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# The hydrogen ab/desorption kinetic properties of doped magnesium hydride $MgH_2$ systems by first principles calculations and kinetic Monte Carlo simulations

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## ABSTRACT

Hydrogen storage ab/desorption kinetic properties of  $MgH_2$  and  $MgH_2$  doped with different metal  $M$  ( $M = Al, Ti, V, Fe$  and  $Ni$ ) are investigated by using both DFT method and kinetic Monte-Carlo simulations. The first principles calculations show that the energy barriers decrease considerably when doping with a small amount of  $M$  element leading to a decreasing of both the stability and the decomposition temperature of the material. Based on the activation energies computed from DFT calculations, we show within the kinetic Monte-Carlo method that the ab/desorption time is reduced considerably without reducing much the hydrogen storage capacity of the material. From our analysis, we observed that the  $Ni$  element exhibits the most appropriate thermodynamical properties for hydrogen storage and the best kinetic of hydrogen absorption/desorption.

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## Introduction

Nowadays, hydrogen is considered as one of the most promising energy carriers alternatively to the fossil fuels including coal, oil and natural gas. The energetic sources will be depleting and also they are involved in the global warming.

However, the development of hydrogen faces a significant problem concerning its storage. Indeed, hydrogen storage method should involve high volumetric, gravimetric capacity, a fast sorption rate at relatively low temperatures, and a recycling high tolerance. Alternative methods have been proposed including high pressure gas cylinders, liquid hydrogen, physisorption of hydrogen on materials with a high

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specific surface area, and hydrogen storage through hydrides (e.g. Boron and Magnesium hydrides). The latter is very promising due to its high hydrogen storage capacities [1–5].

More recently, it has been shown that magnesium hydride is one of the most attractive materials for hydrogen storage applications due to its high gravimetric and volumetric capacities (7.65 wt.% and 110 gH<sub>2</sub>/l, respectively) [5]. However, this material shows slow hydrogen absorption and desorption kinetics as well as high dissociation temperature 573–673 K. These characteristics reduce its application concerning the hydrogen storage [4,6].

In a previous work, we have studied the hydrogen storage ab/desorption kinetic properties for the pure MgH<sub>2</sub> using Kinetic Monte Carlo simulation, then we have characterized it through density distribution of Hydrogen, filling ratios, diffusion time, temperature and pressure. The behavior of ab/desorption agree with the experimental results. The simulated computations show that the material has slow kinetics at high temperature and pressure [7]. Various attempts have been made in order to improve magnesium hydrogen absorbing-desorbing characteristics. Experimentally, it has been shown that the ball-milling with a small amount of transition metals (TM) or their oxides drastically accelerate the hydrogen kinetics. Moreover, they reduce the decomposition temperature of the hydride [4,5,8,9]. In recent experiment, it was shown that adding MnFe<sub>2</sub>O<sub>4</sub> nanoparticles improve considerably the thermodynamic dehydrogenation properties of ball-milled MgH<sub>2</sub> doped with 7 mol% MnFe<sub>2</sub>O<sub>4</sub> [10].

Various theoretical calculations have been performed to understand the relevant mechanism dealing with the alloying effects on the thermodynamic properties on magnesium hydride [11–13]. Based on density functional theory (DFT), we have shown, in a previous work, that alloying MgH<sub>2</sub> with small amounts of transition metals mixture TM (TM = Ti, V and Fe) or alkaline metal AM (AM = Ca, Sr and Ba) improve the stability and the desorption temperature of hydrogen in Mg [14,15].

The aim of this work is to study, using Kinetic Monte Carlo simulation (KMC) based on first principles calculations, the hydrogen storage ab/desorption kinetic properties of MgH<sub>2</sub> doped with different metal M (M = Al, Ti, V, Fe and Ni). To perform such computations, the activation energies that are needed for different elementary processes are estimated by performing ab-initio calculation. The hydrogen diffusion in magnesium hydride (such as dissociation of H<sub>2</sub>, adsorption and diffusion of hydrogen) is then studied using KMC simulation. The paper is organized as follows: in sec. 2, we briefly review our calculation method while sec. 3 is devoted to the presentation and discussion of our numerical results which are compared with those obtained experimentally. The conclusion is given in the last section.

## Model and computational methods

### Kinetic Monte Carlo simulation

The application of the kinetic Monte Carlo (KMC) method [16] to our system is shortly described in this subsection since the detailed model based on has been reported previously in Ref.

[7]. The filling of the H atoms is based on adsorption/desorption dissociation and diffusion processes. The adsorption of H<sub>2</sub>, which is located at the surface (001) of a super-cell containing initially only magnesium and M atoms (M = Al, Ti, V, Fe and Ni), is followed by its decomposition into two H atoms that diffuse from an interstitial site to another one depending on the corresponding activated energies. Such activated energies are obtained from DFT calculation and implemented in the KMC method. Periodic boundary conditions have been considered along X and Y-directions to simulate an infinite system.

Defining the relation between simulated time and Monte Carlo steps (eq (1)), we can predict the hydrogen diffusion time in Mg<sub>0.9375</sub>M<sub>0.0625</sub>H<sub>2</sub> (M = Al, Ti, V, Fe and Ni) systems as function of temperature and pressure such that:

$$\Delta t = -\frac{\ln(u)}{\sum_{i=1}^N \nu_0 \exp\left(-\frac{E_i^a}{k_B T}\right)} \quad (1)$$

where  $\nu_0$  is the jump frequency (usually set to 10<sup>13</sup> Hz),  $E_i^a$  the activation energy of  $i^{\text{th}}$  diffusion process (dissociation of H<sub>2</sub>, adsorption and diffusion) taken from first-principles calculations (see sec. 2.2),  $N$  is the total possible events in the system,  $k_B$  the Boltzmann constant and  $u$  ( $0 < u \leq 1$ ) is a uniformly distributed random variable.

### Density functional theory calculations

For each material more than 300 configurations are needed to determine the different energy barriers required for hydrogen diffusion. In order to compute such barriers, we have used ab-initio calculations based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9.00-34 [17,18] to solve the Kohn–Sham equations using the scalar-relativistic. The parameterization of the exchange-correlation energy has been done within the generalized gradient approximation GGA of the Perdew, Burke, Ernzerhof [19]. To ensure a high accuracy in our calculation, we used self-consistent criteria for both the energy and the density with precision of 10<sup>-8</sup> Ha and 10<sup>-6</sup> Ha<sup>-1</sup> Å<sup>-3</sup>, respectively. A mesh of (6 × 6 × 6) k-points in the Brillouin zone was used in our calculation. The total energy is calculated using the scalar-relativistic scheme, for all configurations.

The hydride MgH<sub>2</sub> is crystallized in the rutile-type structure (P4<sub>2</sub>/mnm, space group N<sup>o</sup>136) at ambient conditions [20]. All our calculations are carried out using a super-cell containing 15 Mg atoms, 1 M atom (M = Al, Ti, V, Fe and Ni) and 32 H atoms, denoted henceforth as Mg15MH32 as shown in Fig. 1. This choice corresponds to an M doped concentration of 6.25%.

The lattice parameters used in all calculation are the relaxed parameters (see Table 1) and the activation energies have been obtained from the maximal energy appearing in the possible paths between the initial H position and the final empty one.

## Results and discussion

To apply Monte Carlo calculations in modeling H diffusion, we should implement some parameters including

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