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A DFT study of dopant (Zr, Nb) and vacancies on the dehydrogenation on MgH_2 (001) surface

Estefanía Germán [a], *Carla Luna* [a], *Jorge Marchetti* [b], *Paula Jasen* [a], *Carlos Macchi* [c], *Alfredo Juan* [a,*]

[a] *Instituto de Física del Sur (IFISUR, UNS-CONICET) and Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, B8000CPB Bahía Blanca, Argentina*
[b] *Department of Mathematical Science and Technology, Norwegian University of Life Sciences, Drøbakveien 31, Ås 1432, Norway*
[c] *IFIMAT, UE CIFICEN (CONICET-UNCPBA), Pinto 399, B7000GHG Tandil, Argentina*

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ABSTRACT

Ab initio calculations were used to study dehydrogenation energy in a set of systems, pure, Nb- or Zr-doped, free of defects and containing vacancy-like defects MgH_2 (001) surface. The preferential location site for dopants was determined by means of occupation energy analysis. Zr atom prefers substitutional and interstitial sites while Nb locates on interstitial site close to the surface. The effect of vacancies in the geometric structure and in dehydrogenation energy was considered. It was found that MgH_2 containing a Mg vacancy doped with Zr, in an interstitial site and the same system containing Mg–H complex vacancy, modify the surface geometry and weakens the Mg–H bonds making easier the dehydrogenation process. When the surface is doped with Nb despite any vacancy generation, the dehydrogenation is less probable energetically in comparison with Zr-doped.

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1. Introduction

Considering the growing world population, the increasing standard of living in developing countries, the limited supply of fossil fuels and its adverse effect on the environment, the need for sustainable and clean energy has never been bigger.

Hydrogen is a promising fuel source that is attractive as an alternative to fossil fuels, it is considered as a possible solution for the automobile industry. This element is an abundant elementary resource with huge energy capacity [1]. Pure hydrogen does not exist in nature, so it must come from other resources. The fossil fuel combustion products; such as carbon dioxide, nitric and nitrous oxides, sulfur dioxide and hydrocarbons is today at considerably high levels. Hydrogen is an environmentally benign, safe and attractive vector; being the most abundant element in the universe, with a high energy density per unit weight (chemical energy of hydrogen; 142 MJ/kg is at least three times larger than that of other chemical fuels [1]) and water as the major by-product of its combustion.

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* *Corresponding author*. Tel./fax: +54 2914888218.
E-mail address: cajuan@uns.edu.ar (A. Juan).

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Recently, solid-state hydrogen storage has received more attention. This methodology is based upon the chemical or physical combination of hydrogen with the materials in question; which are metal/complex hydrides and carbon based structures. Metal hydrides are seen to be a promising, efficient and safe storage media for on-board vehicle applications. A major disadvantage is that store only about 2%–7% hydrogen by weight. Nevertheless, their volumetric storage density is higher than most of other forms of storage [2].

Magnesium hydride (MgH_2) is the parent compound of an important group of hydrogen storage materials and exhibits high gravimetric and volumetric storage density (7.7% and 55 kg/m^3, respectively). Although the practical potential of pure MgH_2 is limited by its high thermodynamic stability and slow kinetics, mechanical treatment and chemical alloying have been shown to improve the kinetics and to reduce the desorption temperatures [3]. However, due to the strong interaction between magnesium (Mg) and hydrogen (H), high desorption temperatures ($\sim$300 °C at 1 atm) are required. This fact gives rise to an unacceptable cost of energy. Undesirable poor hydrogen desorption kinetics of some metal hydrides have tried to be improved by several methods. The hydrogenation/dehydrogenation thermodynamics can be improved altering the chemical composition and mechanical alloying.

There are several studies theoretical and experimental related to the reduction of Mg hydride stability, experimentally [4–14].

Song et al. [15] have found a decreasing effects of Cu, Ni, Al, Nb and Fe to Ti, in terms of descending effectiveness order, on stability of Mg hydride, via total energy methods. The analysis of density of states (DOS) and charge distribution results proved that the bonds between Mg and H were weakened due to the effects of alloying elements.

Vegge and his co-workers [16] performed calculations on $MgTMH_3$ (TM = transition metals) hydrides with perovskite structure. The stability of alloyed hydrides tend to decrease from MgSc to MgFe, where Cu and Zn as impurity elements were not seen to produce the same effect.

In addition to studies on bulk MgH_2, many more have been carried out on surface structures. Mg–H bonds are weaker on surfaces, reducing the high stability of magnesium hydride [17–20].

Wang and Johnson [21] elucidated the catalytic effect of Ti substitutional dopant on H_2 desorption from MgH_2 (110) surfaces using density functional theory (DFT) calculations. In the case of a Ti-doped surface, they identified a concerted mechanism involving H bulk (vacancy-mediated) diffusion to feed H_2 surface desorption, arising from a synchronized diffusion of H atoms around Ti. The kinetic barrier for the Ti-doped surface is reduced and the catalyzed H_2 desorption is mediated by a change in hydrogen coordination number of Ti, altering the associated Ti spin state.

Dai et al. [22] studied the influence of dopants on the dehydrogenation properties of an Al, Ti, Mn, and Ni doped MgH_2 (110) surface by first principles calculations. It was shown that Al prefers to substitute for an Mg atom, whereas Ti, Mn, and Ni prefer to occupy interstitial sites. The dopants followed different mechanisms to improve the dehydrogenation properties of MgH_2. They also carried out a first principle study to investigate the dehydrogenation properties of metal-doped MgH_2 (001) surface [23]. Al and Ti prefer to substitute for Mg atoms, whereas Mn and Ni prefer to occupy interstitial sites.

Periodic DFT and nudged elastic Band (NEB) method have been used by Guangxin Wu et al. to investigate the hydrogen desorption on MgH_2(001) and MgH_2(110) surfaces as a first step towards understanding the dehydrogenation cycle [24]. A study of reaction barriers for different pathways on MgH_2 (001) and MgH_2 (110) surfaces have also been performed.

Previous works reported that generation of vacancies in doped bulk MgH_2 structure diminishes its stability while Mg–H bonds strength decreases [25,13].

In this work we studied the preferential site of two dopants (Nb and Zr) on the MgH_2 (001) surface. We also considered vacancy-like defects (Mg, H or Mg–H complexes) in order to analyze the influence of dopants and vacancies on the dehydrogenation properties and electronic structure. We also studied the evolution of chemical bond during dehydrogenation through overlap population analysis.

2. Computational method and models

Energetic and electronic calculations have been performed within the frame of the density functional theory (DFT) [26] which was implemented in the Vienna Ab initio Simulation Package (VASP) code [27,28]. The projector augmented wave (PAW) pseudopotential [27,28] was used to account the electron–ion core interaction, using the PW91 functional as the generalized gradient approximation (GGA) [29] for the exchange–correlation term.

The studied MgH_2 surfaces were simulated using a (2 × 2) slab containing 5 layers of Mg atoms with a 20 Å vacuum in the [001] direction. We checked the dependence of dopant occupation energy with the size of slabs (1 × 1), (2 × 2) and (3 × 3). This energy value differs 0.12 eV when the calculation is carried out with (1 × 1) and (2 × 2) slabs. The energy value difference is even smaller between (2 × 2) and (3 × 3) slabs. In order to reach a balance between accuracy and time of calculation a (2 × 2) slab model was used. We also checked the influence of strain effect, carrying out a full relaxation of the pure and doped systems and compared the total energy between partial and full relaxation. This difference is lower than 2% in the formation energy calculation implying that the influence of strain effects is weak on the atomic positions in the upper-layers. In the calculation, the Brillouin-zone was sampled using a 6 × 6 × 1 Monkhorst–Pack k-point mesh [30]. For the plane-wave basis set a cut-off of 650 eV was used. We relaxed the first three layers of the slab while the bottom two layers were kept fixed to the bulk positions. The total energy convergence and the forces on the atoms were less than 10^{-4} eV and 0.01 eV/Å, respectively. The self-consistent calculations were considered to converge when the difference in the total energy of the crystal between consecutive steps did not exceed 10^{-5} eV. In the same way, the static calculations were considered to converge using the same criterion. To analyze the electronic structure and bonding we have used the concept of density of states (DOS) and the

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