THEORETICAL PERSPECTIVE ON IMPROVING KINETICS IN Mg HYDROGEN STORAGE

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Introduction

Magnesium, forming ionic, transparent MgH_2 containing 7.6 mass% hydrogen, is among those that are most-promising in hydrogen-storage materials for mobile applications [1]. However, the formation from bulk Mg and gaseous hydrogen is not only extremely slow, but requires elevated temperatures (300 °C at 1 bar pressure) as well, with the reverse process requiring similar conditions [2]. Numerous factors can contribute to the kinetics of the forward and reverse reactions in the hydrogen storage processes [3]. Among them, molecular hydrogen dissociation and hydrogen diffusion are two factors of primary concern. It's already known that hydrogen diffuses only extremely slowly in crystalline Mg, with a diffusion constant in the order of 10^{-16} cm^2/s [4]. This translates to that the mean time ($d^2/6D$, where D is the diffusion constant) for hydrogen to diffuse through a 1 μm Mg particle will be in the order of 10^3 S. One may hope that reducing the particle sizes to nanometers will speed up the kinetics, only to see no significant improvement [5]. It therefore appears that molecular hydrogen dissociation on Mg surfaces is a rate-limiting process.

It had been demonstrated recently [6] that Density Functional Theories (DFT) approach can be used to successfully explore tailoring the energetics of Mg hydrogen sorption/desorption processes, fundamentals that are responsible for properties such as diffusion rate and nucleation. The same principles should apply in exploring aspects in the hydrogen dissociation process, as shown in the literature [7, 8]. In the present work, DFT method was used to look at hydrogen dissociation on both unmodified- and transition metal modified-Mg 100 surface. Energy barrier, surface sorption energy, and surface diffusion barrier are the main focuses of the work.

Method

$Dmol^3$ [9], a Density Functional Theory (DFT) method available in the software package, Materials Studio, was used in the calculations. The setup parameters were similar to those used previously in the thermochemical studies of similar materials [6].

Experimental structure of Mg [10] was used as starting model to obtain the DFT relaxed structure that was identical to what was found in previous study [6]. The 100 surface (Fig. 1A) was constructed based on the DFT optimized bulk structure. Surface suppercell of 4 x 2 was built such that the calculated hydrogen dissociation barrier (see later sections) becomes invariant as a function of cell size, with respect to a set of k-point density. To model the surface environment, a vacuum space of 20 Å was added on top of the surface such that 3D periodic conditions can be used in the summation of the energy terms in the DFT calculations. A total of 4 Mg layers (corresponding to 4-unit cell depth perpendicular to the 100 surface) were used in the calculations. Mg atoms in the surface layer and the layer immediately beneath were allowed to relax prior to introducing hydrogen into the systems. In most cases, one of the surface Mg atoms would be replaced by a transition mental atom (e.g., Fe as in Fig. 1D), and the surface structure reoptimized.

For unmodified Mg 100 surface, two hydrogen dissociation geometries were considered (Fig. 1B&C), corresponding to the hydrogen molecule approaching the surface towards the center of gravity ("atop") of a single Mg atom and towards the "bridge" between two Mg atoms, respectively, and dissociate into the nearby hollows surrounded by 3 Mg atoms. For transition metal-doped surfaces, only the atop configuration was considered, as the bridge configurations were not stable in these circumstances and evolved into atop configuration eventually. A single hydrogen molecule was placed in the middle of the vacuum space (~ 10 Å above the surface) for the initial configuration of the dissociation process.

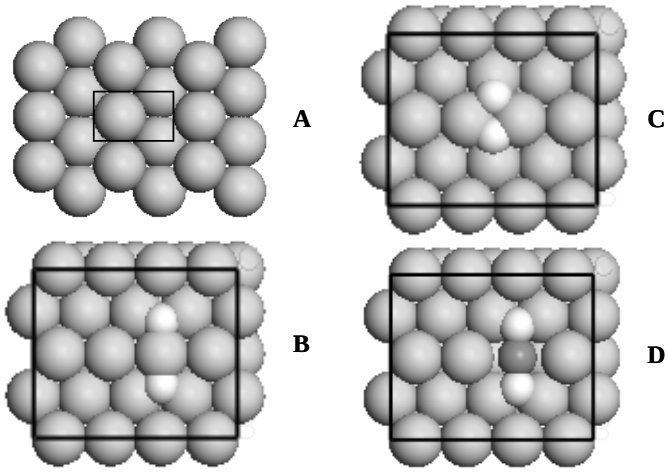

Figure 1. Mg 100 surface used in the calculations. A. the surface layer (1-unit cell depth). The rectangle outlines the original surface unit cell; B. actual simulation cell (4 x 2 x 4) with the adsorbed hydrogens through the "atop" configuration; C. same as B, but with the adsorbed hydrogens through the "bridge" configuration; D. same as B, but with a transition metal (here Fe) atom replacing Mg. Large grey ball: Mg; small, light grey ball: H; small, dark grey ball: Fe.

Transition state search engine available in the Dmol3 package was used for all transition state calculations. Full LST/QST [11] search were performed on each and every sample system, and usually followed by a transition state optimization calculation.

When transition state search failed to produce a transition state (usually associated with transition metal-doped surfaces), the approach of potential energy surface (PES) was used to confirm the nature of unactivated dissociations of hydrogen on such surfaces.

Results and Discussions

The calculated energy barriers, along with the energetic and structural parameters of the corresponding transition states (if exist) are given in Table 1. Note here the enthalpy of reaction (ΔH_f) refers to the difference directly between the total energy of the state when the hydrogen molecule is in the middle of the vacuum space (~ 10 Å above the surface) and that when hydrogen is dissociated into the hollows (state obtained through geometry optimization).

Dissociations on unmodified Mg 100 surface. Hydrogen Dissociations are activated in either atop or bridge configuration (Table 1), with dissociation barriers of ~ 92 kJ/mol. This is in qualitative agreement with earlier theoretical and experimental studies [8, 12] on a different surface (Mg 0001). It's important to note that the enthalpies of reaction are very small (slightly exothermic in atop configuration and slightly endothermic in the bridge configuration) compared to the energy barrier (Fig. 2). In other words, the activation

barrier is the factor that controls the rate of both forward (sorption) and reverse (desorption) processes, and the barrier height dictates the temperature and pressure conditions of both the sorption and desorption processes.

Table 1. Thermodynamic and structural data of H_2 dissociation/absorption on Mg 100 surface

Surface dopent	Ea (kJ/mol)	ΔH_f (kJ/mol)	Ed (kJ/mol)	d_{H-H} (Å)
Unmodified				
atop	91.92	-1.92	minimal	1.28
bridge	92.42	14.52	minimal	1.12
V	51.80	-111.13		1.14
Pd	60.79	-3.56	20.46	1.39
Cu	64.64	-15.86	22.47	1.29
Ni	17.28	-63.85	45.23	1.20
Fe		-100.75	52.05	
Co		-90.04	59.08	
Ti		-105.56	56.44	

Ea: activation energy
ΔH_f: enthalpy of reaction (surface sorption)
Ed: surface diffusion barrier, corresponding to hydrogen diffusion from a hollow with the transition metal being one of the 3 coordinating atoms to a nearby hollow
d_{H-H}: H – H distance at transition state

Dissociation on transition metal-doped surfaces. Most experimental and theoretical studies on the interaction of hydrogen with metal surfaces today involve elemental d-transition metal surfaces; some concern transition alloy surfaces [3]. However, due to the intrinsically low weight percentage of absorbed hydrogen in pure transition metals, and the problem of alloy degradation after repeated cycling of hydrogen sorption and desorption, it becomes increasingly urgent for new thinking in materials design, probably based on the known potential hydrogen storage materials.

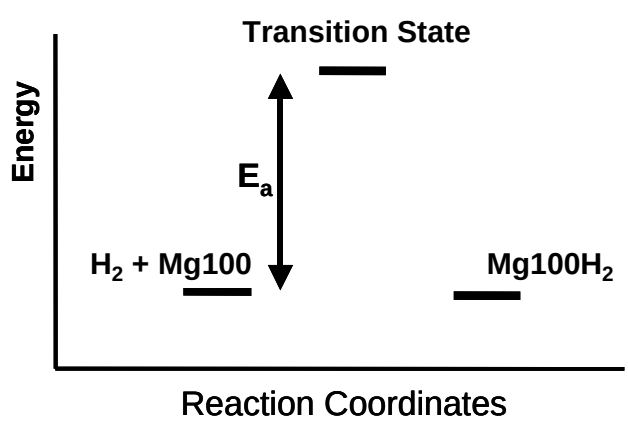

Figure 2. Activated dissociation (with energy barrier, Ea) of hydrogen on Mg 100 surface through the "atop" configuration. Note there is only a minimal difference in system energy (1.92 kJ/mol) between the starting materials (H_2 + Mg 100) and the final product (Mg 100 H_2).

Surface doping on Mg nanoparticles may offer a solution to the dilemma – transition metals doped on the particle surface may accelerate the dissociation of the hydrogen molecules, and particle size in nano-scales will make a very slow diffusion of hydrogen in, e.g., Mg particles to complete in an acceptable time scale.

It can be seen from Table 1 that activation barriers can indeed be lowered substantially, some even become unactivated (when doped with Fe, Co, or Ti). It is interesting to recognize that hydrogen dissociation over a transition metal (when doped on to the Mg 100 surface) may behave differently as appose to that on the corresponding bulk transition metal surface. For example, dissociation over Pd metal surface had been shown both experimentally and theoretically to be unactivated [13, 14, 15]. However, when doped on to the Mg 100 surface, the dissociation on the Pd atom will be activated, with a barrier of ~ 61 kJ/mol (Table 1).

Among the 7 (Table 1) commonly considered transition metals in hydrogen storage applications, 3 (Fe, Co, Ti) show unactivated dissociation when hydrogen molecule approaches the transition metal doped on to the Mg 100 surface. However, notice the associated exothermic enthalpies of reaction between 90 and 106 kJ/mol, which are in the same order of magnitude as that of the energy barrier of hydrogen dissociation over unmodified Mg 100 surface (Fig. 3). That means, while unactivated in the forward (sorption) process, it'll take similar pressure and temperature conditions for the reverse (desorption) process as for pure Mg. It is also important to notice the relatively high diffusion barrier (note there is essentially no surface diffusion barrier on unmodified Mg 100 surface), signifying potentially added difficulty diffusing into the Mg lattice beneath.

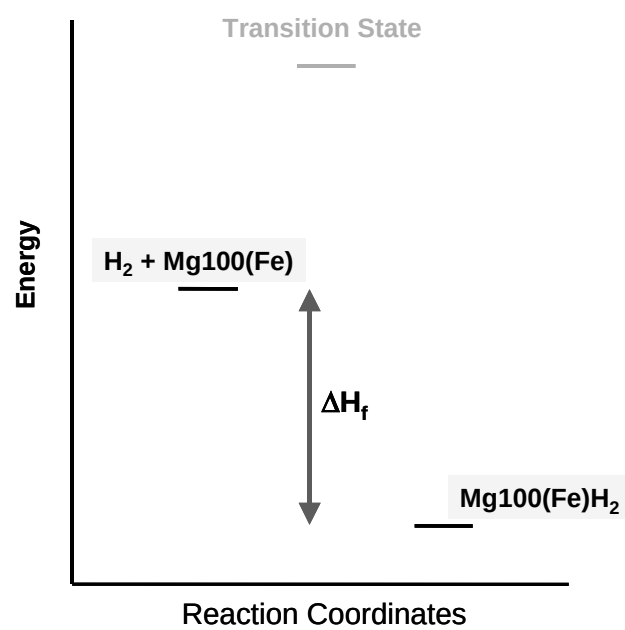

Figure 3. Unactivated dissociation of hydrogen on Fe-doped Mg 100 surface through the "atop" configuration (centered on the Fe atom. Refer to Fig. 1D). The energy barrier (the water-marked "Transition State") of the activated dissociation on unmodified Mg 100 surface was shown as a reference. ΔH_f: enthalpy of formation of the reaction.

Among the 4 doping transition metals (V, Pd, Cu, Ni) that are associated with activated dissociation, although giving a low activation barrier of ~ 17 kJ/mol, Ni is associated with a rather high enthalpy of reaction of ~ 64 kJ/mol. The combined energy needed for the reverse (desorption) process is 81 (17 + 64) kJ/mol, which approaches the barrier associated with unmodified Mg 100 surface. That probably explains why, while the hydrogen sorption process of the Mg2Ni alloy is relatively rapid, the desorption process was found to remain sluggish [1]; Vanadium presented a rather undesirable combination of relatively high activation barrier and the enthalpy of reaction, and was not considered further; Pd and Cu offer a reduction of ~ 30 kJ/mol in activation energy, and relatively low enthalpies of reaction, together with low surface diffusion barriers. In particular, Pd is associated with a minimal enthalpy of reaction (~ 3 kJ/mol), making reduced pressure and temperature conditions possible for both sorption and desorption processes.

Conclusions

Hydrogen dissociations on unmodified Mg 100 surface were found to be activated, with barriers around 92 kJ/mol. When doped with transition metals, the dissociation barrier can be lowered, in some cases to the extent of being unactivated. Pd doping was found to be the most promising, based on the considerations of the activation barrier, energy requirement for reverse (desorption) process, and surface diffusion barrier.

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