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Vacancy mediated desorption of hydrogen from a sodium alanate surface: An *ab initio* spin-polarized study

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Ab initio spin-polarized density functional theory calculations are performed to explore the effect of single Na vacancy on NaAlH₄(001) surface on the initial dehydrogenation kinetics. The authors found that two Al–H bond lengths become elongated and weakened due to the presence of a Na vacancy on the NaAlH₄(001) surface. Spontaneous recombination from the surface to form molecular hydrogen is observed in the spin-polarized *ab initio* molecular dynamics simulation. The authors' results indicate that surface Na vacancies play a critical role in accelerating the dehydrogenation kinetics in sodium alanate. The understanding gained here will aid in the rational design and development of complex hydride materials for hydrogen storage. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721127]

To develop a viable hydrogen storage system is becoming increasingly important for promoting the “hydrogen economy.” Various hydrogen storage materials, such as metal hydrides,^{1,2} carbon-based materials,^{3,4} complex hydrides,^{5,6} metal–N–H systems,⁷ metal organic frameworks,⁸ and clathrate hydrates,⁹ have been considered in recent years. Among them, sodium alanate (NaAlH₄) represents a very promising candidate due to its high reversible hydrogen storage capacity and optimal thermodynamic stability at medium temperature. AlH₄^{−1} is, however, highly stable, necessitating high absorption and decomposition temperatures in the absence of a catalyst.¹⁰ Consequently there has been considerable interest in finding possible destabilization strategies that would facilitate the release of molecular hydrogen at lower temperatures. It has been well established that a small amount of TiCl₃ dopant into NaAlH₄ facilitates accelerated and reversible hydrogen release under moderate conditions,^{5,11,12} a discovery which revitalized the research into complex light-metal hydrides as potential hydrogen storage materials. Since then, substantial progress has been made experimentally in studying the kinetics of Ti-doped sodium alanate for both the hydrogenation and dehydrogenation processes.^{13,14} Currently, it is believed that the final oxidation state of the titanium is zero,^{15,16} which is independent of the initial oxidation state and how Ti is added to NaAlH₄. However, there is still a continuing experimental controversy on precisely where the Ti resides and the exact role of the catalyst. For example, some suggest that Ti is substituted at a Na site or the Al site in the bulk while others find that Ti remains on the surface as a microcrystalline Ti–Al alloy, which could be catalytically active. Distinguishing which if any of these proposed mechanisms are playing a role requires fresh input either from first principle simulations or from experiments.

Theoretically, it has been found that substitution of Na or Al with Ti is energetically feasible and facilitates Al–H bond

breaking through the formation of Ti–H bonds.^{17,18} Surface Ti atoms on NaAlH₄ have been also suggested to be present as TiH_x species.^{19,20} However, the Ti–H bond is too strong to break (130 KJ/mol),²¹ raising further questions about the catalytic mechanism. More recently, Liu and Ge found that an interstitial site beneath the NaAlH₄ surface is the most energetically favorable location for Ti and may also be a precursor of TiAl₃.²² Unfortunately, the energy for the removal of a H₂ molecule from this system is considerable and the release of H₂ may not be facile at typical experimental temperatures.²² Despite intense research efforts, the current understanding of the mechanism responsible for the enhanced hydrogen absorption/desorption kinetics in Ti-doped sodium alanate is still very limited. A detailed understanding of the catalytic mechanism is, however, exceedingly important from the perspective of designing materials with improved desorption kinetics and hydrogen storage capacity.²³

Since there is no experimental evidence to show that such large scale mass transport occurs via diffusion of molecular hydrogen from the bulk, a computational exploration of the surface desorption properties is a logical next step. It is well known that the bond between Na⁺ and (AlH₄)^{−1} is highly ionic in sodium alanate. Generally, the weakening of the ionic bond interaction could significantly suppress the charge transfer between them. Creating neutral Na vacancy should be the most effective way since the anionic charge on the surrounding AlH₄ complexes is thereby reduced. It has been shown that a neutral AlH₄ complex is highly unstable and will result in the rapid formation of a hydrogen molecule.^{24,25} To date, there have been several studies on vacancy mediated H₂ desorption, but these have been limited either to bulk models or have not been spin polarized.²⁶ The energy for formation of single Na vacancy is calculated to be as high as 3.40 eV. However, recent studies by Vegge show that the formation energies of the first and second Na vacancies near a Ti–Na site are decreased to around 1.0 eV.²⁷ The following reaction leading to the two Na vacancies is calculated to be favored by 0.6 eV on the NaAlH₄(001) surface:

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where Ti-Na and Na^v represent a Ti-substituted Na site and sodium vacancy, respectively. This finding is substantiated by the consistent observation of NaCl in diffraction patterns in TiCl_3 -doped samples.^{28,29} Additionally, sodium vacancies may also be produced during the high energy ball milling process.

A very important objective is to understand the intrinsic role of surface Na vacancies in the desorption phase of the hydrogen recycling process in Ti-doped Sodium alanate, since this may help to further understand the mechanism for the experimentally observed fast kinetics that remains unexplained by existing theoretical studies. In a recent preliminary study,²⁵ we carried out initial spin-unpolarized structural optimizations for the NaAlH_4 bulk in the presence of a single Na vacancy. We found that a single Na vacancy in the bulk had little effect on the neighboring AlH_4 complexes—they are surrounded by other Na^+ ions and hence retain much of their negative charge. This is in accord with the earlier findings of Ref. 26. However, after introducing point defects on the NaAlH_4 surface, we have found that the distortion of AlH_4 units around the defect site is stronger, inducing changes in bond length on the order of 2%–3% for AlH_4 complexes adjacent to the point defect within the framework of the spin-unpolarized calculations. This can be understood by the further reduction of the anionic charge of the AlH_4 units adjacent to the defect site compared to the bulk case.

Spin polarization has been shown to be very important for determining the actual energy for substitution of Ti at Na or Al sites.³⁰ In this work, we explore the effect of incorporating spin polarization on the predicted lability of hydrogen in the presence of surface defects, namely, a neutral sodium vacancy—in an attempt to find the lowest energy pathway of H_2 desorption. Both *ab initio* static and dynamics calculations were performed to investigate the decomposition of hydrogen on the $\text{NaAlH}_4(001)$ surface in the presence of a neutral Na vacancy. All the calculations were spin polarized and performed using the plane-wave basis VASP code^{31,32} implementing the generalized gradient approximation of the PBE exchange correlation functional³³ and the projector augmented wave method.^{34,35} The lattice constant of bulk NaAlH_4 was calculated to be 4.993 Å, which was in good agreement with the experimental value and previous theoretical studies.³⁶ The $\text{NaAlH}_4(001)$ surface was modeled in a (4×4) surface unit cell containing six layers of Al, a total of 96 NaAlH_4 molecular units (576 atoms), which is significantly larger than the existing studies.^{17,22,26} The minimum distance between vacancies exceeds 15 Å so the interaction among periodic images of neutral vacancies is assumed to be negligible. All atoms in the bottom layer are fixed at their bulk position while the top five layers are allowed to relax. The energy cutoff for plane waves was chosen to be 250 eV and the vacuum space was larger than 16 Å. Only gamma point calculation is used for surface Brillouin zone sampling. Structural relaxations were considered to be converged for residual force components are small than 0.01 eV/Å.

Remarkably, the final structure in the presence of a single surface Na vacancy after full optimization, Fig. 1(a), is in significant contrast to that predicted in the former unpolarized calculation.²⁵ Due to the charge reduction, one AlH_4 complex adjacent to the Na vacancy becomes strongly distorted. The lengths of two Al–H bonds are increased from

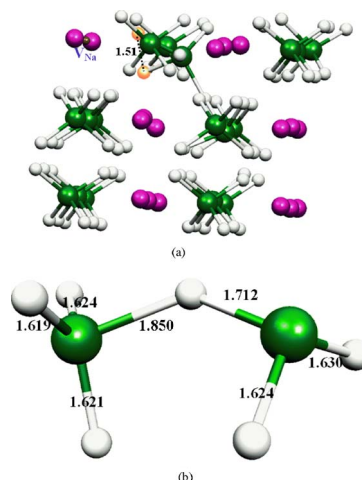


FIG. 1. (Color online) (a) Local structure for the equilibrium configuration of a $\text{NaAlH}_4(001)$ surface in the presence of a neutral Na vacancy. (b) The formed Al_2H_6 anionlike structure after full relaxation of the structure with one hydrogen molecule removed in (a). Purple, green, and white balls represent Na, Al, and H atoms, respectively. Small brown ball represents a neutral sodium vacancy.

1.643 to 1.71 and 1.79 Å, while the remaining two are decreased from 1.643 to 1.61 Å. Correspondingly, the H–H distance for the elongated pair is reduced from 2.65 to 1.50 Å. Generally, longer chemical bonds imply weaker bond strength. Apparently, these two hydrogen atoms are bound dissociatively and close to nearly molecular form of H_2 . These can be understood by the fact that H will form covalent interaction with neighboring H to compensate the reduced anion charge. Very interestingly, more than one elongated Al–H pair will be produced when more Na vacancies are created on the sodium alanate surface. The spin-polarized calculation converged to a magnetic ground state with one unpaired electron. The magnetic charge density (spin up minus spin down) showed that the unpaired electron is localized around the elongated H pairs. The energy is 0.35 eV lower compared to that in the spin-unpolarized calculation. Figures 2(a) and 2(b) present the total density of states for a pure $\text{NaAlH}_4(001)$ surface and one with a single Na vacancy, respectively. Clearly, sodium alanate is semiconducting with a wide band gap (4.5 eV), which is in accord with Ref. 37. A defect state appears in the band gap for the defect surface, corresponding to the unpaired electron.

We now turn to study the energetics of hydrogen desorption on the basis of the final configuration obtained above. The desorption energy is obtained by calculating the difference between the total energy computed for the Na-vacancy-containing slab and the sum of the total energies computed for the stoichiometric geometry with two hydrogen atoms removed and a hydrogen molecule (in all cases fully optimized). The desorption energy is calculated to be -0.68 eV—significantly exothermic. To further study the effect of temperature, we then perform *ab initio* spin-polarized molecular dynamics at 300 K for the geometry shown in Fig. 1(a). Our molecular dynamics simulation was based on the canonical (*NVT*) ensemble using the Nose algorithm.³⁸ Time step is 0.5 fs and nuclear deuterium is used instead of hydrogen to increase the time step. As might be expected on the basis of the computed desorption energy, we observed the spontaneous recombinative desorption of a H_2 molecule on the $\text{NaAlH}_4(001)$ surface within the time scale of 1 ps. After

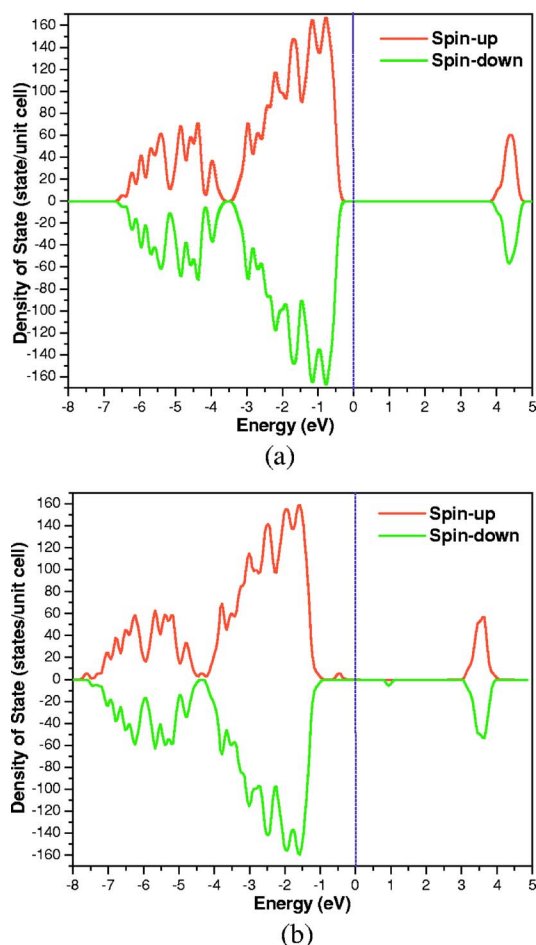


FIG. 2. (Color online) (a) Density of states (DOS) for the relaxed $\text{NaAlH}_4(001)$ surface. (b) The same as (a), but that for a $\text{NaAlH}_4(001)$ surface in the presence of a neutral Na vacancy. The vertical dotted blue line represents the Fermi level.

removing one hydrogen molecule, AlH_2 will move towards another neighboring AlH_4 anion and form the Al_2H_6 anionic structure as reported in Refs. 24 and 39 Figure 1(b) presents the local structure cut from the relaxed NaAlH_4 structure. The unpaired electron is localized around the Al atom. At the same time, the Fermi level is decreased from -2.158 to -1.236 eV.

We should note that the recycling performance in Ti-doped sodium alanate involves not only the desorption of H_2 but the rehydrogenation as well. The role of Ti dopant in the latter case has been recently identified as catalytic role on Al surface in the chemisorption of molecular hydrogen.⁴⁰ Here we have demonstrated that two Al-H bond lengths will become elongated and weakened due to the presence of a Na vacancy on the $\text{NaAlH}_4(001)$ surface. Spontaneous recombination from the surface to form molecular hydrogen is observed in the spin-polarized *ab initio* molecular dynamics simulation. Our results indicate that surface Na vacancies could be a mechanism by which the desorption kinetics of H_2 in NaAlH_4 is accelerated, as observed in experiments. Since NaAlH_4 is prototypical among the complex metal hydride candidates for hydrogen storage materials, the understanding gained here will aid in the rational design and development of such materials.

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