Hydrogen evolution on a pseudomorphic Cu-layer on Ni(1 1 1) – A theoretical study

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ABSTRACT

Hydrogen evolution on a monolayer of copper on Ni(1 1 1) has been investigated by a combination of density functional theory and a model developed in our own group. The lattice constant of nickel is only about 2.5% shorter than that of copper; therefore the nickel substrate has only a minor effect on the surface d band of the adsorbed copper. However, there is a strong chemical effect which enhances the interaction of hydrogen with the Cu/Ni(1 1 1) surface as compared to Cu(1 1 1). Consequently, the adlayer promises to be a cheap catalyst that is significantly better than pure copper.

1. Introduction

In the search for better and cheaper catalysts, core–shell systems with an active layer of catalyst on a less active metal have recently gained much attention. In particular, layers of platinum on cores composed of metals from the iron group have been found to be good catalysts for oxygen reduction [1,2]. But even though the platinum content in these systems is low, they are still expensive. In addition, their stability may be a problem under working conditions. It therefore certainly worthwhile to look for cheaper and more stable catalyst.

Nickel and copper form interesting combinations; they are chemically quite different, but they mix readily since their lattice constants are quite similar. Polycrystalline Ni–Cu alloys have been well investigated, e.g. by Conway et al. [3], but they did not show any promising catalytic activity. In this communication we do not concern ourselves with alloys, but with pseudomorphic monolayers of copper on Ni(1 1 1), which are stable at ambient temperatures [4]. Although, to the best of our knowledge, their electrocatalytic properties have not been investigated experimentally, we believe that they are interesting systems. Therefore, we have investigated their electronic properties and their catalytic activity for the hydrogen evolution reaction. As we shall demonstrate below, they promise to be much better catalysts than

expected. Naturally, it would be interesting to know if they are good catalysts for oxygen reduction as well, but the absence of a proper theory for the kinetics of this reaction prevents us from answering this question.

2. Our model

In a recent communication, we have systematically investigated hydrogen electrocatalysis on a number of metals covered by monolayers of foreign metals [5]. These calculations, based on the Santos–Koper–Schmickler (SKS) Hamiltonian [6,7], showed that, in general, both the chemical effect of the substrate and a geometric effect – compression or extension of the adsorbate lattice – determine their reactivity. Here, we want to study a particular system, not investigated before, in greater detail using an extension of the SKS formalism which involves more quantum chemical calculations on the basis of density functional theory (DFT). The details of our model have been presented in a recent article [8]; here we give a short summary in order to make this article self contained.

We focus on the Volmer reaction:

$$H^+ + e^- \rightarrow H_{ad} \tag{1}$$

which is always the first step in hydrogen evolution, and determines the rate at least at short times. The initial state is a fully solvated proton at a certain distance from the surface, the final state an

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adsorbed, discharged, and unsolvated hydrogen atom. Therefore, we calculate free energy surfaces for the reaction as a function of two variables: The distance d of the reactant from the metal surface, measured with respect to the first lattice plane, and the solvent coordinate q. The latter is a concept familiar from Marcus theory [9]; it indicates the configuration of the solvent. In our convention it is normalized such that a value q indicates a state of the solvent which would be in equilibrium with a charge of $-q$ on the reactant. Thus, a fully solvated proton would correspond to $q = -1$, an adsorbed, discharged hydrogen atom to $q = 0$.

For $q = 0$ the solvent plays no role, and the electronic energy can be calculated directly as a function of d by DFT. In order to extrapolate these values to solvated states with $q \neq 0$, we use a model proposed by one of us [10], which combines elements of the Anderson–Newns model [11,12] with Marcus theory. For the present purpose, the key quantity is the density of states (DOS) $\rho_a(\epsilon)$ of the reactant, which takes the following form:

$$\rho_a(\epsilon) = \frac{1}{\pi} \frac{\Delta(\epsilon)}{[\epsilon - (\epsilon_a + \Lambda(\epsilon) - 2\lambda q)]^2 + \Delta(\epsilon)^2} \tag{2}$$

Here, $\Delta(\epsilon)$ and $\Lambda(\epsilon)$ are the chemisorption functions:

$$\Delta(\epsilon) = \sum_k |V_k|^2 \pi \delta(\epsilon - \epsilon_k), \quad \Lambda(\epsilon) = \frac{1}{\pi} \mathscr{P} \int \frac{\Delta(\epsilon')}{\epsilon - \epsilon'} d\epsilon' \tag{3}$$

$|V|^2$ is the interaction of the reactant with the metal d band, and ϵ_a the energy of the 1s orbital of hydrogen without this interaction. λ is the reorganization energy of the solvent. The quantities $|V|^2$ and ϵ_a depend on the distance from the metal surface. They are obtained by fitting the hydrogen density of states to Eq. (2) with $q = 0$.

Our theory focuses on the effect of the d band. The role of the sp band is roughly the same on all metals [13,14]; it makes a contribution to the chemisorption function $\Delta(\epsilon)$ which we have set to $\Delta_{sp} = 0.7$ eV. This has been estimated from the width of the hydrogen DOS when its main peak lies outside the d band. For the details of our procedure to obtain the free energy surfaces, we refer to our original publication [8].

The only quantity which we cannot obtain from DFT is the energy of reorganization λ of the solvent. This is determined by the solvation of the proton, and should be independent of the nature of the metal. The appropriate value has been discussed extensively in our previous works [8,15]; based on the solvation energy of the proton, we have estimated a value of the order of $\lambda = 3$ eV. In Ref. [8] we have performed calculations for several values of λ and also investigated a model, in which λ decreases by a factor of two towards the metal surface for steric reasons, an effect which one of us had suggested before [16], and which is supported by computer simulations [17]. As expected, we found that the order of the activity of the metals did not depend on the exact value of λ, and also was the same for a model with a spatially constant λ; however, the model with a varying λ gave surfaces which are more in line with computer simulations [17]. Therefore, we shall here give the results for an energy of reorganization which has a value of 3 eV for the proton in the initial state, and half that value at the adsorption site. Our main focus in this work is the catalytic activity of a monolayer of copper on Ni(111) in comparison with Cu(111). The relative activity is independent of the model we use for the solvent reorganization.

The free energy of the Volmer reaction, or hydrogen adsorption, depends on the electrode potential. It is convenient to refer all values to the standard hydrogen potential SHE at pH 0. Under these conditions the solvated protons are in equilibrium with hydrogen gas under standard conditions. Following the procedure outlined in [18], the free energy of adsorption was obtained from the energy of adsorption per hydrogen atom by adding a value of 0.2 eV for the entropy of the hydrogen gas.

3. Results

The lattice constant of Cu is about 2.5% larger than that of Ni. Thus, the adsorbed Cu-layer is slightly compressed, but the geometric effect should be small. This expectation is verified by the adsorption energy: On the adlayer, the free energy of adsorption of a hydrogen atom is 0.05 eV vs. SHE, on Cu(111) it is 0.1 eV, so they are almost equal. The bond distance, taken with respect to the plane of the uppermost copper atoms, is somewhat larger on the adlayer: 1.05 Å as compared to 0.9 Å on Cu(111). This small shift is caused by the shorter lattice constant of the substrate. In fact, the bond distance at the Cu adlayer is the same as for hydrogen on pure Ni(111).

Since the lattice mismatch is small, we do not expect a major change in the density of states of the d band; this is indeed borne out by our calculations (see Fig. 1). The smaller lattice constant of the adsorbate layer entails a slight broadening of the d band, which has acquired a tail extending to the Fermi level, which here and elsewhere has been taken as zero. Since the density close to the Fermi level remains low, this should have only a minor effect on hydrogen adsorption.

Thus, from the d band structure alone we would not expect a major difference between hydrogen evolution on bare copper and on the adlayer. However, surprisingly the adlayer interacts much more strongly with the 1s orbital of hydrogen than Cu(111). As an example, we show the density of states of the hydrogen atom at a distance of 1.6 Å for Cu/Ni(111) (Fig. 2 – left) and 1.5 Å for Cu(111) (Fig. 2 – right), i.e. 0.6 Å in front of the equilibrium position on both surfaces. At Cu(111) the hydrogen DOS has a major peak that lies well below the d band, which with it overlaps a little. There is also a small antibonding peak at about -2.5 eV. On Cu/Ni(111), the hydrogen DOS lies higher and interacts more strongly with the d band. The overlap is substantial, and both a bonding and an antibonding peak are clearly visible. Fig. 2a also shows the fit according to Eq. (2); it captures well the main features, even though the situation of strong overlap is the most difficult to fit.

A quantitative evaluation of the fits shows that the coupling between the hydrogen 1s and the d band is much stronger on Cu/Ni(111) than on pure Cu(111), by about 50% (see Fig. 3). Interestingly, the two curves run parallel and thus decay in the same way. For comparison, we also show the coupling constants on Pt(111), which are higher and decay less rapidly. Since Cu/Ni(111) and Cu(111) have very similar d bands, this enlarged interaction must be caused by the effect of nickel on the properties of the adsorbed Cu monolayer. Thus, it is principally caused by a chemical (or ligand) effect, and not by the slight compression of the layer. This effect has nothing to do with the spin polarization of nickel, since spin-polarized and non-polarized calculations gave the same results.
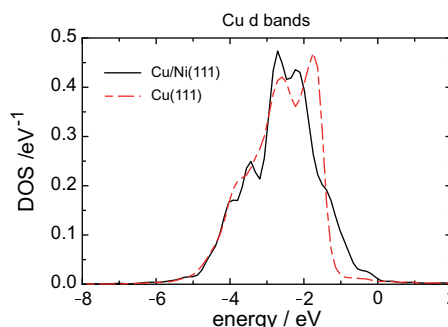

Fig. 1. d bands at the surface of Cu/Ni(111) and of Cu(111). The Fermi level has been taken as the energy zero.
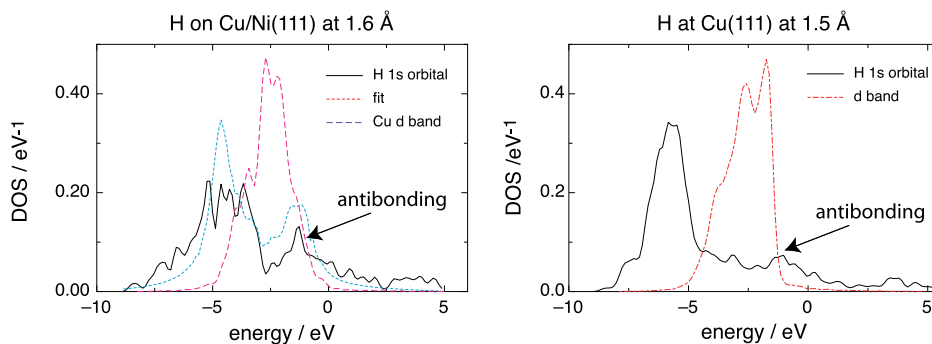
Fig. 2. Density of states of the hydrogen 1s orbital at a distance of 1.6 Å in front of Cu/Ni(1 1 1) (left) and at a distance of 1.5 Å in front of Cu(1 1 1) (right).
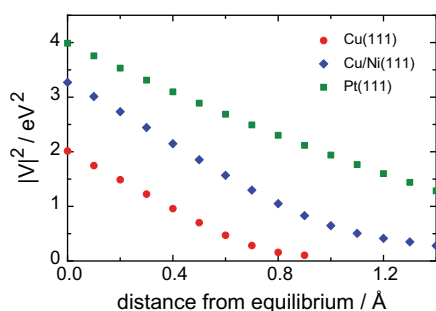

Fig. 3. Coupling constants between the hydrogen 1s orbital and the metal d band as a function of the distance from equilibrium.

The stronger coupling entails a substantial lowering of the energy of activation. Fig. 4 shows the free energy surfaces for the Volmer reaction. The valley near $q = -1$, $d = 2.5$ Å corresponds to a solvated proton close to the metal surface; the minimum near $q = 0$, $d = 1.0$ Å represents the adsorbed hydrogen atom. The two minima are separated by a barrier with a saddle point of $E_{act} = 0.45$ eV height. For comparison, on Cu(1 1 1) [8], using the same model, we have obtained a free energy of activation of

$E_{act} = 0.70$ eV. This difference is outside of the uncertainty of our model, and is certainly caused by the larger interaction of Cu/Ni(1 1 1) with hydrogen.

In our model we can perform calculations for various overpotentials [7], an opportunity which so far we have little explored. Therefore, in Fig. 4 we also show the free energy surface for a cathodic overpotential of 200 mV. In our convention, this raises the energy of the proton in the solution by 200 meV, while the energies on the metal surface are kept fixed. The absolute value of the saddle point energy is raised by about 100 meV, resulting in a reduction of the activation energy for the forward reaction also by 100 meV, and a transfer coefficient of about 1/2, a value often encountered for the Volmer reaction.

4. Conclusions

In this work we have investigated hydrogen evolution on Ni(1 1 1) covered by a mesomorphic monolayer of copper. The adlayer is only slightly compressed with respect to bulk copper, so that there is little change in the d band structure. Nevertheless, we found that the monolayer of copper interacts much more strongly with hydrogen than Cu(1 1 1), which we attribute to a chemical effect of the nickel substrate. The stronger interaction results in a substantially reduced energy of activation for the
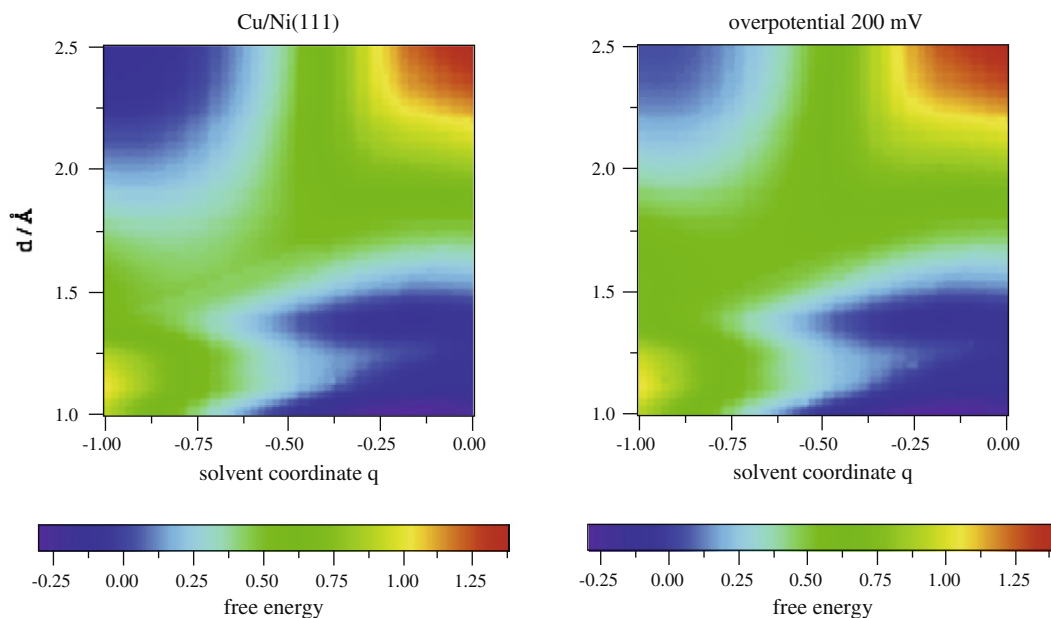

Fig. 4. Free energy surfaces for the Volmer reaction at Cu/Ni(1 1 1) at equilibrium (left) and at a cathodic overpotential of 200 mV (right).

Volmer reaction, which should make this surface a cheap and decent catalyst, even though its reactivity cannot quite compete with that of platinum.

We have focused here on the Volmer reaction, which determines the reaction rate at least at short times. Since at zero overvoltage the Volmer reaction is almost isoenergetic, the desorption in a second step should not be a major problem. Judging from experiments on bulk copper [19], this is likely to be the Heyrowski reaction. However, this needs to be verified by detailed calculations – or by experiments.

In summary, on the basis of our model we predict that a Ni(1 1 1) surface covered by a monolayer of copper should be cheap and fairly good catalyst for hydrogen evolution.

Acknowledgements

Appendix A. Details of the DFT calculations

All calculations were performed using the DACAPO code [20]. 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 wave functions, and the inner electrons were represented by ultrasoft pseudopotentials [21], which allows the use of a low energy cutoff for the plane-wave basis set. An energy cutoff of 400 eV, dictated by the pseudopotential of each metal, was used in all calculations. The electron–electron exchange and correlation interactions are treated with the generalized gradient approximation (GGA) in the version of Perdew, Burke and Ernzerhof [22]. The Brillouin zone integration was performed using a $8 \times 8 \times 1$ k-point Monkhorst–Pack grid [23] corresponding to the (1×1) surface unit cell. The surfaces were modeled by a (2×2) supercell with four metal layers and 10 layers of vacuum. Dipole corrections were used to avoid slab–slab interactions [24]. The first two layers were allowed to relax, while the bottom two layers were fixed at the calculated next neighbor distance. The

optimized surfaces (pre-relaxed) in the absence of the hydrogen atom were used as input data to carry out the calculations to study the hydrogen desorption. For each systems, we performed a series of calculations for a single hydrogen atom adsorbed on a hollow site, and varied its separation from the surface. The pre-relaxed surface was kept fixed while the H was allowed to relax in the xy-coordinates during these calculations. At each position we calculated the adsorption energy, and the DOS projected onto the 1s orbital of hydrogen. We performed both spin-polarized and non-polarized calculations. While spin polarization led to the expected lowering of the total energy, it had no effect on hydrogen adsorption.

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