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The role of steps in the dissociation of H_2 on Mg(0001)

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Abstract

The role of steps in the dissociation of molecules on metal surfaces has been extensively investigated in the past. In particular, both theoretical calculations and experimental results for H_2 dissociation on transition metal (TM) surfaces show that steps can significantly increase the reactivity, leading to higher metal–H binding energies and lower activation energies. Here we have used density functional theory (DFT) with the generalized gradient approximation (GGA) to investigate the role of steps on the Mg(0001) surface in the dissociation of H_2 and the binding of H to the metal surface. Our results follow those found for TM surfaces as far as H adsorption energies are concerned, namely that adsorption energies are higher near the steps. However, we find that the activation energy for the dissociation of hydrogen is hardly affected by the presence of steps, with a DFT–GGA value of 0.85 eV, only marginally lower than the value 0.87 eV found on the flat Mg(0001) surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnesium is a light material that when combined with hydrogen forms the hydride MgH_2. When heated above 300 °C the hydride decomposes back to Mg metal and H_2 gas, making this material interesting for hydrogen storage purposes. A number of theoretical studies on the properties of various flat Mg surfaces when interacting with hydrogen have been performed in the past, including studies on pure surfaces, and surfaces doped with traces of transition metals [1–12]. It is well known, however, that real surfaces are often far from being flat. Reactions on real systems are more complex due to the presence of imperfections/defects in the form of steps edges or kinks vertices. It is therefore important to investigate the effects that steps may have on the dissociation of H_2 on such surfaces.

It has been shown both theoretically and experimentally that steps significantly increase the reactivity of transition metal surfaces (but not that of noble metal surfaces; see [13] and references therein), with adsorption occurring to or near a step site where the energy barrier for molecular dissociation is smaller and the adsorption energy is larger (see for example [14–18] and references therein).

In particular, the influence of steps on the interaction between hydrogen and stepped metals (such as Ni, Rh, Cu, Pt, Pd) surfaces has been largely investigated (see for example [19–22] and references therein). These theoretical studies show that steps sites are more reactive: they are responsible for larger H–metal binding energies and for significantly lower activation barriers for H_2 dissociation. Molecular beam and low-energy electron diffraction experiments on stepped transition metal systems (see [20, 23] and references therein) confirm the theoretical findings.

The increase in chemical activity near the steps can be understood in terms of the local atomic structure. For a molecule adsorbed near a step edge there is a larger number of orbitals from the metal available to interact with the molecule,

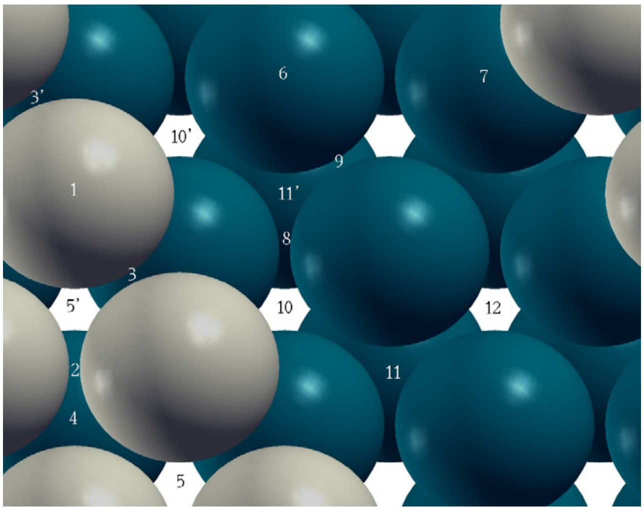

Figure 1. Possible adsorption sites for hydrogen on the stepped Mg(0001) surface (denoted by site number, as listed in table 1). Mg atoms of the top terrace are shown in light grey while those belonging to the bottom terrace are shown in dark grey.

Table 1. Hydrogen adsorption energies on the stepped Mg(0001) surface for the different sites investigated (see figure 1).

Adsorption sites	E_{ads} (eV)
Top (1)	0.47
Bridge (2)	0.20
Bridge (3)	−0.19
Hollow hcp (4)	−0.06
Hollow fcc (5)	−0.11
Top (6)	0.67
Top (7)	0.24
Bridge (8)	0.25
Bridge (9)	0.11
Hollow fcc (10)	0.04
Hollow hcp (11)	0.05
Hollow fcc (12)	−0.08

the d orbitals in the case of transition metal surfaces, because the number of nearest neighbours of the atoms near the step is smaller.

Here we have performed density functional theory calculations on a stepped Mg(0001) surface in order to study the role of steps on the dissociation of H_2 and its subsequent adsorption on the surface. In line with results on different systems, we find that the adsorption energy increases somewhat on sites near the step edges, but the energy barrier for the dissociation of the molecule is only marginally affected by the presence of steps.

2. Computational method

DFT calculations were performed with the *ab initio* simulation package VASP [24] using the projector augmented wave (PAW) method [25, 26] and the PBE exchange–correlation functional [27]. An efficient charge density extrapolation was used to speed up the calculations [28]. The electronic wavefunctions were expanded in plane-wave basis sets with an energy cut-off of 270 eV, which guarantees convergence of adsorption energies to within 1 meV.

The Mg(0001) surface was modelled by a five layer slab repeated periodically where two rows of Mg atoms have been removed from the topmost layer to create the step. The first three atomic layers were allowed to relax, while the bottom two were held fixed to the positions of bulk Mg. The vacuum gap was 10 Å. The step is modelled by using a 4×2 unit cell with a $4 \times 8 \times 1$ **k**-point grid. Tests have also been performed on a larger unit cell (6×2, with a $3 \times 9 \times 1$ **k**-point grid) to check for possible interactions between adjacent steps. In particular, we calculated the adsorption energy of atomic hydrogen in the most stable site (a bridge site on the step edge, see below) using the 4×2 surface unit cell and three possible 6×2 surface unit cells (with a top terrace width of two rows and a bottom terrace width of four rows, or vice versa of four rows on the top terrace and two on the bottom one, or three rows on the top and three on the bottom), and we found that these adsorption energies are all within 0.01 eV. We therefore decided to use the 4×2 surface unit cell for all the calculations. We found that the topmost layer (top of the step) has an inward relaxation of about 3.5% with respect to the second layer (bottom of the step), and this result is essentially unchanged if six layers are used instead of five.

H adsorption and H_2 dissociation have been investigated at both terrace and step edge sites of the Mg(0001) surface. Activation energies have been calculated using the climbing image nudged elastic band (NEB) method [29], using nine replicas for most of the calculations. Tests performed with 17 images showed that activation energies were already converged to within 1 meV and displayed all the main features of the minimum energy path.

Figures 1 and 3 have been made using the XCRYSDEN software [30].

3. Results

3.1. H adsorption on the stepped Mg(0001) surface

We have studied the adsorption of atomic hydrogen at all possible adsorption sites on the terraces and near the step edge. Figure 1 shows the adsorption sites investigated here, including top, bridge, hollow fcc (empty hollow) and hollow hcp (filled hollow) sites. Adsorption energies for the reported sites are listed in table 1. They are defined as $E_{\mathrm{ads}}(H) = E_{\mathrm{slab}}(\mathrm{MgH}) - [E_{\mathrm{slab}}(\mathrm{Mg}) + 1/2E(\mathrm{H}_2)]$, where $E_{\mathrm{slab}}(\mathrm{MgH})$ is the energy of the stepped slab with one H adsorbed on the surface, $E_{\mathrm{slab}}(\mathrm{Mg})$ is the energy of the pure stepped slab and $E(\mathrm{H}_2)$ the energy of the isolated hydrogen molecule, calculated by placing the H_2 molecule in a large cubic box of sides 13.5 Å.

The preferred site for H adsorption is the bridge site (3) situated on the top of the step and overlooking the bottom of the step itself. The adsorption energy in this site is 0.19 eV, larger than the value of 0.05 eV found on the flat metal surface [10].

Next, we have investigated the adsorption of two H atoms on the surface, and we list all possible sites in table 2, together with their adsorption energies. We investigated various possible combinations, including both sites on the top of the step, both on the bottom, or one on the top and one on the bottom.

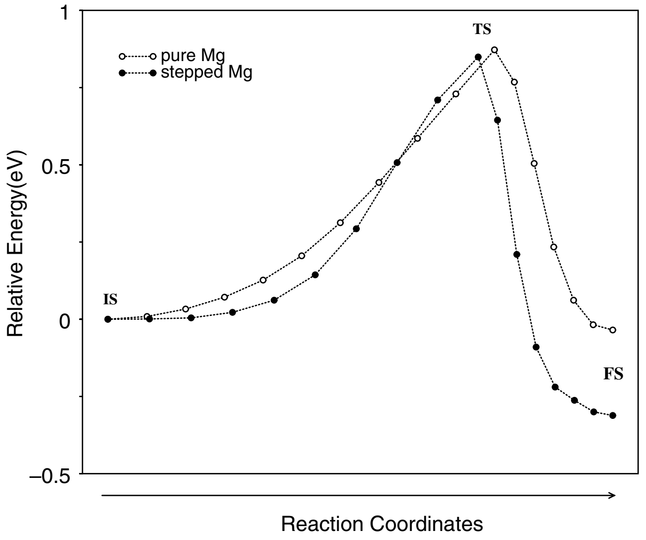

Figure 2. Minimum energy path barrier for H_2 dissociation on the stepped Mg(0001) surface as compared to that on the pure Mg(0001) surface.

The most energetically favourable configuration is the one with both H atoms in a bridge position, slightly shifted towards the edge of the step, overlooking the bottom of the step itself (which is denoted by (3)–(3′) in table 2). The next most energetically favourable configuration (with an adsorption energy lower by about 0.08 eV) is the one with one H atom in a bridge position and the other in a nearby hcp site (which are denoted by (3)–(4) in table 2). Other possible adsorption sites are reported in table 2.

3.2. *H_2 dissociation on the stepped Mg(0001) surface*

To study the dissociation of the H_2 molecule, we performed a number of NEB calculations, trying to look for many possible minimum energy paths. The initial state of the NEB calculations was represented by the hydrogen molecule sitting at a distance of about 5 Å from the top of the step. We tested two different sites, placing the molecule above a bridge site or above a top site. The energy of the initial state is our reference, and it is essentially equal to the energy of the isolated slab plus the energy of the isolated molecule (within 4 meV), so that the energy of the final states are also representative of the adsorption energy of the two H atoms on the surface. In table 2 we report the activation energies for all the paths investigated here, in which we indicate the positions of the two sites where the two H atoms adsorb after the dissociation of the molecule (final states).

Table 2. Activation energies (E_{diss}) and energy difference between the initial and final states (E_{ad}) for the dissociation of H_2 on the stepped Mg surface, reported for different possible adsorption sites for the two H atoms after dissociation of the molecule (see also table 1 and figure 1).

H–H dissociation sites	E_{diss} (eV)	E_{ad} (eV)
(3)–(4)	0.85	−0.31
(3)–(3′)	1.06	−0.39
(4)–(5)	0.85	−0.24
(3)–(5)	1.07	−0.34
(5)–(5′)	1.07	−0.24
(3)–(10)	1.13	−0.20
(4)–(10)	0.95	−0.05
(3)–(11′)	0.96	−0.14
(10)–(11′)	0.87	0.07
(10)–(10′)	1.18	0.07

There are two equally most energetically favourable pathways (denoted by (3)–(4) and (4)–(5) in table 2), which both show an activation energy of 0.85 eV. This value is only slightly smaller than the value 0.87 eV that we found on the pure Mg(0001) surface [10]. The energy of the final state E_{ad} is lower than the value −0.04 eV found for the pure Mg surface [10], reflecting the larger H binding energy on the stepped surface. As we can see from table 2, all the other dissociation sites give similar or larger barrier values than that on the flat Mg(0001) surface.

Figure 2 compares the minimum energy paths for the dissociation of H_2 on the stepped Mg surface for one of the two most favourable pathways with that found on the flat Mg(0001) surface. Figure 3 shows the dissociation on the stepped Mg surface as viewed from the top at the initial state (IS), transition state (TS) and final state (FS) of the NEB calculations.

These results show that the role of steps on the activation energy for the dissociation of H_2 is marginal on the Mg(0001)

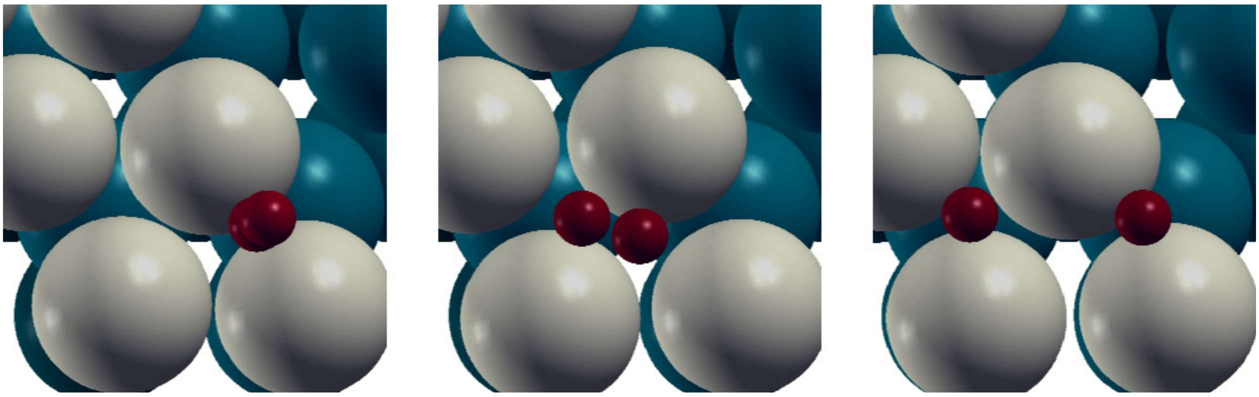

Figure 3. H_2 (black) dissociation on the stepped Mg (grey) surface as viewed from top at IS (left), TS (centre) and FS (right) of the NEB calculations.

surface. This perhaps is not unexpected: the low reactivity of the Mg surface even in the presence of steps can be understood in terms of the electronic properties. Contrary to TM surfaces, Mg has no partially occupied d shell that can be used to reduce the dissociation energy barrier by donating electrons to the anti-bonding states of the molecule and accepting back-donation from the bonding orbitals of the molecule. The Mg surface resists back-donation of charge from the H_2 molecule, and the presence of a step does not significantly modify the electronic structure. This behaviour is similar to that of noble metal surfaces, which also show a marginal effect of steps on the activity of the surface [13].

4. Conclusions

We have presented DFT calculations to investigate the role of steps on the dissociation of H_2 and the adsorption of H on a Mg(0001) surface. We find that steps increase the H adsorption energy with respect to the flat Mg(0001) surface (about 0.19 eV against 0.05, respectively), in line with the well known behaviour on other surfaces, mainly transition metal surfaces. By contrast, on a Mg surface the presence of steps does not significantly change the energy barrier for the dissociation of the hydrogen molecule, with an activation energy of about 0.85 eV, only slightly lower than the value 0.87 eV found on the flat Mg(0001) surface [10]. This behaviour is in line with that observed on noble metals, which also show a marginal role of steps on the activity of surfaces. The present results make a connection between the often idealized theoretical modelling of perfect surfaces and the real experimental situations, where steps and defects are almost unavoidable. Here we have showed that, for the reaction of interest, studies performed on idealized surfaces should also be representative of real systems.

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