



# Thermodynamics is not enough – The case of the Volmer reaction on silver



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## ABSTRACT

The energy of activation for the Volmer step of the hydrogen evolution reaction on silver electrodes is evaluated using our own theory of electrocatalysis. The reactivity at the hollow sites of the flat Ag(1 0 0) surface and the vicinal Ag(1 1 5) surface is compared. Although the adsorption energy calculated by Density Functional Theory is similar for both systems, we found a substantially higher value for the activation energy in the case of the (1 1 5) crystal orientation. Our analysis shows that other important factors, such as the electronic interactions between reactant and substrate at the transition state, play a decisive role. Thermodynamics is not enough to explain reactivity.

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## 1. Introduction

The reactivity of electrode materials is frequently estimated from the adsorption energy of the reactant. In a framework based on the Sabatier principle [1], electrodes showing similar adsorption energies for the reactant are expected to have similar catalytic properties. Although the attempt to understand catalytic reactions with the aid of a single descriptor, typically the energy of adsorption of a single intermediate, is sometimes useful, the kinetics of complex reactions are often not so simple. Following the ideas of Polanyi, Nørskov et al. [2] have proposed a roughly linear function between the reaction energy and the activation energy. They introduced two parameters ( $\alpha$  and  $\beta$ ) that represent electronic and geometrical effects. We have also addressed this issue in a recent publication [3], and concluded that not only the adsorption energy but also other factors must be considered in order to explain electrocatalytic properties. One of these factors is a strong, long-range interaction between the electronic states of the substrate and the orbitals of the reactant. The electron transfer to the reactant occurs at a certain distance, which in most cases is  $<1$  Å from the adsorption site (for example, in the case of the Volmer reaction it is of the order of 0.5 Å). In this work, we present an example in which the electronic interactions between reactant and substrate at the transition state play a decisive role.

Stepped surfaces usually show greater reactivity than flat surfaces [4–7]. The electrochemical response is a combination of current contributions from terrace and step sites. Frequently it is found that reactions

are faster on step sites than on terrace sites. However, sometimes the correlation between step density and reactivity is complicated [7].

In a previous communication to this journal [8], we have shown from potentiostatic transient measurements that on stepped silver surfaces the rates of both Volmer and Heyrovsky reactions are faster on the steps than on the terraces. However, the rate constants of these reactions do not vary linearly with step density. We have qualitatively explained these results by assuming that adsorption on shorter terraces is less favourable. According to calculations based on the Density Functional Theory (DFT), a certain anisotropy exists for the hydrogen adsorption energy on hollow sites along a terrace or stepped surface [9]. However, the dispersion of these values ( $<0.1$  eV) is too low to explain the difference in reactivity.

In this work, we take a step forward. We solve this puzzle by means not only of thermodynamics, but also through a rigorous analysis of the whole reaction path using our own theory of electrocatalysis.

## 2. Theoretical approach

The calculations follow our previous works [10,11], to which we refer for the details. Our theory of electrocatalysis is based on a model Hamiltonian, quantum statistics, and DFT. The planar (1 0 0) surface has been described using a  $(2 \times 2)$  supercell with five metal layers, while the vicinal Ag(1 1 5) surface was modelled using a unit cell with 6 silver atoms exposed to the surface, and the  $(2 \times 1)$  supercell contains 15 metal layers. All the adsorbate atoms and either the 2 or the 6 top-most metal layers were allowed to relax in the case of planar or vicinal surfaces, respectively.

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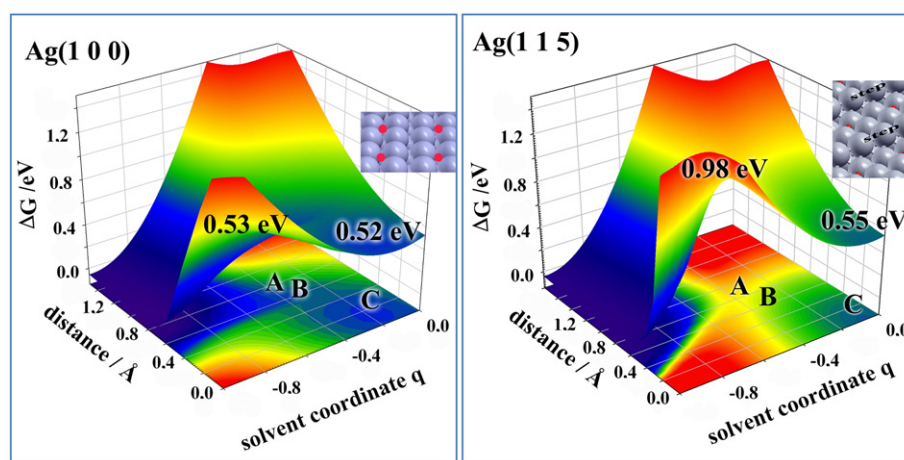


Fig. 1. 3D potential energy surface for the Volmer reaction at the hollow sites of the Ag(1 0 0) (left) and the Ag(1 1 5) surfaces (right).

The spatial redistribution of the electronic charge  $\Delta\rho(x,y,z)$  has been calculated according to the usual procedure [12–14].

The reorganization of the solvent around the proton during the path reaction is obtained using molecular dynamics.

### 3. Results and discussion

We have calculated the free energy surface for the electrochemical hydrogen adsorption (Volmer step) on Ag(1 0 0) and Ag(1 1 5). We use as coordinates the distance of the reactant from the surface, and the solvent coordinate  $q$ , which characterizes the state of the solvent. The initial state is a solvated proton far away from the electrode (Zundel ion), which corresponds to  $q = -1$ . The final state is an adsorbed hydrogen atom at the equilibrium distance with  $q = 0$ . An activation barrier results from the interplay between the interactions with the solvent (reorganization of the solvation shell) and the electronic interactions with the metal.

The most reactive site is the bridge position at the upper part of the step, as expected from experiment. However, we shall focus on the hollow site of the small terrace and compare its reactivity with the hollow site of the plane (1 0 0) surface.

Fig. 1 shows the results for both systems. The adsorption energy for the final state is similar: 0.52 eV and 0.55 eV for the Ag(1 0 0) and Ag(1 1 5) surfaces, respectively. However, we found a much higher value for the activation energy on the (1 1 5) crystal orientation (0.98 eV compared with 0.53 eV for Ag(1 0 0)). This is almost a factor of two in the activation energy, and this corresponds to a ratio of  $10^7$  in the rate constant. This is a clear example of a situation in which thermodynamics alone cannot explain the reactivity. The obvious question is why?

When the hydrogen is adsorbed, the environment is similar for both systems. The equilibrium position is very close to the surrounding silver atoms. In contrast, when the proton approaches the surface, because the hollow site at the (1 1 5) surface is near the step, the electronic environment is different to that of the flat (1 0 0) surface. Its position is particularly crucial when it crosses the saddle point of the energy surface (between 0.5 Å and 0.8 Å from the equilibrium distance).

An analysis of the density of states projected onto the 1s orbital of the approaching hydrogen atom (HPDOS) near the saddle point shows that coupling with the electronic states of the surface is stronger in the case of the Ag(1 0 0) than for the Ag(1 1 5) surface. Fig. 2 shows the HPDOS for the three positions labelled in the potential energy surfaces as A, B (around the transition state), and C (at the final adsorbed state). While the densities of states for the adsorbed state are very similar, those corresponding to the transition state are essentially different. In the case of Ag(1 0 0), they are broader and deeper in energy, revealing stronger coupling than for the Ag(1 1 5) surface, which causes a decrease in the activation barrier. Indeed, the coupling parameters with the sp band and d band at the transition state are larger for the (1 0 0) orientation:  $|V_{sp}^{100}|^2 = 5.42 \text{ eV}^2$  and  $|V_d^{100}|^2 = 2.52 \text{ eV}^2$  than the corresponding values  $|V_{sp}^{115}|^2 = 1.85 \text{ eV}^2$  and  $|V_d^{115}|^2 = 1.64 \text{ eV}^2$  for the (1 1 5) orientation.

The occupation of the 1s orbital at a distance of 0.8 Å from the equilibrium (A in the plots) is 0.57 for Ag(1 0 0) while it is 0.73 for Ag(1 1 5).

Additional evidence for the distinct interactions comes from the spatial electronic density redistribution when the hydrogen approaches both hollow sites. Fig. 3 shows these results for the positions A and C. At the equilibrium distance for the adsorption (position C) both systems show similar electronic density changes. Electronic charge

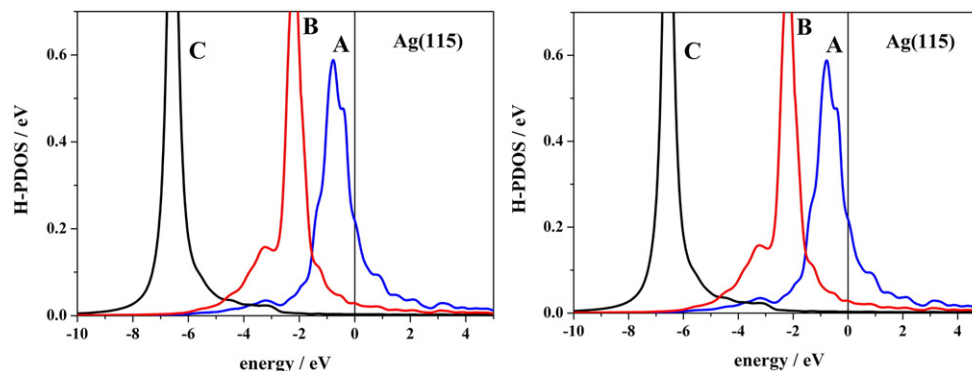
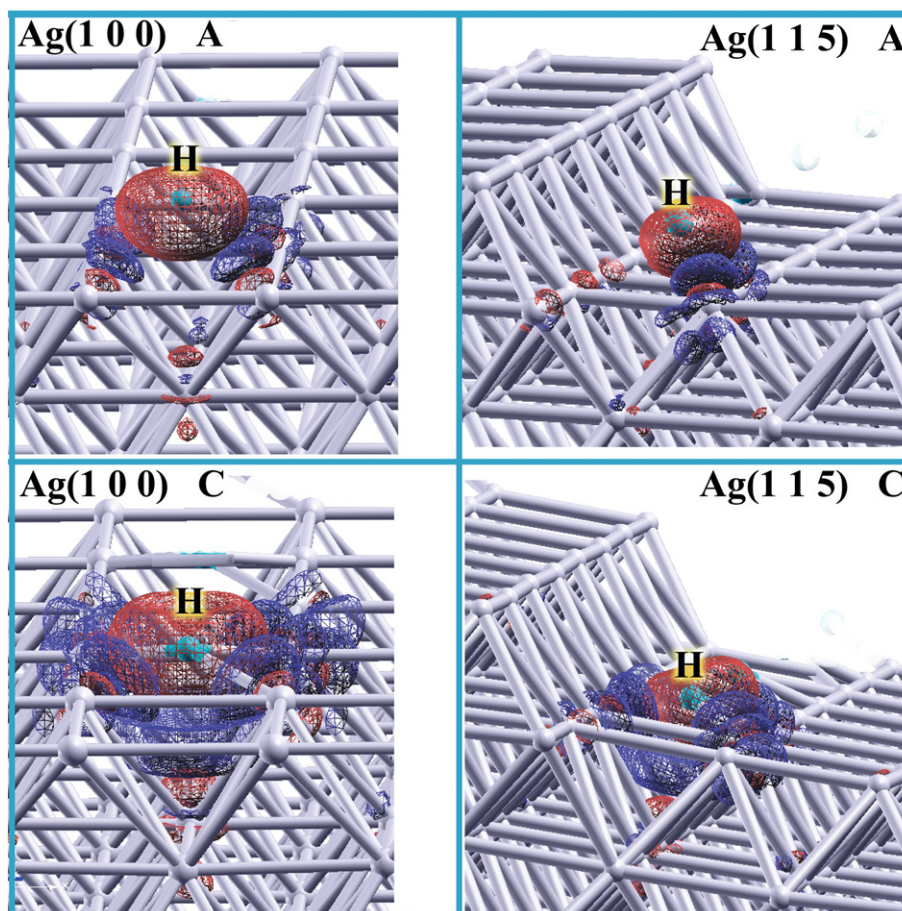


Fig. 2. H-PDOS for the hydrogen atom approaching the Ag(1 0 0) and the Ag(1 1 5) surfaces. The letters indicate the positions given in the potential energy surfaces of Fig. 1. C corresponds to the adsorbed hydrogen in the final equilibrium state. B and A correspond to the proton crossing the barrier.



**Fig. 3.** Electronic charge density redistribution when the hydrogen approaches the hollow sites of the Ag(1 0 0) and the Ag(1 1 5) surfaces. Red and blue colours correspond to electron accumulation and depletion, respectively. Isosurface:  $0.0012 \text{ e } \text{\AA}^{-3}$  (plotted with the XCRYSDEN package [13]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

displacements occur between the four Ag atoms of the hollow site surrounding the hydrogen, with a small additional contribution from the Ag atom corresponding to the second layer. The situation at a distance of 0.8 Å from equilibrium (position A) near the saddle point is particularly interesting. Here the differences in the strength of the hydrogen–substrate interactions become clear. While at this stage the hydrogen already strongly interacts with the four Ag atoms of the hollow site of the Ag(1 0 0), in the case of the approach to the hollow site of the Ag(1 1 5) near the step, the interactions with the Ag atoms on the bottom of the step are substantially weaker.

Previously, a strong geometrical effect on the transition state has been observed for molecular dissociation reactions, such as  $\text{N}_2$  dissociation reactions on flat and stepped Ru(0 0 0 1) surfaces [15]. However, in the case of molecules different atoms interact with different sites during the reaction path, therefore different behaviour may be expected. One N atom is positioned close to the most stable hcp site while the other N atom is at a bridge position. On the stepped surface, the latter site is located at the step, which is more active in reducing the barrier. In our example, the hydrogen approaches a hollow site on the terrace of the stepped surface and the same site on the flat surface. This implies that in the Volmer reaction, in contrast to molecular dissociation, only one type of site is involved in the transition state. The decrease in the barrier is therefore unexpected.

#### 4. Conclusions

We have investigated the Volmer step of the hydrogen evolution reaction (HER) at the hollow sites of the flat Ag(1 0 0) surface and compared it with the same process at the same geometrical location on

the vicinal Ag(1 1 5) surface. The adsorption energy is similar for both systems. However, the electronic interactions when the hydrogen atom approaches each surface are very different due to the different spatial environment. As a consequence, there is a considerably higher activation barrier for the reaction on the Ag(1 1 5) surface. These results clearly demonstrate that thermodynamics is not enough to explain the reactivity in such cases. A rigorous analysis of the whole reaction path is necessary.

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