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The role of V_2O_5 on the dehydrogenation and hydrogenation in magnesium hydride: An *ab initio* study

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Ab initio density functional theory calculations are performed to study the experimentally observed catalytic role of V_2O_5 in the recycling of hydrogen in magnesium hydride. We find that the Mg–H bond length becomes elongated when MgH_2 clusters are positioned on single, two, and three coordinated oxygen sites (O_1, O_2, and O_3) on the $V_2O_5(001)$ surface. Molecular hydrogen is predicted to spontaneously form at the hole site on the $V_2O_5(001)$ surface. Additionally, the activation barrier for the dissociation of hydrogen on V-doped Mg(0001) surface is 0.20 eV, which is only $\frac{1}{5}$ of that on pure Mg(0001) surface. Our results indicate that oxygen sites on the $V_2O_5(001)$ surface and the V dopant in Mg may be important facilitators for dehydrogenation and rehydrogenation, respectively. The understanding gained here will aid in the rational design and development of Mg-based hydrogen storage materials. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2916828]

The development of efficient, safe, and lightweight storage materials for hydrogen is a key technological objective within the drive toward the hydrogen economy. Magnesium and its alloys have been considered among the most promising candidates for automotive applications due to its high capacity in the stoichiometric limit (7.6 wt %) and low cost.[1–3] Unfortunately, the application is primarily limited by the hydrogenation reaction temperature and slow kinetics. One of the possible reasons is that the hydrogen molecules do not readily dissociate on Mg surface.[4–6] Experimentally, many studies have been devoted to the catalytic effect on hydrogen adsorption of mixing transition metals or their oxides in small quantities into Mg hydride powder during ball milling.[7–10] The transition metals, such as Ti, Nb, V, etc. are believed to act as catalysts for enhancing the surface dissociation of molecular hydrogen into adsorbed atoms,[11–15] albeit at the cost of a partial reduction in the weight-percent capacity. Ball milling MgH_2 with 1 mol % of a transitional metal oxide such as V_2O_5, Mn_2O_3, Fe_3O_4, or Nb_2O_5, etc. leads to a similar improvement of magnesium-H sorption properties.[10,16] Moreover, some oxides such as Fe_3O_4, V_2O_5, and Nb_2O_5 also show the enhanced *desorption* kinetics.[17] Clearly, the use of a cheap metal oxide compared to the pure metal for catalytic purposes is an advantage from the cost perspective. However, the underlying mechanism for how this works is completely unresolved.

To explore the role of V_2O_5 on fast dehydriding (hydriding) kinetics of Mg, herein, we perform state-of-the-art *ab initio* density functional theory (DFT) calculations to investigate the dehydrogenation of a MgH_2 cluster supported on the $V_2O_5(001)$ surface and the rehydrogenation of Mg in the presence of a V dopant on Mg surface. We predict that the oxygen and hole sites on the $V_2O_5(001)$ surface are catalytically active for the destabilization of a MgH_2 cluster. Additionally, a V dopant on the Mg surface is predicted to

greatly modify the minimum energy pathway (MEP) for the dissociation of H_2 on a Mg(0001) surface compared to that on the clean magnesium surface.[6,12–14] In the next section, we outline our computational method. Section III presents the calculated results for optimized geometries of MgH_2 cluster supported on the $V_2O_5(001)$ surface and the dissociation of H_2 on a V-doped Mg(0001) surface. The last section is devoted to the conclusions.

All calculations have been performed by using the plane-wave basis Vienna ab initio simulation package (VASP) code[18,19] implementing the generalized gradient approximation of Perdew–Burke–Ernzerhof exchange correlation functional[20] and the projector augmented wave method.[21,22] The $V_2O_5(001)$ surface is modelled as a one-layer (1×3) surface slab with all the atoms allowed to relax. This one-layer model is justified because bulk V_2O_5 has a layered structure, with interlayer bonding based on van der Waals interactions. A $2 \times 2 \times 1$ Monkhorst–Pack grid of k points was used for the Brillouin-zone sampling and the cutoff energy for plane waves was 312.5 eV. The vacuum space was up to 16 Å, which is large enough to guarantee a sufficient separation between periodic images. Additionally, the lattice constant of bulk Mg was calculated to be 3.191 Å, which was only 0.5% in error compared with the experimental value. The V incorporated Mg(0001) surface was modelled by using a (4×4) surface unit cell with five layers of Mg atoms. Only gamma point was used in this calculation. To determine dissociation barriers of H_2 on the V-doped Mg(0001) surface, the nudged elastic band (NEB) method was used.[23,24] This method involves optimizing a chain of images that connect the reactant and product states. Each image is only allowed to move into the direction perpendicular to the hypertangent. Hence, the energy is minimized in all directions except for the direction of the reaction path. A damped molecular dynamics was used to relax ions until the force in each image are less than 0.02 eV/Å.

The single-layer V_2O_5 sheet was first fully optimized by conjugate gradient methods. Figures 1(a) and 1(b) present a

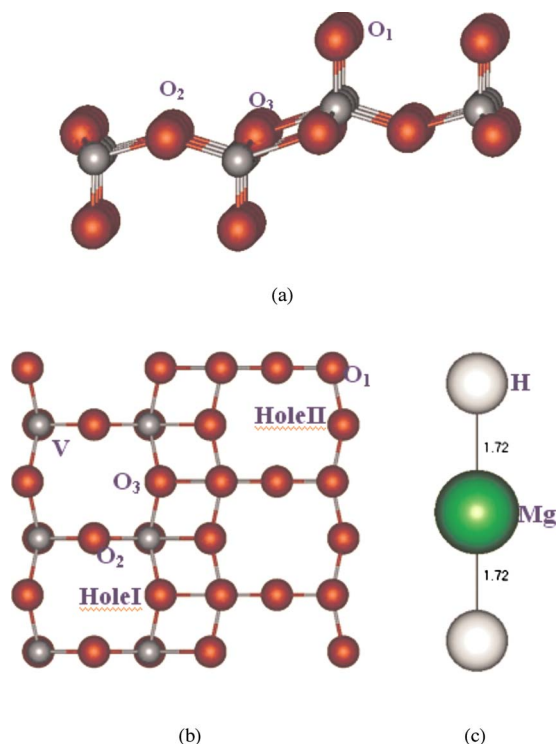a)Author to whom correspondence should be addressed. Electronic mail: s.smith@uq.edu.au.

(a)

(b)   (c)

FIG. 1. (Color online) (a) A side view of (1×3) $V_2O_5(001)$ surface. (b) The same as (a) but from a top view. (c) The optimized MgH_2 cluster. O_1, O_2, and O_3 represent single, two, and three coordinated oxygen sites, respectively. The red, grey, green, and white balls represent O, V, Mg, and H atoms, respectively.

FIG. 2. (Color online) Fully relaxed configurations for MgH_2 clusters on (a) O_1, (b) O_2, (c) O_3, and (d) Hole I sites as shown in Fig. 1. The Mg–H bond lengths were also presented.

side and top view of the fully relaxed $V_2O_5(001)$ surface. The $V_2O_5(001)$ surface is characterized by single, two-, and three-coordinated oxygen sites (O_1, O_2, and O_3) and two types of fourfold hollow sites (Hole I and Hole II). As reported in Refs. 25 and 26, the physical properties of MgH_2 could be determined in a localized region and, thus, we use a MgH_2 cluster model as in Refs. 25 and 26 to explore the possible role of the oxide-hydride interactions in facilitating the dehydrogenation of MgH_2. In our calculation, MgH_2 clusters were positioned onto six specific sites (O_1, O_2, O_3, V, Hole I, and Hole II) on the $V_2O_5(001)$ surface and then fully relaxed. The Mg–H bond length in free MgH_2 cluster is around 1.72 Å, as shown in Fig. 1(c), and the desorption energy of H_2 from MgH_2 is known to be high.[25,27] However, the Mg–H bond lengths in the presence of the V_2O_5 support are found to be 1.76, 1.75, and 1.77 Å for O_1, O_2, and O_3 sites, respectively. In Figs. 2(a)–2(d), we present the optimized geometries for MgH_2–O_1,O_2,O_3, and Hole sites, respectively. Generally, longer chemical bonds imply weaker bond strength. The activation barrier for the recombination of two H atoms to form hydrogen molecule should, thus, be significantly decreased. Most interestingly, a hydrogen molecule can be spontaneously formed during geometry optimization of the MgH_2 cluster on Hole I and Hole II sites of the $V_2O_5(001)$ surface [see Fig. 2(d)]. This can be understood by the fact that charge transfer from the Mg atom to the O atom will be induced and, thus, weaken the Mg–H bonds. Additionally, the MgH_2 cluster was found to be repelled from the top of the V site and, hence, the V site on the $V_2O_5(001)$ surface is not catalytically active for desorption of hydrogen.

Having studied the dehydrogenation of the MgH_2 cluster on a single-layer V_2O_5 sheet, we now turn to study rehydrogenation of Mg, which is important for reversible loading
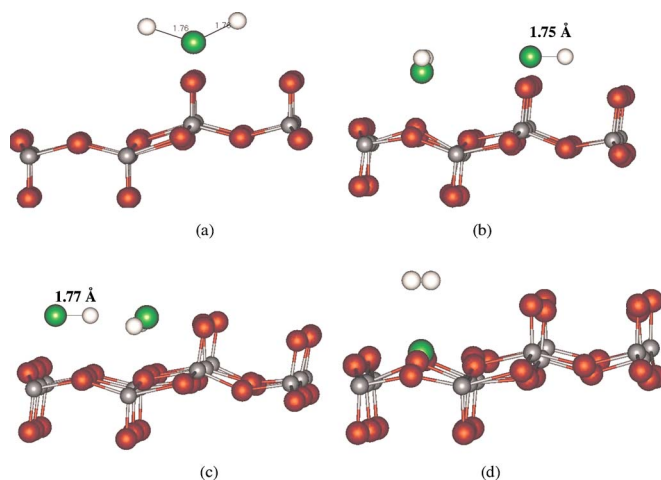
and unloading of hydrogen. It may plausibly be suggested that, during high energy ball milling experiments, the reduction of V_2O_5 (phase transformation) can occur, yielding MgO and metallic V.[28] This, however, could be difficult to detect due to the low addition levels of V_2O_5. Motivated by our previous theoretical studies on catalytic effects of Ti and Pd dopants on a Mg surface,[13,14] as well as more recent work on Ni,[29] we have explored the possible role of V dopants in facilitating the surface dissociation of H_2 on the Mg(0001) surface. Experimentally, a V-incorporated Mg(0001) surface (V@Mg(0001)) may not be difficult to form by creating a Mg vacancy and then be filled by a V atom. The formation energy (E_f) for a V@Mg(0001) surface (coverage $\theta = 1/16$) was calculated according by the following equation:[30]

$$E_f = E_{V/Mg(0001)} + E_{Mg} - E_{V\text{-atom}} - E_{Mg(0001)},$$

where $E_{V/Mg(0001)}$, E_{Mg}, $E_{V\text{-atom}}$, and $E_{Mg(0001)}$ represent the total energy of the relaxed V-incorporated Mg(0001) surface, the bulk Mg atom, the isolated V atom, and the clean Mg(0001) slab, respectively. The formation energy is up to -2.86 eV, which indicates a high thermodynamic stability.

The activation barrier for the dissociation of a hydrogen molecule on the V@Mg(0001) surface was then calculated by utilizing the NEB method. We set one H_2 molecule a large distance from the relaxed V-doped Mg(0001) surface as the initial state. In the relaxed final state, the positions of two H atoms were located around 0.75 Å from the surface with a V–H distance of 1.745 Å. Figure 3 presents the energy profile along the MEP for the dissociation of H_2 on the V@Mg(0001) surface. The effective barrier for the dissociation of H_2 on V@Mg(0001) surface was calculated to be 0.20 eV, which is only $\frac{1}{5}$ of that on a pure Mg surface. Clearly, the dissociation event on the V@Mg(0001) surface should be fast near room temperature. The underlying mechanism can be understood in terms of the strong interaction between the molecular orbital of H_2 and d orbitals of transitional metal. First, there is a charge donation from the σ orbital of H_2 to the d orbital of V. Then, the binding is stabilized by back donation of electrons from the filled orbital of V to the antibonding orbital (σ^*) of the bound H_2 and, finally, two V–H bonds are formed.[31]

We should note here that the hydrogenation of Mg involves not only the dissociation of hydrogen onto the
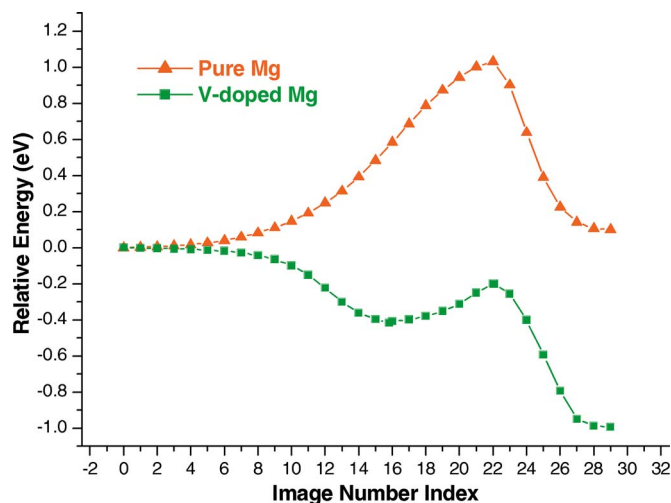
FIG. 3. (Color online) The energy profiles for the dissociation of H_2 on a pure and V-doped Mg(0001) surface.

Mg(0001) surface in the first step, but also the subsequent diffusion of dissociated surface H atoms away from catalytic active site. As clearly shown in Fig. 3, the final state (VH$_2$) is very stable compared to the initial state. It is not clear whether this stability would lead to a subsequent barrier to diffusion of atomic H away from the V site, analogous to the case recently elaborated for Ti.[14] While the present spin-polarized calculations are very time consuming, preventing us from addressing these subsequent stages of the sorption process in the present article, it is worthy to note that experimentally, V hydride was reported to decompose easily even though V displays a high affinity for hydride formation.[32,33] The reaction (VH$_2 \rightarrow$ V+2H) was reported to occur at 35 C with an activation barrier of 0.04 eV for the diffusion of atomic H from free V surface.[34] Subsequently, the atomic H transfers to Mg atoms, forming MgH$_2$ around the V site and, thus, V can be regarded as an "atomic hydrogen pump," which facilitates the adsorption of atomic H. While our results presented herein shed light on the nature of the initial surface adsorption of hydrogen onto V sites in the Mg surface, they do not provide a full rationalization of the experimentally observed catalytic role of V for hydrogen sorption into ball milled Mg nanocomposite materials. In order to probe for possible low-energy diffusion pathways that might provide a more complete theoretical explanation of the catalytic role, further studies on H diffusion away from the V site will be required. Additionally, our initial study deals only with MgH$_2$ cluster on the V$_2$O$_5$(001) surface, a more ambitious model based on the MgH$_2$−V$_2$O$_5$ interface might be expected to provide a more complete mechanistic elaboration. Both H migration away from the V site and MgH$_2$/V$_2$O$_5$ interface model are reserved as the subject of fuller subsequent studies.

In summary, *ab initio* DFT calculations were performed to explore the catalytic effect of V$_2$O$_5$ on the hydrogenation and dehydrogenation of magnesium hydride. We found that Mg–H bond length became elongated and weakened when MgH$_2$ clusters were positioned on single, two, and three coordinated oxygen sites on the V$_2$O$_5$(001) surface. Most interestingly, hydrogen molecule could be spontaneously formed at the hole site on the V$_2$O$_5$(001) surface. On the other hand, the activation barrier for the dissociation of H$_2$ on top of V atom was calculated to be only 0.20 eV, which is

$\frac{1}{5}$ of that on pure Mg(0001) surface. Our results indicate that oxygen and hole sites on the V$_2$O$_5$(001) surface are catalytically active for the destabilization of MgH$_2$ and V dopant on Mg surface could accelerate the dissociation of H$_2$ on Mg(0001) surface. The understanding gained here will aid in the rational design and development of Mg-based hydrogen storage materials.

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