Surface Science 603 (2009) 304–310

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

# Density functional and dynamics study of the dissociative adsorption of hydrogen on Mg (0001) surface

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ARTICLE INFO

*Article history:*
Received 8 July 2008
Accepted for publication 17 November 2008
Available online 30 November 2008

*Keywords:*
Density functional calculations
Molecular dynamics
Magnesium hydride
Hydrogen adsorption

ABSTRACT

A first principles study is performed to investigate the adsorption characteristics of hydrogen on magnesium surface. Substitutional and on-surface adsorption energies are calculated for Mg (0001) surface alloyed with the selected elements. To further analyze the hydrogen–magnesium interaction, first principles molecular dynamics method is used which simulates the behavior of $H_2$ at the surface. Also, charge density differences of substitutionally doped surface configurations were illustrated. Accordingly, Mo and Ni are among the elements yielding lower adsorption energies, which are found to be −9.2626 and −5.2995 eV for substitutionally alloyed surfaces, respectively. In light of the dynamic calculations, Co as an alloying element is found to have a splitting effect on $H_2$ in 50 fs, where the first hydrogen atom is taken inside the Mg substrate right after the decomposition and the other after 1300 fs. An interesting remark is that, elements which acquire higher chances of adsorption are also seen to be competent at dissociating the hydrogen molecule. Furthermore, charge density distributions support the results of molecular dynamics simulations, by verifying the distinguished effects of most of the 3*d* and 4*d* transition metals.

## 1. Introduction

The fact that fossil fuel reserves are expected to diminish in the near future and cause serious environmental pollution highlights the significance of hydrogen, as being an abundant, environmentally benign and efficient energy carrier. The reversible storage of hydrogen for both stationary and mobile applications can be in several forms, such as gaseous, liquid, carbon nanotubes, metal and complex hydrides [1]. Besides the advantage of metals being highly reactive with hydrogen, in the hydride form they are capable of storing hydrogen in large amounts on a reversible basis [2]. The generally searched criteria for an ideal metal hydride are high storage capacity, fast hydrogenation/dehydrogenation kinetics, low desorption temperatures as well as low cost. Magnesium hydride ($MgH_2$), in this respect is a promising material being economic, light weight and storing high amounts of hydrogen (7.6 wt.%), despite its high reactivity towards air and oxygen and high thermodynamical stability, which leads to poor hydriding/dehydriding kinetics [3]. In order to decrease the hydrogen desorption temperature which is above 300 °C, there are several methods such as altering the chemical composition, mechanical alloying and addition of catalysts. Zaluska et al. [4] pointed out two major reasons for poor dehydrogenation kinetics as, oxide layer formation and slow dissociation rate of hydrogen on magnesium surface. It was also mentioned that since the MgO layer impedes hydrogen penetration inside the surface, the oxide layer needs to be cracked by annealing at a temperature above 400 °C, so that the metal surface would be exposed to hydrogen. Furthermore, in their study, the conclusion has been raised that small amounts of catalysts (like Pd or Fe) would induce the improvement of hydrogenation kinetics. Besides palladium, Baer et al. [5] claimed that nickel is also an outstanding catalyst since it holds the ability to dissociate and adsorb the hydrogen molecule. Titanium and vanadium, as stated by Liang et al. [6] are as well favored catalysts for hydrogen absorption. Although their strong tendency towards oxidization makes the catalytic effect disappear. Moreover, addition of oxide catalysts, such as $Cr_2O_3$, $V_2O_5$ and $Fe_3O_4$ [7], were found useful in achieving improved hydriding properties at lower temperatures. Dornheim et al. [8], have stressed the effect of 3*d* transition metals in their study, in terms of the reduction of hydride formation enthalpies. Nevertheless, alloying with 3*d* elements was seen to give rise to a decline in the hydrogen storage capacity below 3.6 wt.%.

Sprunger and Plummer [9], on the other hand, executed a study based on the comparison of experimental and theoretical results. Regarding the interaction of $H_2$ with Mg (0001) surface, the tools used were electron energy loss spectroscopy (EELS), thermal desorption spectrometry (TDS), core level spectroscopy and work-function measurements. In their study, as a result of the

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doi:10.1016/j.susc.2008.11.017

exposure of pure Mg (0001) surface (≥110 K) to hydrogen at room temperature, not only it was unlikely to observe molecular adsorption of $H_2$, but also dissociative chemisorption did not take place under the temperature conditions in question. This result is supported with the outcome of theoretical calculations, which stress the high activation barrier for H/simple metal systems. Bird et al. [10] indicated that, as a result of the interaction between hydrogen and metal surface, the non-bonding orbital of the metal is being filled. Moreover, their study revealed that with a barrier of 0.4 eV, the adsorption site preferred by $H_2$ is the bridge site between the two metal atoms. Furthermore, Ravindran et al. [11] have studied complex hydrides, making use of charge density, charge transfer, electron localization function, partial densities of states, Mulliken population analysis and Born effective charges. Finally, they have reached the conclusion that, due to their weaker bonding characteristics, the interstitial sites are favored by hydrogen in metals, alloys and intermetallic structures. Vegge [12] in his study, where he made use of the nudged elastic band method (NEB), presented the rate-limiting step for adsorption of hydrogen on Mg (0001) surface as the dissociation, whereas that for desorption was concluded to be the rejoining of $H_2$. The potential energy surface (PES) results for hydrogen action on magnesium put forward the rate-limiting character of dissociation step by yielding large activation energies for this and diffusion of dissociated hydrogen into the first layer of Mg slab. In another study of Vegge and his co-workers [13], it was deduced that 3*d* transition metals would be beneficial in improving both the adsorption and desorption kinetics for $MgH_2$, in case magnesium is properly alloyed with 3*d* transition elements. In addition, Pozzo et al. [14] detected the improvement of $H_2$ intake kinetics through Mg surface, via doping Ni and Ti as the adsorbates, where the interaction of their unfilled *d* orbitals and *s* electron of hydrogen is seen to be predominant over Mg–H bonding.

Apart from the studies on hydrogen interaction with magnesium surface, Kiejna et al. [15], have examined the adsorption of low-coverage alkali adatoms on (0001) surface of Mg. The results show that, potassium would prefer hollow sites, where its relatively large size disables the adsorption on substitutional sites.

In this study, we aimed to investigate the manners for hydrogen dissociation and adsorption on Mg surface and suggest a systematic trend within the periodic table in terms of the catalyzer effects of selected elements. Correspondingly, substitutional and on-surface adsorption energies regarding Mg (0001) surfaces doped with one adatom were computed via the ab-initio total energy pseudopotential methods. In addition, first principles molecular dynamics calculations were performed for structures also including the hydrogen molecule. Finally, charge density difference distributions were illustrated for substitutionally alloyed Mg surface systems.

## 2. Computational method

All computations in this study have been performed using plane-wave pseudopotential where fully self-consistent density functional theory (DFT) calculations were used to solve Kohn-Sham equations. Ab-initio total energy and molecular dynamics calculations were executed using the VASP (Vienna ab-initio simulation package) code developed at the Institut fur Materialphysik of the Universitat Wien [16–18]. The generalized gradient approximation (GGA) implementation by Perdew et al. [19] was exploited where the core electrons were replaced by Vanderbilt ultrasoft pseudopotentials (US-PP) [20].

For surface calculations of magnesium, a slab consisting of 3 × 3 × 1 unit cells (six atomic layers) of Mg was created. The positions of atoms in surface structure of magnesium were set according to the relaxed coordinates in bulk Mg. One atomic layer at the bottom was fixed during the calculations. A vacuum range of up to 20 Å has been used in modeling the surface and approximately after 11 Å, no appreciable difference was seen in the top layer atomic coordinates after relaxation. During the relaxation calculations of alloyed surface systems, we have initially used the relaxed coordinates of pure Mg surface. Furthermore, we have calculated the percent change in coordinates of atoms located just above the fixed bottom layer, for pure Mg and Co doped surfaces due to relaxation. They are 4.5% and 0.14%, respectively, from which slab thickness chosen was decided to be adequate.

We first aimed to investigate the substitutional adsorption behavior of selected alloying elements on (0001) surface of Mg. There are 53 Mg atoms and one M atom (substituted in place of a magnesium atom at the center of the uppermost layer, creating a concentration of 0.93 at.%) in the slab. Within the alloying elements studied, there are 3*d* transition metals (the entire row), 4*d* transition metals from Zr to Mo and Pd to In, some heavy metals such as Au and Pb, some alkaline elements and also some nonmetals like P and Ge. For the purpose of obtaining the lowest energy configuration, systems were allowed to relax in terms of all atomic degrees of freedom, while the cell size and shape were kept constant. *k*-point implementation was performed on the gamma point only. The differences in the substitutional adsorption energy for some of the elements studied between gamma point only and 2 × 2 × 1 *k*-point mesh calculation were found to be less than 19 meV per cell. Additional spin polarized calculations performed for Fe, Ni and Co doped systems were not seen to create a significant effect energetically, with respect to the non-spin polarized calculations.

Adsorption energy for substitutionally doped Mg (0001) surface structures (represented by $E_{\text{sub-ads,Mg(0001)}}$) is calculated via the following equation [21]:

$$E_{\text{sub-ads,Mg(0001)}} = E_{\text{M/Mg(0001)}} - E_{\text{Mg(0001)}} - E_{\text{M-atom}} + E_{\text{Mg-step}} \tag{1}$$

where $E_{\text{M/Mg(0001)}}$ and $E_{\text{Mg(0001)}}$ represent the total energies of substitutionally alloyed and pure magnesium surface structures, respectively. $E_{\text{M-atom}}$ represents the energy of the adatom, which was put as a single atom in a box of 10 × 10 × 10 Å, calculated with single *k*-point. Besides, $E_{\text{Mg-step}}$ stands for the energy of Mg atom (to be substituted by M atom) which is considered to be removed from the top plane and brought to a step or kink site at the surface. For the calculation of this term, one magnesium atom was located on the surface at a regular lattice point as if the surface extends towards vacuum. Next, the difference between total energies calculated for this configuration and normal Mg surface without this extension was taken, which yields the term $E_{\text{Mg-step}}$.

For all relaxation calculations, $10^{-3}$ eV energy difference was set as the convergence criterion between successive ionic steps. We have also determined the dipole corrections to the total energy. It was found to be less than 1 meV per cell, which was then neglected in all calculations.

We then studied on-surface (normal) adsorption. Adatoms were placed slightly above the surface (1.6–1.8 Å) which were then relaxed, in three different positions, which are hollow, top and bridge, as illustrated in Fig. 1, produced by VESTA [22]. Calculation of on-surface adsorption energies for normally doped Mg (0001) surface (expressed as $E_{\text{nor-ads,Mg(0001)}}$) is via the equation shown as follows [21]:

$$E_{\text{nor-ads,Mg(0001)}} = E_{\text{M/Mg(0001)}} - E_{\text{Mg(0001)}} - E_{\text{M-atom}} \tag{2}$$

where $E_{\text{M/Mg(0001)}}$ and $E_{\text{Mg(0001)}}$ represent the total energies of normally doped and pure Mg surfaces, respectively. Here again, $E_{\text{M-atom}}$ is the energy of the adsorbed species. In addition, the vibrational frequencies for the alloying elements adsorbed on-surface were also calculated to elucidate the nature of each site.