A precursor state for formation of $TiAl_3$ complex in reversible hydrogen desorption/adsorption from Ti-doped $NaAlH_4$†

Jianjun Liu and Qingfeng Ge*

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The structure of a $TiAl_3H_x$ complex for the formation of a $TiAl_3$ binary phase that could play important roles in the reversible de-/hydrogenation of Ti-doped $NaAlH_4$ has been identified on the basis of first principles density functional theory studies.

One significant barrier that prevents the widespread use of hydrogen as an energy carrier for on-board applications is the lack of efficient hydrogen storage systems that provide the needed quantity of hydrogen in regard to volume, weight, cost, and safety risk as compared with the current petrol-driven combustion engine.[1–3] Alanate-based complex metal hydrides offer perhaps the best opportunities for meeting the requirements of on-board application due to the breakthrough work of Bogdanovic and co-workers who demonstrated that Ti-doped $NaAlH_4$ could reversibly desorb and readsorb hydrogen under mild conditions.[4,5] Extensive studies of Ti-doped $NaAlH_4$ have led to considerable improvement in the kinetics and cycling performance at the conditions that are relevant to the practical operation of a proton exchange membrane fuel cell. Despite these improvements, the mechanism and process by which the $NaAlH_4$ system is catalyzed by a small amount of Ti are not well understood.

In general, heterogeneous reactions such as hydrogen release and uptake in Ti-doped $NaAlH_4$ are complex and difficult to study. Many experimental studies have attempted to provide an answer to one of the most important questions: what is the role of added Ti in the reversible dehydrogenation/reformation of $NaAlH_4$? A microcrystalline $TiAl_3$ alloy formed during high energy ball-milling of $TiCl_4$ and $LiAlH_4$ has been assumed catalytically active.[6] Recent studies of Ti-doped $NaAlH_4$ indicated that Ti exists at zerovalent state in the form of Ti–Al alloy in the amorphous phase.[7] A combined TEM-EDX and XAFS study showed that Ti was atomically dispersed in the Al phase and formed a Ti–Al alloy.[8,9] Combining the Ti–Al binary phase diagram and the fact that Ti–Al compounds have favorable formation energies, the authors concluded that $TiAl_3$ is likely to be formed in the Ti-doped $NaAlH_4$. An alternative mechanism that involves Ti hydrides, formed during the doping or hydrogenation processes, contributes to the enhanced performance in the reversible de-/hydrogenation processes.[10] Although the strong affinity of Ti to hydrogen makes the formation of Ti hydride favorable, the catalytic role of the Ti hydride was only supported by limited experimental evidence.[11–13] Coexistence of $TiAl_3$ and Ti hydrides phases may produce a synergetic effect.

Correlating experimental observations with the atomic scale transformation is critical in understanding materials properties and performance. However, it is extremely challenging to accurately determine the structure of materials involving hydrogen. It is even more difficult to track the chemistry of hydrogen at an atomic scale in solid state transformations. On the other hand, computational chemistry and molecular simulation are advantageous for studies of well-defined model systems, including those containing hydrogen. DFT calculations have been applied previously in the studies of Ti-doped bulk $NaAlH_4$[14,15] and $NaAlH_4$ surfaces.[16] Herein, we performed DFT planewave slab calculations of total energy, force, and structures of Ti-doped $NaAlH_4(001)$ using the VASP code.[17,18] The projector-augmented wave potentials were used to describe electron–ion interactions and the PW91 form of the generalized gradient approximation[19] was employed to calculate exchange and correlation energy. The cutoff energy of the plainwave was set to 400 eV. A supercell with a vacuum space larger than 15 Å along the z directions was used for constructing a slab to simulate the surface. The k-points for surface Brillouin zone sampling were generated by the Monkhorst–Pack scheme with a space less than $0.05\ \text{Å}^{-1}$. The convergence criteria in energy and force are 1.0×10^{-6} eV and 0.05 eV/Å, respectively. A similar parameter set was used in our previous study of $LiBH_4$.[20]

We first established the preferred site of Ti in Ti-doped $NaAlH_4(001)$. It has been shown that Ti prefers a Na site for substitutional doping.[14] In the present study, we focused on three types of sites: (1) Ti is adsorbed on the surface and linked with two neighboring AlH_4^- hydrides; (2) Ti replaces Na^+ in the lattice, making Na^+ displace upward or downward; (3) Ti is located in the interstitial sites and connected with three hydrides. The slab containing 6 layers of Al, total twenty-four $NaAlH_4$ molecular units, was then optimized with the bottom two layers of Al and Na atoms being fixed at their corresponding bulk positions. The remaining Na and Al atoms as well as all the hydrogen atoms in the slab were allowed to relax. Structures and Ti binding energies with respect to the pure (001) surface and a free Ti atom after relaxation have been provided in the supplementary information. Our results clearly show that Ti in the interstitial sites, with a binding energy of 4.182 eV, is most stable among all these structures. In the relaxed structures, the Ti atom occupies the interstitial space among three hydrides and is bound directly with three Al atoms, as shown in Fig. 1(a). This interstitial space is accessible directly from the surface. The stronger affinity of Ti toward H than Al makes Ti strip hydrogen from Al. We refer to it

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Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA. E-mail: qge@chem.siu.edu; Fax: 1-618-453-6408; Tel: 1-618-453-6406

† Electronic supplementary information (ESI) available: A figure showing GGA-relaxed structures and binding energies of Ti-doped $NaAlH_4(001)$ with Ti in different positions. See DOI: 10.1039/b600679e

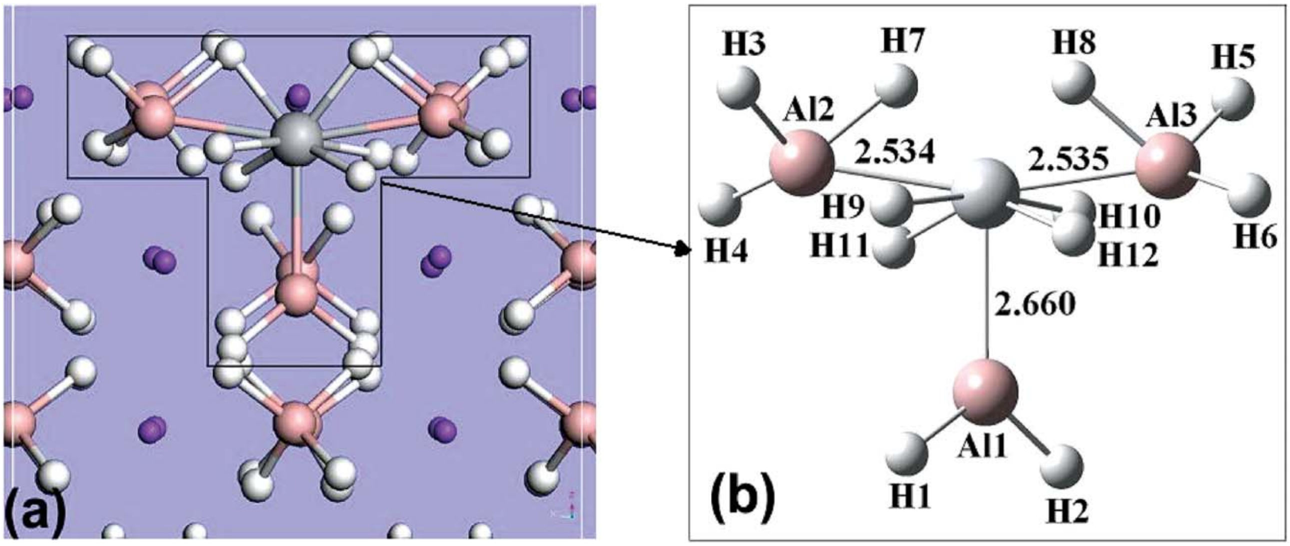

Fig. 1 (a) GGA-relaxed structure of Ti-doped $NaAlH_4$(001) with Ti in the interstitial space; (b) detailed local structure of the $TiAl_3H_x$ (x = 12) complex shown in (a).

as $TiAl_3H_x$ for simplicity but note that Ti–H bonds are formed in the complex structure. The detailed local structure of a $TiAl_3H_x$ complex with x = 12 is shown in Fig. 1(b). The distance between two top original AlH_4^- units that are bound to Ti does not change significantly but the original AlH_4^- underneath Ti was pushed downward by ~ 0.1 Å. Insertion of Ti also causes slight expansion of AlH_4^- that are not bound to the Ti atom. In this complex, Ti coordinates with three Al atoms, which is consistent with the XAFS measurements.[8,9] Furthermore, our results showed that Ti–Al bond lengths vary within 0.2 Å from the initial fully hydrogenated complex to the completely dehydrogenated state in the slab, which indicates an invariant local environment around Ti during dehydrogenation. The bond lengths are also in agreement with the measured Ti–Al bond lengths from the experiments.

We then studied the energetics of hydrogen desorption on the basis of the most stable structure determined above. Herein, we define desorption energy as the total energy difference between the Ti-doped stoichiometric slab and the sum of the slab with hydrogen atoms removed and hydrogen molecules. Hydrogen desorption energies with hydrogen atoms from different positions of the complex structure shown in Fig. 1b are summarized in Table 1. For example, the energy cost to desorb hydrogen from positions H1 and H2 in Fig. 1b and form one H_2 molecule is only 0.515 eV. On the other hand, to desorb four almost symmetrical hydrogen atoms (H3, H4, H5, and H6) bound on two Al-atoms on opposite sides costs 0.921 eV per H_2 molecule. The combinative desorption of hydrogen atoms H9 and H10 has a similar energy cost of 0.934 eV. These two hydrogen atoms bound directly with the Ti atom. The hydrogen atoms H11 and H12 as well as the two H atoms shared by Ti and Al atoms have significantly higher desorption energy than the other hydrogen atoms in the complex. For comparison, we also calculated the energy cost to desorb a pair of hydrogen atoms from the same AlH_4^- unit on the (001) surface of pure $NaAlH_4$. This energy is 1.383 eV per H_2 molecule. Clearly, to desorb hydrogen from the Ti-containing complex is energetically favorable over the direct desorption from pure $NaAlH_4$. Furthermore, the energy required to desorb the first 4 hydrogen molecules from the complex is ~ 3.3 eV, indicating that the heat released from doping the Ti atoms would be sufficient to maintain the energy balance. Of course, atomization energy of Ti from its precursor and the kinetic barrier for desorption will ultimately determine the overall energy cost and desorption rate.

Table 1 DFT-GGA hydrogen desorption energies with different combinations of hydrogen atoms in the local structure $TiAl_3H_x$ (x = 12) shown in Fig. 1b

Combination of hydrogen atoms	Desorption energy (eV/H_2 molecule)
H1, H2	0.515
H3, H4, H5, H6	0.921
H9, H10	0.934
H11, H12	1.265
H7, H8	2.067

In order to understand the origin of the reduced desorption energy of hydrogen from the Ti-doped $NaAlH_4$(001), a cluster of $TiAl_3H_{12}$, shown in Fig. 1(b), was constructed with the same structure as the complex embedded in the $NaAlH_4$(001) slab. The electronic structure of the complex was calculated and analyzed using Gaussian'03[21] without further geometry optimization. The results of Gaussian calculations with different charges in the range from −3 to +1 indicate that the complex with one negative charge is most stable. Natural bond orbital analysis showed that the charge on Ti in the −1 charged complex is close to zero (−0.01). The highest occupied molecular orbital (HOMO) and HOMO-1 are shown in Fig. 2. In fact, there are two degenerate HOMO-1 orbitals and only one is shown in Fig. 2(b). The HOMO is an antibonding orbital (σ^*) formed between Ti-3d_{z^2} and H-s orbitals and helps to strengthen Ti–Al interactions but weakens the Al–H bonds. In fact, this orbital involves strong bonding interactions between two hydrogen atoms bound to the lower Al atom from underneath. On the other hand, the HOMO-1 orbitals contain weak antibonding characteristics (π^*) between Ti-3d_{yz} and side H-s orbitals. The collective effects of these orbitals are the lowered desorption energy of hydrogen, especially the two hydrogen atoms bound to the lower Al atom from underneath.

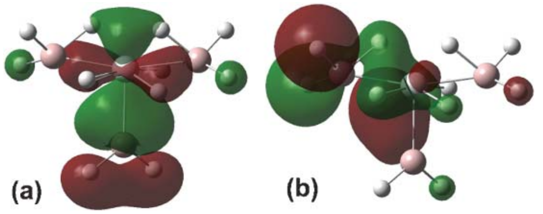

Fig. 2 Isosurface of (a) HOMO and (b) HOMO-1 of the $TiAl_3H_x$ (x = 12) complex structure shown in Fig. 1(b) calculated at the B3LYP/6-311++G(d, p) level.

The complex structure may play important roles in the reversible hydrogen release/uptake in Ti-doped $NaAlH_4$. Our calculations showed that desorption of two bottom hydrogen atoms and four side hydrogen atoms caused hydrogen atoms of the neighboring AlH_4^- units to migrate to the Al atoms of the complex. The migration of hydrogen during relaxation after desorbing hydrogen indicates that the barrier for hydrogen diffusion across different AlH_4^- units is small. The small diffusion barrier of hydrogen from surrounding AlH_4^- units to the complex structure helps to sustain the hydrogen desorption until the hydrogen in the surrounding region becomes sufficiently depleted. Complete dehydrogenation will lead to the formation of $TiAl_3$ dispersed in a predominantly Al phase.[3] Rehydrogenation may start at the dispersed $TiAl_3$ complex with the formation of $TiAl_3H_x$ complex structure. A plausible pathway for rehydrogenation *via* the $TiAl_3$ phase has been previously explored.[22] As the structure becomes saturated with hydrogen, diffusion of hydrogen from $TiAl_3H_x$ to the neighboring Al site may take place. Alternatively, Ti may migrate to a new Al dominated site and form a new $TiAl_3$ complex. Hydrogenation will be repeated at the new complex structure. All these arguments support the proposal that the $TiAl_3H_x$ complex structure is active in dehydrogenation/hydrogenation processes. Furthermore, this complex does not exclude the presence of Ti hydrides during hydrogenation and reformation of $NaAlH_4$. The high desorption energy of two bridging hydrogen atoms bound to Ti and two side Al atoms may provide an explanation of the Ti-hydrides observed experimentally.[10,13] We are currently working on mapping out the reaction pathways for hydrogen desorption through this complex and determining the transition states and reaction barriers for hydrogen migration and desorption. The understanding from these studies will not only help us to establish the mechanism for this particular system but also to understand the mechanism of similar heterogeneous reactions.

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