of solvent introducing the energy of reorganization $\lambda(z)$ and the solvent coordinate q. We assume that $\lambda(z)$ increases from the surface toward the bulk from 0 to 5.5 eV and use a polynomial interpolation between these two values.[40] Variation of this parameter within a reasonable range has only small effects on the barrier (about 0.05 eV according to our previous estimates[40]).

From the H-PDOS calculated with the fitted parameters for the different distances to the surface and for the different solvent coordinates, we obtained one of the electronic contribution terms to the total energy, $E_{el}(z,q) = \int^{E_F} \rho_H(z,q,\varepsilon) \times \varepsilon \, d\varepsilon$.

In order to account for the entropy of the hydrogen gas and the zero-point energy of the hydrogen molecule, we added an amount of 0.2 eV to the energy values.[55] Henceforth, we calculated the free energy surface for the Volmer reaction $H^+ + e^- \rightarrow H_{ads}$ as a function of the solvent coordinate q and the distance of the reactant from the substrate:

$$\Delta G_{tot}(z, q) = E_{el}(z, q) + \lambda(z)q^2 + 2\lambda(z)q$$
$$+ (1 - n_H(z))\lambda(z) - n_H(z)(E_{el}(z, q = 0) - E_{DFT}$$
$$+ S_{term})$$
$$(2)$$

The terms containing λ account for both slow and fast contributions of the solvent modes. The solvent coordinate q, which has been already mentioned above, describes the configuration of the solvent during the approach of the proton to the surface. When the system passes from the solvated proton to the adsorbed hydrogen atom, the occupancy of its 1s orbital ($n_H(z) = \int^{E_F} \rho_H \, d\varepsilon$) increases gradually from zero to unity, and the solvent coordinates goes from −1 to zero. The latter term in (2) accounts for the correlation and exchange between the electrons on the metal and on the hydrogen that we obtain from extrapolation of DFT calculations. For details we refer to our previous papers[1,40] and the Supporting Information.

The results obtained for three different systems, that is, , the Volmer reaction on Pd(111) surface (taken as reference system), on Au(111) covered by one monolayer of Pd (1MLPd/Au(111) system), and on Au(111) covered by two monolayers of Pd (2MLPd/Au(111) system), are shown in Figure 3. There are represented as three-dimensional plots of
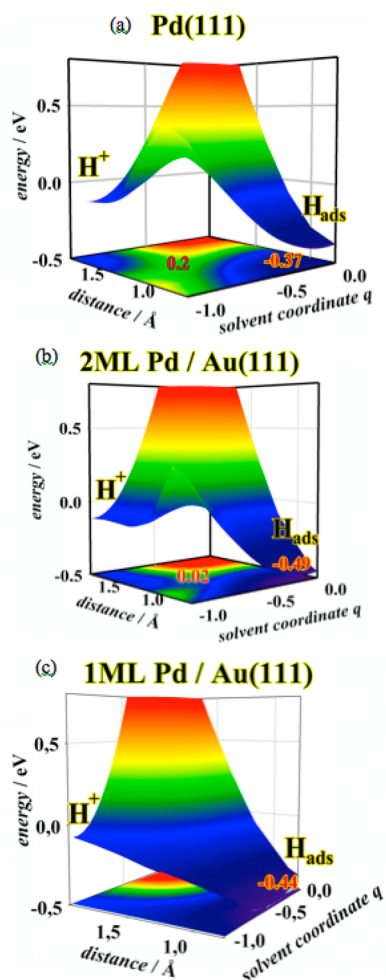
Figure 3. Potential free energy surface for the Volmer reaction on three different bimetallic systems: (a) Pd(111), (b) two monolayers of Pd on Au(111), and (c) one monolayer of Pd on Au(111). In the lower parts of the plots are shown the contours of the three-dimensional surfaces.

the free energy as a function of the solvent and distance coordinates. The two-dimensional projections onto the plane of these two coordinates are also shown.

We have calculated these free energy surfaces for the equilibrium potential of the overall hydrogen reaction ($2H^+ + 2e^- \rightarrow H_2$), which we have taken as reference (0 V SHE). Therefore, at large distances from the surface and for a solvent coordinate of $q = -1$, the proton is solvated and its free energy is zero. The line on the contour plots along $q = 0$ reflects the electronic energy of the neutral hydrogen atom as a function of distance as obtained from DFT; in this case, the interaction of the uncharged atom with the solvent is almost negligible. The line on the contour plots along $q = -1$ corresponds to the proton, whose electronic energy is zero. When the proton approaches the surface, the free energy becomes slightly negative due to the interaction with its image charge on the metal. At shorter distances, the proton starts to lose its solvation shell and its energy increases. The minima corresponding to the equilibrium positions of the adsorbed hydrogen atom appear at a distance of about 0.8 Å from the surface and it is centered at $q = 0$. This is also the equilibrium distance obtained by DFT calculations[36,37] for the dissociation reaction ($H_2 \rightarrow 2H_{ads}$) on Pd(111). In all the cases, the reaction is exergonic, although the adsorption is slightly more favorable on the bimetallic systems than on pure Pd(111) by about 0.1 eV.

During the course of the reaction, the system passes a saddle point around 1.2 Å from the surface. We use this opportunity to point out some important differences between adiabatic outer-sphere electron transfer, and electrocatalytic reactions as considered here. In exergonic outer sphere reactions, the value q of the solvent coordinate at the saddle point is closer to the value of q at the initial state. For the Volmer reaction, this means that $q < -1/2$ for the exergonic case, which is also observed in Table 1. In the adiabatic outer-sphere electron transfer at equilibrium, for $\Delta G = 0$, the transition state should be half occupied: $n_H = 1/2$, a result which was first intuitively assumed in Marcus−Hush theory and later established by Schmickler.[56] However, another relation that holds for the outer-sphere mode is not even approximately obeyed in the electrocatalytic case: In outer-sphere reactions, the occupation of the reactant at the saddle is given by $n_H = 1 + q$, which would give much smaller occupancies than we observe here. The corresponding proof is based on the assumption that the electronic density of states on the metal is wide and featureless.[56] In our case, by far, the larger part of the d-

Table 1. Different Thermodynamic and Kinetic Parameters for the Investigated Systems Obtained in the Calculation of the Free Energy Surfaces for the Volmer Reaction[a]

system	ε_c^d	ΔG_{ad}^{fcc} ($\theta = 1/4$)	ΔG_{act} ($H^+ + e^- \rightarrow H_{ad}$)	ΔG_{act} ($H_{ad} \rightarrow H^+ + e^-$)	q_{act}	n_H^{act}
Pd(111)	−1.86	−0.37	0.2	0.57	−0.68	0.75
	(−1.83)[42]	(−0.2)[37RPBE]				
		(−0.4)[37PW91]				
		(−0.3),[49] ($\theta = 2/3$)				
		(0.2),[34] ($\theta = 1$)				
		(0.43),[53] ($\theta = 0.22$)				
1ML Pd/Au(111)	−1.63, (−1.66)[42]	−0.44	0.0	0.44	−0.7	0.5
		(−0.48)[49]				
2ML Pd/Au(111)	−1.63	−0.49	0.02	0.49	−0.72	0.63
		(−0.55)[49]				
2ML Pd (H_{abs})/Au(111)	−2.29	−0.19	0.09	0.28	−0.7	0.78
		(0.18),[34] β-PdH(111), ($\theta = 1$)				

[a]The values of the literature are given in parentheses for comparison. The coverage and functionals used in the calculations are also given. In the case of 1ML Pd/Au(111), there is no transition state.
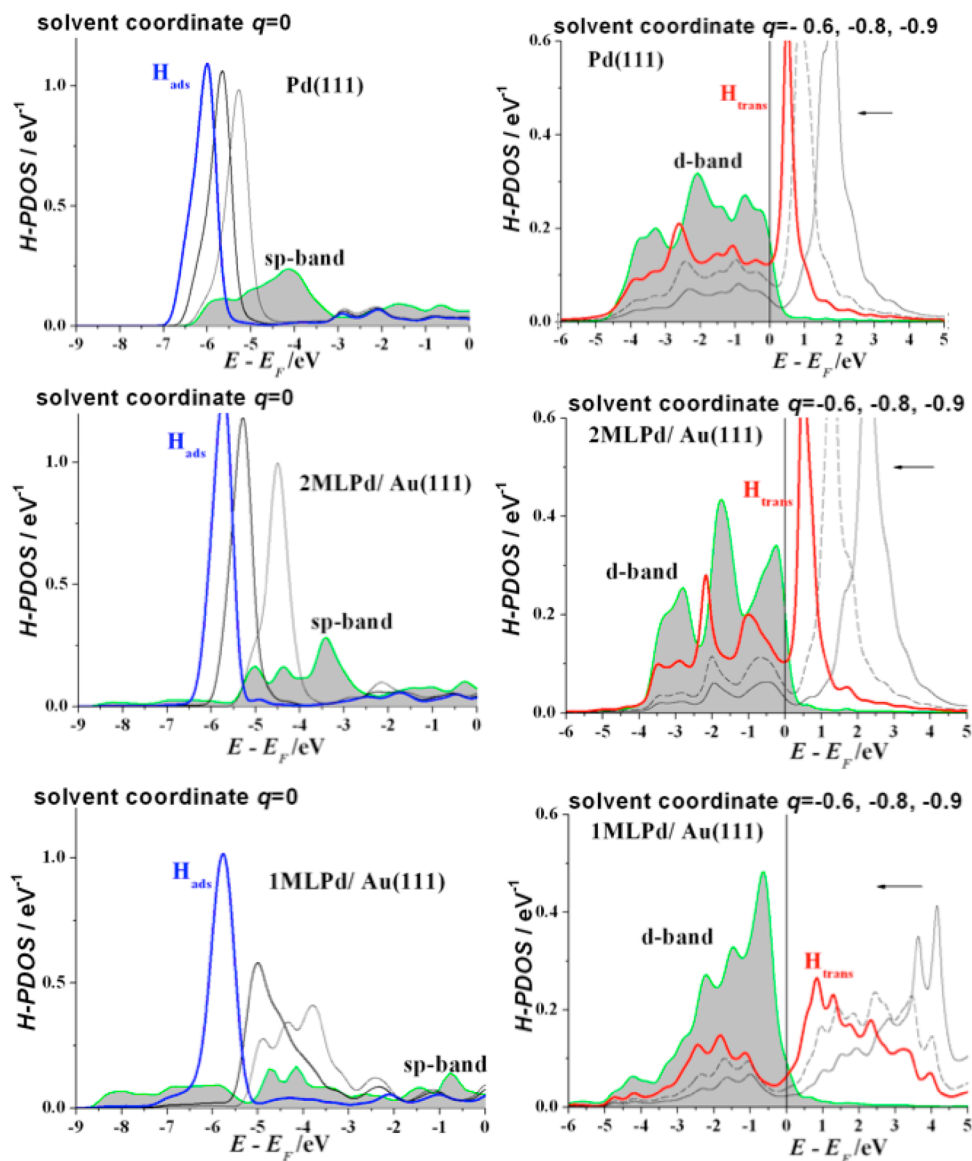
Figure 4. PDOS on the 1s orbital of the hydrogen during the Volmer reaction at the different systems shown in Figure 3. At the left are shown the H-PDOS obtained by DFT when the H atom approaches the equilibrium position for the adsorption at a distance between 0.8 and 1.2 Å ($q = 0$). At the right are shown the H-PDOS obtained from our theory of electrocatalysis at the saddle point of the potential free energy surfaces of Figure 3. The sp- and d-bands of the Pd surface layer are also shown in the presence (full lines) and in the absence (dotted lines) of adsorbed hydrogen.

band, to which the hydrogen couples strongly, lies below the Fermi level. Therefore, the part of the density of states that lies below the Fermi level has a much larger weight than in the outer sphere case, and the occupancies n_H at the saddle point are much larger. We note in passing that ref 56 considers explicitly the case in which $q = 0$ at the initial state; we have adapted the corresponding relations to our case.

It is noticeable that the Volmer reaction for the system consisting of one monolayer of Pd on Au(111) occurs barrierless. In the case of the system involving two monolayers of Pd on Au(111), the barrier is very low (0.02 eV) and it is about 0.2 eV for Pd(111). Table 1 summarizes our calculations and compares them with the literature. We shall discuss these results below.

In a previous publication,[54] we have discussed the different possible mechanisms for the hydrogen evolution reaction for diverse systems, inclusive for a monolayer of Pd on Au(111). We have emphasized that in many cases (like on Pt(111)) the

most strongly adsorbed hydrogen is often only a spectator, while the reaction proceeds via a weakly adsorbed species. For 1ML Pd/Au(111), the free energy of adsorption of the weak species is about 0.3 eV uphill, and the adsorption reaction goes over a barrier of about 0.6 eV.[54] For the dissociation of hydrogen over a Pd/Au(111) surface covered with a monolayer of strongly adsorbed hydrogen we obtained an activation energy of about 0.8 eV.[54] The chemical dissociation of the hydrogen molecule on a bare surface of Pd occurs with a low activation barrier or barrierless, depending on the boundary conditions, and frequently through a precursor state (weakly adsorbed molecule).[25,38,48,54] Consequently, the dissociation over a bare Pd/Au(111) surface to form the strongly adsorbed species is also expected to be a nonactivated process. If the Tafel reaction should be the second step, from the energetics and in contrast to Pt(111), the evolution reaction on Pd/Au(111) could occur either through the weakly or the strongly adsorbed species as intermediate.[21] Gabrielli et al.[22] suggested

that hydrogen evolution occurs from weakly adsorbed hydrogen. However, other experimental data[29] indicate that the electrochemical desorption (Heyrovsky) could also play an important role in the overall rate.

Figure 4 shows the density of electronic states projected onto the 1s orbital of the hydrogen atom at different positions of the distance−q coordinates corresponding to the potential free energy surfaces shown in Figure 3. At the left are shown the H-PDOS obtained by DFT near the equilibrium position for the adsorption of the neutral atom at $q = 0$. The orbital 1s is occupied by one electron and mainly interacts with the sp-band. It lies deep in energy and hardly overlaps with the bottom of the sp-band in the case of the surface layer of Pd(111). The position and shape of the H-PDOS for the Pd(111) system are very similar to the results obtained by Dong et al.[36] In the cases of the bimetallic systems, the position of the 1s states in the energy scale is slightly shifted toward higher values. For these systems, the sp-band extends toward lower energies due to the interaction with the underlayer of Au and therefore the overlap with 1s states of hydrogen is larger. When the hydrogen is near to equilibrium position, as it is clear from the width of the 1s peak, the interaction seems to be stronger with the system with only one monolayer of Pd (see Figure 4, bottom part) than with that having two monolayers (see Figure 4, middle part) and this appears stronger than with Pd(111) (see Figure 4, upper part). In the case of both bimetallic systems, the H-PDOS resemble the electronic structure of the metal. This is especially clear for the 1ML Pd/Au(111) system, where a one to one correspondence between the peaks at −4.7, −4.2, and −3.5 eV of hydrogen and sp-band is observed. For this system, the d-band already starts at −5 eV; therefore, it seems that now near the equilibrium the electronic states of hydrogen could also start to interact with the d-band.

The right-hand side of Figure 4 shows the PDOS of hydrogen near the saddle points of the potential free energy surfaces of Figure 3 calculated in the framework of our theory of electrocatalysis with eq 1.[1,40] Now, near the transition state, fluctuations of the solvent shift the position of the 1s orbital by $-2\lambda q$ (with $q = -0.6$ at the top of the barrier) in the energy scale. Since an electron transfer process to the metal starts to occur, the 1s orbital is partially occupied. At the transition state, the position in energy of the 1s orbital overlaps very well with the d-bands; its features follow subtly the features of the d-bands. The H-PDOS becomes much broader at energies above the Fermi level in the case of the 1ML Pd/Au(111) system, indicating a stronger interaction in comparison to the other systems. These results are in line with the values of the activation barriers. Effectively, while the Volmer reaction occurs barrierless on the 1ML Pd/Au(111) system, a small barrier appears in the other systems.

Effects of an Underlayer of Absorbed Hydrogen on the Volmer Reaction. It is well-known[23] that H binds less strongly to Pd hydride than to Pd. It has also been found that the activation barrier for desorption at the H coverage of one monolayer is slightly lower on Pd hydride, whereas the activation energy for adsorption is similar for Pd and Pd hydride. Therefore, we were interested in investigating the electroadsorption process (Volmer reaction) in the presence of a complete submonolayer of hydrogen. We chose 2ML Pd/Au(111) containing hydrogen absorbed in the octahedral site $(\Delta G_{abs} = -0.237$ eV$)^{35}$ as test system, since in the case of 1ML Pd/Au(111) the submonolayer is not stable.

The effects of the presence of absorbed hydrogen on the electronic properties of the surface layer of Pd are very strong (see Figure 5). Similar results have been given in the
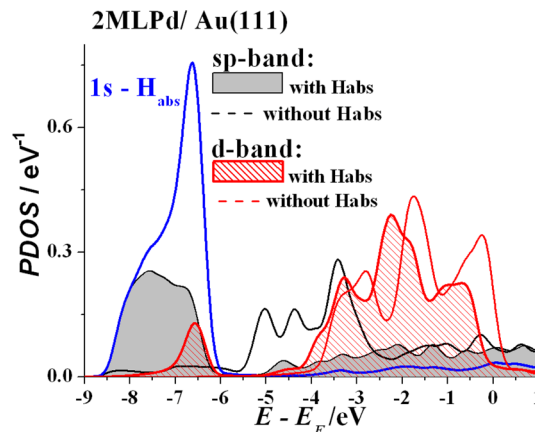

Figure 5. Effects of the presence of an absorbed complete submonolayer of hydrogen on the electronic states of the surface layer of Pd. PDOS of the 1s orbital of the absorbed hydrogen are also shown.

literature.[38−41] Electronic states corresponding to both sp- and d-bands are shifted to lower energies in order to overlap with the 1s states of the absorbed hydrogen. These states between −8.5 and −6 eV below the Fermi level become strongly localized, and between −6 and −5 eV a gap of about 1 eV appears in the remaining delocalized electronic states of the bands above −5 eV. Therefore, important changes in the catalytic activity are expected.

Figure 6 shows the free potential energy surface for the Volmer reaction on this system. The adsorption is practically a
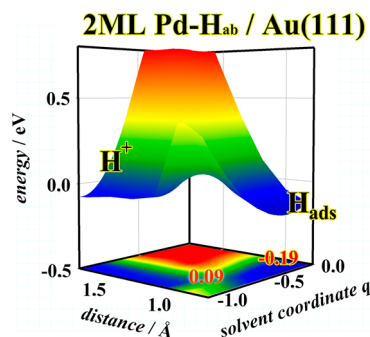

Figure 6. Potential free energy surface for the Volmer reaction on two monolayers of Pd on Au(111) containing a submonolayer of absorbed hydrogen In the lower part of the plot is shown the contour of the three-dimensional surface.

nonactivated process. The equilibrium minimum for the adsorbed hydrogen is slightly shifted to negative values of the solvent coordinate q, indicating that the hydrogen retains a slight positive charge, probably due to the repulsion with the absorbed hydrogen. The free energy of adsorption is about 0.2 eV higher than for the bare system; this is also an indication of repulsion. According to this value, it is also expected that the chemical recombination (Tafel reaction) should have a lower barrier. These two effects, lower barriers and an adsorption energy nearer to zero for the Volmer reaction, increase the catalytic activity for the global hydrogen evolution reaction for

the 2ML Pd/Au(111) system in the presence of absorbed hydrogen.

Figure 7 shows the density of states projected onto the 1s orbital of the hydrogen atom approaching the surface of the
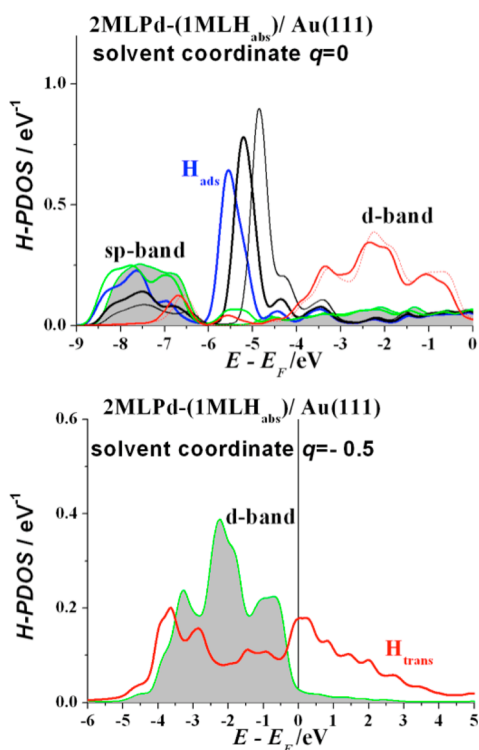

Figure 7. PDOS on the 1s orbital of the hydrogen during the Volmer reaction at 2ML Pd/Au(111) system in the presence of a monolayer of absorbed hydrogen. At the top are shown the H-PDOS obtained by DFT when the H atom approaches the equilibrium position for the adsorption at a distance between 0.8 and 1.2 Å ($q = 0$). At the bottom are shown the H-PDOS obtained from our theory of electrocatalysis at the saddle point of the potential free energy surfaces of Figure 6. The sp- and d-bands of the Pd surface layer are also shown in the presence (full lines) and in the absence (dotted lines) of adsorbed hydrogen.

2ML Pd (H_{abs})/Au(111) system. The H-PDOS near the adsorption equilibrium are shown at the top of Figure 7. The strong interaction with the sp-band is evident from the split into two parts, one between −9 and −6 eV overlapping both the sp-band and the 1s states of the absorbed hydrogen, and a peak that becomes broader and shifts to lower energies at shorter distances. New localized sp- and d-states appear in the energy region of this main peak (also small peaks at about −5.5 eV). The H-PDOS at the transition state are shown at the bottom of Figure 7.

About half of these states lie spread out below the Fermi level and overlap very well with the d-band, much more than in the case of the bare surface (compare with the middle part of Figure 4), which explains the good catalytic activity.

Finally, Figure 8 shows the various parameters for the different systems used in the calculation of the free energy surfaces, and Table 1 summarizes the kinetic and thermodynamic results obtained for the Volmer reaction. It is clear that there is a complicated interplay of the various factors. Equation 2 shows that different terms contribute to the total energy. Each of them depends on the distance and on the solvent coordinate in a different way. The occupation of the 1s states also changes
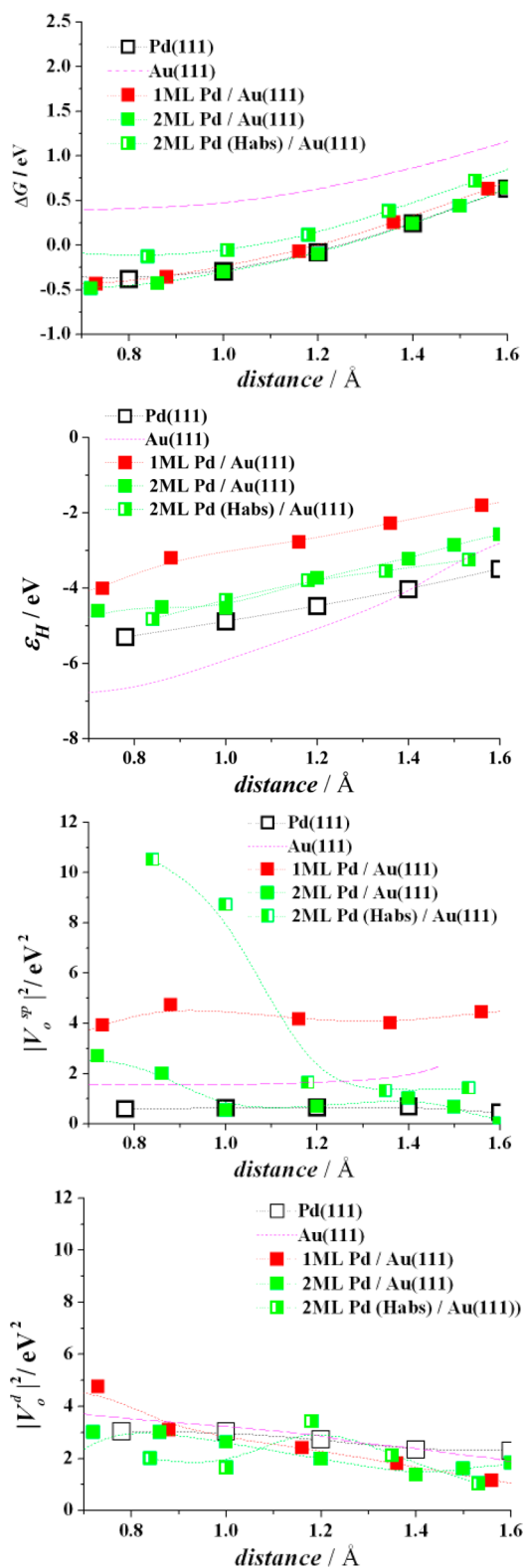

Figure 8. Distance dependence of different parameters obtained for the Volmer reaction at the different systems when the hydrogen atom approaches the surface. From top to bottom: DFT energies, position of the 1s states of H, coupling constant with the sp-band, and coupling constant with the d-band.

with distance and solvent configuration. It is not possible to explain the electrocatalytic properties of the investigated systems through a simple model like the *d-band-model*. While

the thermodynamic values for the adsorption energy almost follow the tendency of the position of the d-band center, this is not the case for the activation barriers and the electronic energy at the transition state. Particularly astonishing is the result for the system with two layers of Pd containing absorbed hydrogen. Here, the center of the d-band has shifted negatively by about more than 1 eV relative to Pd(111); nevertheless, the barrier is much lower than that for the latter system.

The interaction of the 1s states of hydrogen with the d-band is very similar for all the systems, while the coupling constant with the sp-band varies not only with the distance, but also from system to system. In the case of the 2ML Pd (H_{abs})/Au(111) system, $|V_o^{sp}|^2$ strongly increases at short distances due to the indirect interaction with the sublayer of hydrogen.

CONCLUSIONS

We have investigated the electrocatalytic properties of multi-layers of Pd epitaxially deposited on Au(111). In contrast to the numerous previous works in this area, we have focused on the electrochemical step for the hydrogen adsorption (Volmer reaction). We have analyzed in detail different factors that determine both the kinetics and thermodynamics of the Volmer reaction. We have used a combination of DFT calculations and our own theory of electrocatalysis, which allows us to investigate the systems in an electrochemical environment. Electronic and solvent interactions play a complicated role. The free adsorption energy at the more favorable site (fcc) for the 2ML Pd/Au(111) system is the most negative and for Pd(111) the less favorable in agreement with the literature. Concerning the kinetics, the activation barrier for the hydrogen adsorption process from proton is very low or almost zero for all bimetallic systems. It is about 0.2 eV for pure Pd(111). The similarities of the electronic structures between the systems makes it difficult to find simple correlations like those found with the d-band center for other systems. In the case of the reverse reaction (oxidation of adsorbed hydrogen), the bimetallic systems also show lower barriers than that of pure Pd(111). Particularly interesting is the case of two layers of Pd on Au(111) containing absorbed hydrogen in the subsurface. Here, the adsorption free energy is less negative and the barrier lower than for the other investigated systems in agreement with experimental data that shows a larger activity for hydrogen oxidation with hydride Pd systems.

Finally, we like to add a few words about the factors that determine the accuracy of our theory of electrocatalysis. A critical issue is the quality of the fit of eq 1. It is important to obtain reliable values for the coupling constants between the electronic states of the substrate and the adsorbate. In the Supporting Information, we have provided some examples. The other critical factor is the reorganization energy of the solvent. The total energy of solvation of the proton is about 11 eV. At the surface, the solvation is considerably reduced, and partially replaced by the image force as the stabilizing interaction. In previous work,[40] we have performed calculations varying the value of λ. Fortunately, the trends and the order of magnitude for our results do not depend on its exact value.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional details on the methodology for calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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