A first principles study of the hydrogen reaction in alkaline media: OH effect

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ABSTRACT

The effect of the electrolyte on the hydrogen electrode reaction (HER) has been investigated. As a starting point, we centered our studies on the Volmer reaction in alkaline media $-H_2O + e^- \rightarrow H_{ad} + OH^-$ − on a Pt(111) surface. The adsorption process of the reaction intermediate H_{ad} was investigated by quantum chemical calculations. Our analysis focused on the interaction of the OH and the H_{ad} with the electronic bands of the metal electrode.
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1. Introduction

New technologies related to the generation and storage of electrical energy center their attention on electrochemical devices because of their known advantages [1−4]. In this context, the fuel cell has become a promising option for the search of new methods of production, conversion and storage of clean energy compared to conventional fossil fuels, which are highly pollutant. However, there are still many problems to be solved to ensure that the systems based on hydrogen become a competitive force.

For decades, a great number of groups worldwide have investigated the hydrogen reaction experimentally and theoretically in order to improve the electrocatalytic properties of electrode materials and contribute to the general understanding of the reaction. For instance, the role of the electrolyte, the electrode material, the behavior of the reaction intermediate, among others, are the most studied topics. In th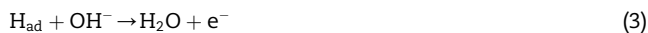is context, our group has investigated the hydrogen electrode reaction (HER) in the light of a theory for electrocatalysis proposed by two of us (E.S. and W.S.) [5−8]. The theory presents a unified model for electrochemical electron transfer reactions which explicitly accounts for the electronic structure of the electrode. It provides a framework to describe the whole course of bond breaking during an electron transfer, and explains catalytic effects caused by the presence of d bands. Particularly during the last years, we have focused on the electrochemical adsorption of a proton from the solution (Volmer reaction) $-H^+ + e^- \rightarrow H_{ad}-$ in acid media in a variety of systems of technological interest, such as bare single crystals [9−12] and nanostructures (clusters, monolayers, nanowires, etc.) on different substrates [13−16]; and our focus has been the interaction of the metal electrode d band with the valence orbital of the reactant and its effect on the catalytic activity as well as other aspects that influence the surface electrode reactivity such as strain and chemical factors [13].

Much information has been collected concerning the effect of the electrolyte; in most of the cases the HER in acidic media

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was investigated [17,18], but only few theoretical works have considered the effect of alkaline media [19−23]. It is well known that the HER in these media consists of the following elementary steps, Tafel (1) or Heyrovsky (2) and Volmer (3):

$$H_2 \rightarrow 2H_{ad} \tag{1}$$

$$OH^- + 1/2H_2 \rightarrow H_2O + H_{ad} + e^- \tag{2}$$

$$H_{ad} + OH^- \rightarrow H_2O + e^- \tag{3}$$

Reactions (1) and (2) are alternatives, which often compete. The reaction always evolves through an adsorbed intermediate (H_{ad}) on an active site on the metal electrode. Although during the last decades much effort has been spent on clarifying the behavior of the adsorbed intermediate and the role of the electrolyte, there is still a lack of knowledge in understanding the nature of the hydrogen electrocatalysis, the adsorption process of OH on metal electrodes and the influence of alkaline electrolytes on the hydrogen reaction.

As was discussed in detail in Ref. [5,9], E.S and W.S. have proposed a theory based on a model Hamiltonian for electrochemical bond breaking reactions which explain catalytic effects caused by the presence of surface d bands. In application to real systems, the parameters of this model – interaction strengths, densities of states (DOS), and correlation energies – are obtained from density-functional theory. The most important properties of the metal catalyst that determine their effectivity are the position of the d band and its coupling strength to the molecular orbitals: a good catalyst usually has a d band extending across the Fermi level, which interacts strongly with the reactant. When the interaction is weak, the level is just broadened, and when the interaction is strong, the level is split into a bonding and an antibonding orbital but in this case with respect to the metal. When the interaction is strong, a considerable decrease on the activation energy is produced. Actually, first applications of this theory for electrocatalysis in alkaline media are in progress in our group.

In this context, the focus of the present work is to investigate the effect of the electrolyte on the HER. As a starting point, we centered our studies on the Volmer reaction in an alkaline electrolyte $-H_{ad} + OH^- \rightarrow H_2O + e^-$ – on a Pt(111) surface, one of the best electrocatalysts for this reaction. The adsorption phenomena of the reaction intermediate H_{ad} has been investigated by quantum chemical calculations to understand the processes involved in the HER. Specifically, we focus on the effect of the hydroxyl radical on the strongly adsorbed hydrogen H_{ad}[1] and the electronic bands of the metal electrode.

2. Computational details

2.1. First principles calculations

All calculations were performed using the DACAPO code [24]. This utilizes an iterative scheme to solve the Kohn−Sham

equations of density-functional theory self-consistently. A plane-wave basis set is used to expand the electronic wavefunctions, and the inner electrons were represented by ultrasoft pseudopotentials [25], which allow the use of a low-energy cutoff for the plane-wave basis set. An energy cutoff of 450 eV was used in the calculations. The electron−electron exchange and correlation interactions are treated with the generalized gradient approximation in the version of Perdew et al. [26]. The Brillouin-zone integration was performed using a $4 \times 4 \times 1$ k-point Monkhorst-Pack grid [27] corresponding to the 1×1 surface unit cell. The energy accuracy was reached when the change in the absolute energy value was less than 10 meV. For relaxations, the convergence criterion was achieved when the total forces were less than 0.02 eV/Å. Unless mentioned spin-polarization was not considered. Dipole correction was used to avoid slab−slab interactions [28].

2.2. Slab modeling and OH processes

To understand the influence of an alkaline electrolyte, the effect of OH on a pre-adsorbed H atom (H_{ad}) on Pt(111) electrode has been investigated. The surface was considered to be covered with a submonolayer of pre-adsorbed hydrogen ($\theta_{H_{ad}} = 1/9$) and was modeled by a (3×3) supercell with 4 metal layers. In all the calculations 8 layers of vacuum were considered. For the relaxations, the two bottom layers were fixed at the calculated next-neighbor distance corresponding to bulk, and all the other layers were allowed to relax. The optimized surfaces – pre-relaxed H_{ad}/Pt(111) – in the absence of OH were used as input data to carry out the calculations for the involved processes. The interaction of OH with the H_{ad}/Pt(111) system has been evaluated. The OH radical was located
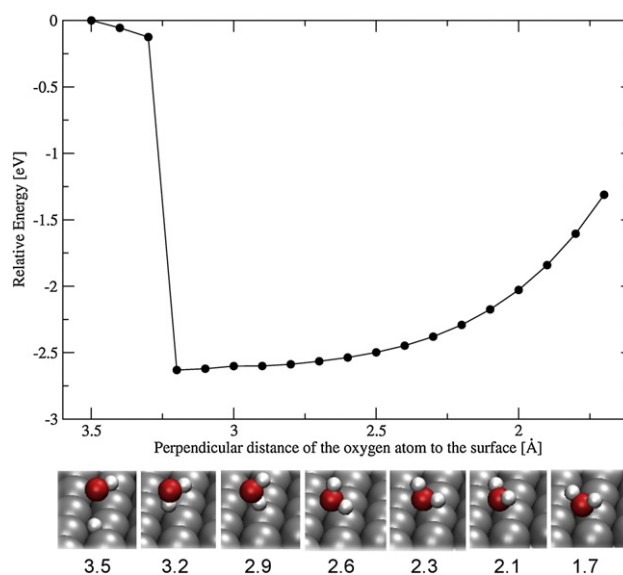

Fig. 1 − Initial structures (before the water formation): H_{ad} on a fcc site on Pt(111) and OH situated on top of the adsorbed hydrogen and at a distance of 3.5 Å from the metal surface. Final structure (after the water formation) at 3.2 Å from the metal surface. Rotation of the water molecule can be seen at shorter distances of the oxygen atom to the electrode.

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[1] The strongly adsorbed hydrogen is also known in electrochemistry as underpotential deposited hydrogen (H_{UPD}), for detailed information see Ref. [1] and references therein.
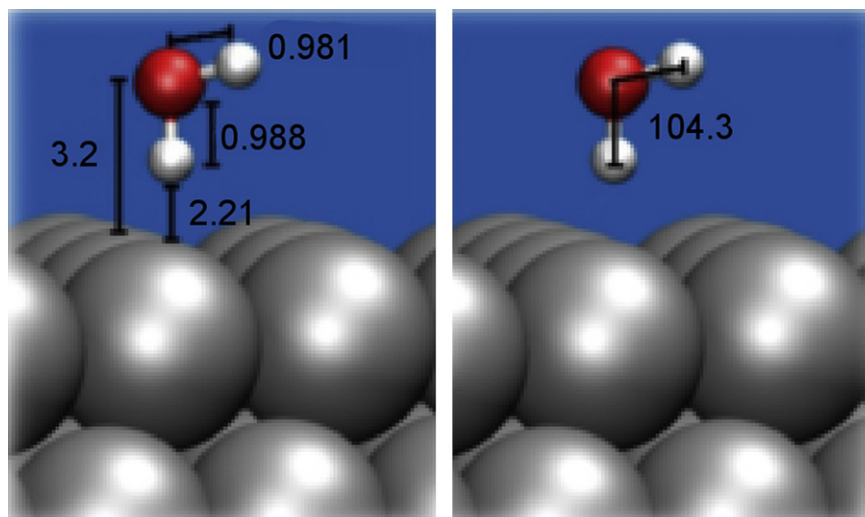
Fig. 2 – Geometric information of the most stable water structure on an fcc hollow site on Pt(111) in the condition of our calculations: O-metal distance: 3.2 Å, H-down-metal distance: 2.21 Å, H-down-O bond distance: 0.988 Å, lateral H–O bond distance: 0.981 Å and finally H–O–H angle: 104.3°.

on top of the pre-adsorbed H atom situated on a fcc site. The pre-relaxed surfaces were kept fixed while adsorbed hydrogen (H_{ad}) and the H in OH radical were fully optimized. The O was frozen in all the coordinates at different z-distances perpendicular to the surface.

3. Results and discussions

As detailed previously, the first approach of our theoretical model is focused on the study of the Volmer reaction (3) in alkaline media on a platinum metal electrode. Our analysis mainly centered in the position of the surface d band and its interaction with the 1s orbital of the adsorbed hydrogen atom; as well as the hydroxyl influence at several distances from the metal electrode.

3.1. Geometry

Fig. 1 shows the behavior of OH when it approaches the adsorbed hydrogen. In this condition, the formation of water was detected at ≈3.2 Å of the oxygen atom from the metal. Subsequently the molecule was fixed at several distances ($3.2 \leq d/Å \leq 1.7$) to the electrode as described previously (Section 2.2). Water rotation was found at shorter distances (<3.2 Å) from the electrode to minimize the repulsive character (Fig. 1).

The different positions of the molecule when it comes closer to the surface can be appreciated from Fig. 1. The favored structure was found at 3.2 Å of the oxygen atom to the surface with a hydrogen pointing down to the electrode and the other one lying almost parallel to the metal. For completeness, geometric information related to H_{down}[2]-metal

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[2] The hydrogen of the water molecule which points to metal surface.

and O-metal distances as well as H–O bond distances and H–O–H angle is shown in Fig. 2.

As mentioned before, the water molecule begins to rotate to minimize the repulsive interaction with the metal surface. The energy smoothly increases with decreasing the H_2O distance to the electrode. For closer distances (<2.3 Å of the oxygen to the surface), the molecule sits with both hydrogens pointing up with respect to the surface (Fig. 1). Although in all these configurations the H–O–H angle and the H–O bond distances slightly oscillate around 106°–107° and 0.98 Å–0.99 Å respectively; the water structure is practically preserved.

In addition, we perfomed a DFT calculation to verify the optimized position of a water molecule on Pt(111) without the constrains of our technical procedure. In this case, the water molecule was allowed to relax in all three coordinates. As expected, our results are comparable with the theoretical data reported by other groups [29]. A water molecule on Pt(111) is adsorbed on a slightly shifted top site (O-Metal distance: 2.46 Å) with the hydrogens atoms lying in a plane almost parallel to the surface (H–O–Pt angle: ≈96°). In accord with the values shown in Fig. 3 the water structure remains geometrically unchanged; with values of ≈0.986 Å for H–O bond distances and 104.7° for the H–O–H angle.

3.2. Electronic structure

The interpretation of the electronic structure of this system –OH, H_{ad}/Pt(111)– is rather complicated due to the presence of several interactions between the species, H_{ad} and OH radical, plus the electronic states of the metal surface. Therefore, in order to understand the nature of these interactions, the local density of states – LDOS – was examined. All the DOS presented in this contribution are normalized and the energy values are refered to the Fermi level taken as zero energy.

Fig. 4 shows the behavior of the H_{ad}/Pt(111) while the hydroxyl is approaching the surface for two specific distances
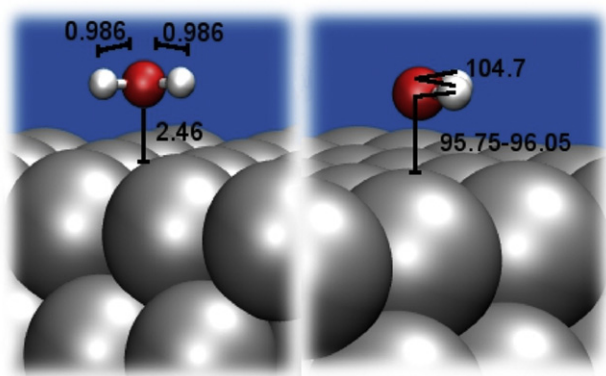
Fig. 3 − A water molecule on Pt(111) surface. Geometric parameters: O-metal distance: 2.46 Å, H−O bond distance: 0.986 Å, H−O−H angle: 104.7° and H−O−Pt angles: 95.75°−96.05°.

of the oxygen to the metal: 3.5 Å (before water formation, Fig. 4: top row) and 3.2 Å (after water formation, Fig. 4: bottom row). The LDOS at 3.5 Å (Fig. 4: top row (a)), shows the expected profile of an adsorbed hydrogen on a fcc hollow site on a platinum (111) surface. A peak appearing at ≈ -7 eV can be assigned to bonding states between the 1s hydrogen orbital and the platinum d states (see blue line and gray area−black line in Fig. 4: top row (a)). An interaction between the 1s hydrogen orbital with the broadened platinum sp band is also detected but not shown in this contribution. In addition, it is

noticeable that at larger distances (>3.2 Å) there is no interaction between the adsorbed hydrogen (H_{ad}) and the OH radical. There is no overlap between the 1s orbital of the adsorbed hydrogen and the 2s and 2p states of the oxygen or with the 1s hydrogen orbital in the hydroxyl (Fig. 4: top row (b) and (c)).

Finally, Fig. 4: top row (c) shows the expected behavior for the OH (comparable to the isolated radical). In principle three groups of contributions can be distinguished. A peak at ≈ -3 eV can be assigned to a bonding state between the hydrogen and oxygen; contributions of the 1s hydrogen orbital and 2s and 2p oxygen orbitals are also found. The peak above the Fermi level corresponds to antibonding states, and the last contribution can be attributed to the non-bonding states situated across the Fermi level, which indicates partial occupation (presence of lone electrons).

In accord with the constrains established in our calculations, the oxygen atom is completely frozen for each perpendicular distance to the electrode, but both hydrogens are fully free to relax. Hence, when the oxygen atom is fixed at 3.2 Å from the surface and localized on top of the adsorbed hydrogen, the result of the calculation suggests that an attractive interaction appears and suddenly the adsorbed hydrogen jumps to form a water molecule. Consequently, at 3.2 Å, water formation takes place; hence the peak at ≈ -7 eV assigned to the bond between the adsorbed hydrogen and Pt d states has disappeared (Fig. 4: bottom row (a)). The presence of water shows a weak interaction with the platinum surface. This behavior can be seen in Fig. 4: bottom row (a) where no modification in the electronic structure of Pt is found. It is
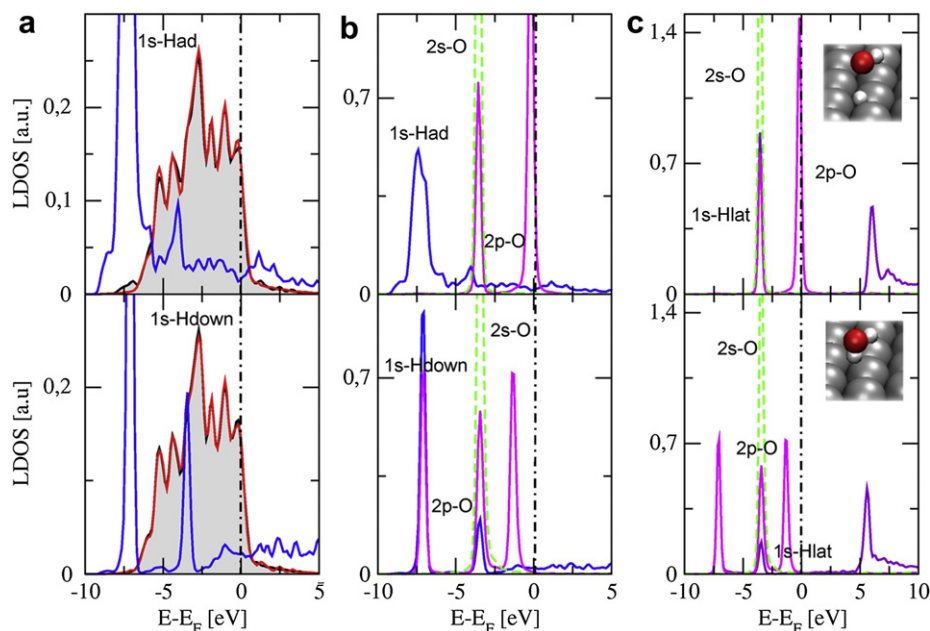

Fig. 4 − Local density of states, LDOS for the system. Top row: OH at 3.5 Å before water formation (a) gray area−black line: d band of platinum in the presence of H_{ad} at the fcc hollow site, red line: d band of bare platinum, blue line: DOS of 1s absorbed hydrogen orbital. (b) blue line: DOS of 1s absorbed hydrogen orbital, green dotted line: DOS of 2s oxygen orbitals, magenta line: DOS of 2p oxygen orbitals. (c) indigo line: DOS of 1s orbital of the hydrogen bonded to the oxygen atom, green line: DOS of 2s oxygen orbital, magenta line: DOS of 2p oxygen orbital. Bottom row: water formation at 3.2 Å (a), (b) and (c) DOS similar to the upper panel. In the inset in (c) pannels shown the corresponding geometric structures of the systems. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

important to notice that in spite of our different technical procedure, this result is in accordance with the trends found in the literature [29—32].

In Fig. 4: bottom row (b) the appearance of two peaks situated below the Fermi level at ≈ -7 eV, ≈ -4 eV are attributed to the bonding orbitals (overlaps between 1s H—2s O and 1s H—2p O) and another one localized higher than the bonding orbitals at ≈ -1 eV below the Fermi level, which corresponds to the lone electron pairs of water.

4.   Conclusions

The first steps in understanding the Volmer reaction in alkaline media has been investigated in the framework of DFT as a starting point to understand its electrocatalysis.

In particular, the effect of the OH on the adsorbed hydrogen on a platinum metal surface was studied. Our results indicate that water formation takes place when the OH is at a distance of ≈ 3.2 Å from metal surface; for closer distances, the rotation of water was found to minimize the repulsion between the molecule and the metal. As mentioned previously and in accord with the literature, no significant interaction between the H_2O states and the metal d bands is observed.

Acknowledgments

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