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A first-principles study of Sc-doped $NaAlH_4$ for reversible hydrogen storage

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Abstract

Density function theory calculations have been carried out to investigate energetics, structure, and NMR chemical shielding of Sc-doped $NaAlH_4$ (0 0 1) surface. Sc atom was found to occupy the interstitial site and interact directly with three immediate neighboring AlH_4^- groups and indirectly with two additional AlH_4^- groups, forming an extended complex structure of $ScAl_3H_{12}$–$2AlH_4$. In the $ScAl_3H_{12}$–$2AlH_4$ structure, the Al–Al distances between the Al atom in $ScAl_3H_{12}$ and the Al in the neighboring AlH_4^- are 3.154 Å. Hydrogen desorption energies from many positions of the complex were reduced significantly from that of the clean surface. This extended structure is more efficient for dehydrogenating $NaAlH_4$ than the similar $TiAl_3H_{12}$ complex that was identified in the Ti-doped $NaAlH_4$ surfaces. Furthermore, our calculated NMR shielding of Sc-doped $NaAlH_4$ shows that the Al atoms in direct contact with Sc have very different shielding values from the Al atoms in the center of H tetrahedra. These result may provide an explanation for the ^{27}Al MAS NMR chemical shifts observed experimentally.

Keywords: Complex metal hydrides; Hydrogen storage; Catalysis; Surfaces; Density functional theory; NMR shielding

1. Introduction

There have been great interests in developing transition metal-catalyzed light-weight complex metal hydrides as hydrogen storage materials for transportation application due to the pioneering work of Bogdanovic and Schwickardi [1]. These authors demonstrated that a small amount of transition metal compounds such as $TiCl_3$ can increase the rates of hydrogen adsorption and desorption. Although $NaAlH_4$ will not be able to meet the hydrogen capacity target set by US DOE, it has been used as a model system to understand the role of the transition metal additives in catalyzing the reversible dehydrogenation and rehydrogenation processes in materials of similar structures [2,3]. Many transition metal elements including Sc, Ti, V, Cr, Fe, Zr, and Cd have been tested and shown to accelerate dehydrogenation and rehydrogenation reactions [4–6]. In particular, Bogdanovic et al found that $NaAlH_4$ ball milled with 2 mol.% $ScCl_3$ was highly efficient with respect to storage capacity and kinetics but the cyclic stability was not as good as Ti-doped $NaAlH_4$ [6], as manifested by the fact that the system was not rehydrogenated to reach the same level of storage capacity as quickly as prior to the low-pressure dehydrogenation. They demonstrated that the problem can be alleviated by adding other compounds containing transition metal elements such as Ce and Pr. Many analytical techniques including solid state NMR have been used to characterize these potential hydrogen storage materials [7–10]. Recently, Bowman and co-workers performed a MAS NMR study of Sc-doped $NaAlH_4$ [11]. They observed an unknown feature with a shift of 20 ppm below the Al atoms of the AlH_4^- hydrides in their ^{27}Al MAS NMR spectra after two cycles of dehydrogenation and rehydrogenation, in addition to the Al chemical shifts associated with the normal tetrahedral AlH_4^- and AlH_6^{3-}.

In our recent studies [12,13], we showed that Ti energetically favors the interstitial sites formed by three neighboring $(AlH_4)^-$ groups and interacts directly with them. The resulting local structure corresponds to a formula of $TiAl_3H_x$ with $x = 12$ before hydrogen desorption starts. The hydrogen desorption energies from many positions of $TiAl_3H_{12}$ were reduced considerably as compared with that from the corresponding clean, undoped $NaAlH_4$ surfaces. The almost invariant local environment surrounding Ti during dehydrogenation led us to

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conclude that the $TiAl_3H_x$ complex is a precursor state for the formation of experimentally observed $TiAl_3$. We also showed that the $TiAl_3H_x$ complex has extended effects beyond reducing locally the hydrogen desorption energy. It facilitates low energy hydrogen desorption by either transferring hydrogen to the $TiAl_3H_x$ complex or by reducing hydrogen desorption energy in the neighboring hydrides by linking these hydrides with the complex structure [13].

In the present paper, we extend our study to Sc-doped $NaAlH_4$ (0 0 1) surface. In addition to computing the structures and energetics of Sc doping in $NaAlH_4$ (0 0 1), we also report our preliminary results of NMR chemical shielding of Al in Sc-doped $NaAlH_4$ (0 0 1) surface.

2. Computational methods

Periodic density function theory (DFT) calculations have been carried out using the VASP package [14]. The electron–ion interactions were described by projector augmented wave and the valence electrons were treated with a plan-wave basis set of 400 eV cutoff energy. The exchange-correlation energy was calculated with PBE form [15] of generalized gradient-corrected functional. The surface Brillouin zone was sampled with the $4 \times 4 \times 1$ K-points generated by Monkhorst-Pack scheme [16]. Slabs with six-layer metal atoms (Al and Na) consisting of 24 $NaAlH_4$ units were constructed on the basis of the relaxed bulk lattice constants to simulate the surfaces. The dimensions of the super-cell to simulate the (0 0 1) surface are $9.96\,Å \times 9.96\,Å \times 27.8\,Å$. The super-cell of this size has a vacuum space of >15 Å along z direction. A Gaussian smearing of 0.1 eV was employed to improve the convergence of electronic self-consistent cycles. The convergence criteria of energy and force are 1.0×10^{-6} eV and 0.05 eV/Å, respectively. The Al and Na atoms in bottom three layers of slab were fixed at their corresponding bulk positions during the relaxations. On the other hand, the Na and Al atoms in the top three layers as well as all the hydrogen atoms were allowed to relax according the calculated forces. A similar set of parameters has been applied successfully in our previous studies of Ti doping in $NaAlH_4$ [12,13].

A linear response theory as implemented in the CPMD program [17,18] was used to calculate the NMR chemical shielding in the present study. The NMR calculations were performed with the VASP-relaxed structure and using the Perdew-Becke form of gradient-corrected functional and norm-conserving Goedecker pseudopotentials [19]. The valance electronic wavefunction

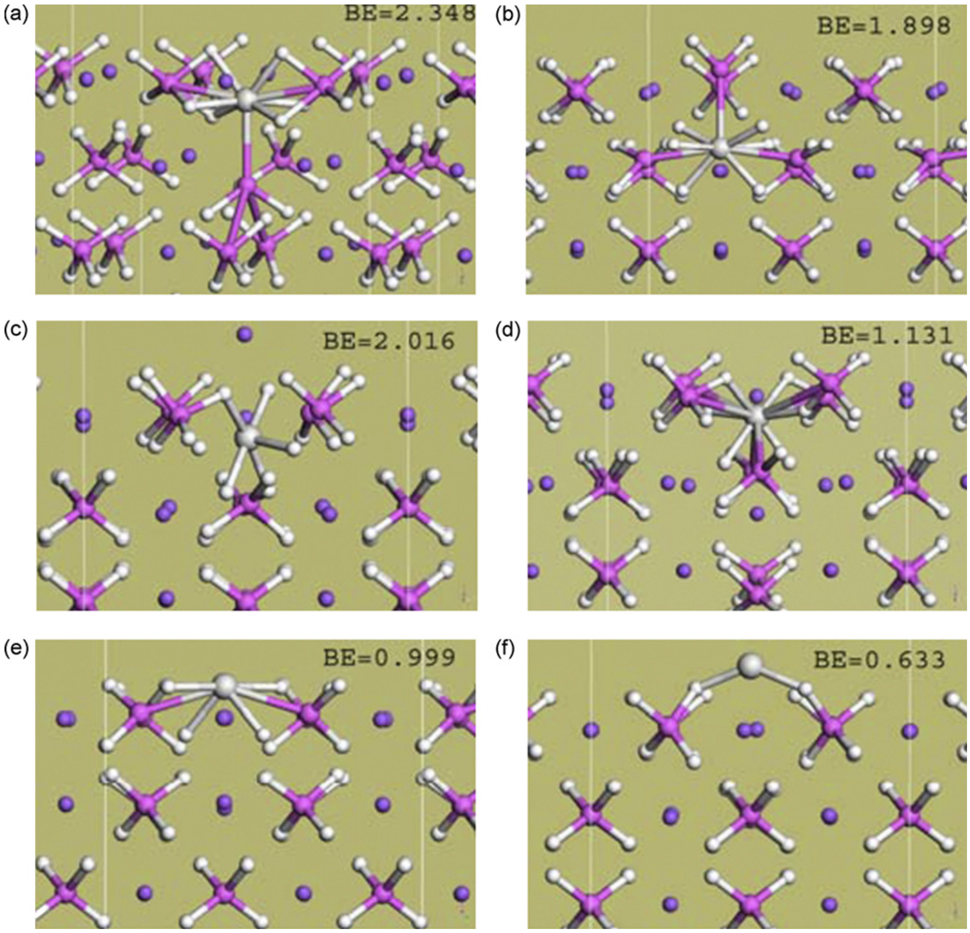

Fig. 1. The DFT–GGA relaxed structures of Sc-doped in $NaAlH_4$ (1 0 0) surface. (a) Sc occupies the interstitial site in the first layer; (b) Sc occupies the interstitial site in the second layer; (c) Sc substitutes Na and moves Na up; (d) Sc substitutes Na and pushes Na down; (e) Sc adsorbed between two surface $AlH_4{}^-$ units; (f) Sc adsorbed between two surface hydrogen atoms.

were expended on a plane-wave basis set with a cutoff energy of 952 eV.

3. Results and discussion

3.1. Structures and stabilities of Sc-doped $NaAlH_4$ (0 0 1) surface

We used the stable structures in Ti-doped $NaAlH_4$ (0 0 1) as initial input and replaced their Ti with Sc before allowing further relaxation. All these initial structures were relaxed to similar stable geometries. The binding energy of Sc in $NaAlH_4$ (0 0 1), calculated with respect to an isolated Sc atom and relaxed clean $NaAlH_4$ (0 0 1) surface, was used to characterize the relative stabilities of the relaxed structures. All six structures together with the corresponding Sc binding energies are shown in Fig. 1. Although the structures are similar, the detailed structural parameters are different when Ti was replaced by Sc. The surface interstitial sites are most stable for both Sc and Ti doping. The stability of Sc in $NaAlH_4$ (0 0 1) follows the same general order: interstitial > substitutional > surface adsorption.

As shown in Fig. 1, the surface interstitial site (1(a)) is the most stable configuration for Sc with a binding energy of 2.348 eV. In Fig. 1(a), the insertion of Sc leads to a complete hydrogen transfer from the hydrides in second layer to Sc in the first layer. Six hydrogen atoms bridge Sc and two Al atoms in the first layer, leading to the formation of two short Sc–Al bonds (2.675 Å) in the first layer. The stretched Sc–Al bond (2.839 Å) perpendicular to the surface pushes the AlH_2 moieties in the second layer downward, making the Al atom form Al–Al bonds with two neighboring AlH_4^- units in the next layer. Accordingly, we referred this complex to as $ScAl_3H_{12}$–$2AlH_4$ in which the main part $ScAl_3H_{12}$ is extended to connect with two neighboring AlH_4^- groups. The complex structure is boxed in Fig. 1(a). Fig. 2 shows the detailed local structure in a cluster representation in order to avoid interference caused by the periodic condition.

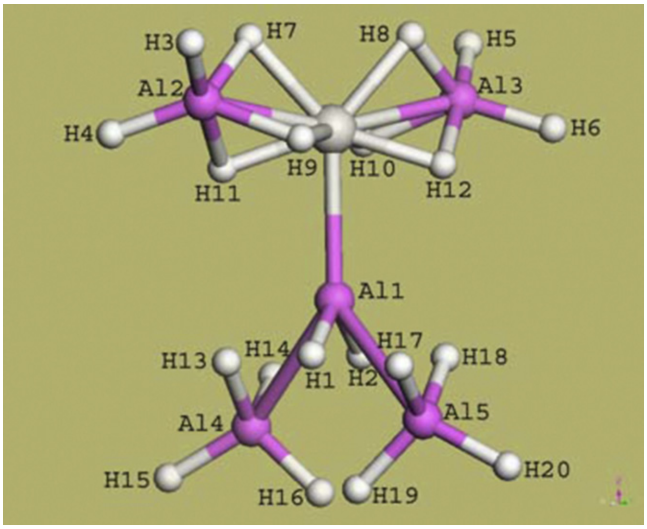

Fig. 2. Detailed local structure of $ScAl_3H_{12}$–$2AlH_4$ shown in the box of Fig. 1(a).

Table 1
Comparison of DFT–GGA calculated hydrogen desorption energies from the complex $ScAl_3H_{12}$–$2AlH_4$ structure in Sc-doped $NaAlH_4$ (0 0 1) and from the $TiAl_3H_{12}$ structure in Ti-doped $NaAlH_4$ (0 0 1)

Combination of hydrogen atoms	Sc-doped $NaAlH_4$	Ti-doped $NaAlH_4$
H1, H2	0.642	0.515
H3, H4 (or H5, H6)	0.937	0.668
H4, H11 (or H6, H12)	0.546	0.605
H11, H12	0.759	0.934
H9, H10	2.200	1.265
H7, H8	2.180	2.067
H3, H4, H5, H6	0.794	0.921
H4, H6, H11, H12	0.918	1.207
H1, H14 (or H2, H17)	0.058	–
H1, H13 (or H2, H18)	0.335	–
H15, H16 (or H19, H20)	1.228	–
H13, H15 (or H18, H20)	1.143	–

The numbering of hydrogen atoms was shown in Fig. 2.

3.2. Dehydrogenation from $ScAl_3H_x$–$2AlH_4$

The effect of doping Sc in $NaAlH_4$ on hydrogen desorption was measured on the basis of the most stable $ScAl_3H_{12}$–$2AlH_4$ complex. Herein, the hydrogen desorption energy is defined as $\Delta E_{\text{des}} = 1/n(E_{\text{stoi}} - nE_{H_2} - E_{\text{Hdes}})$, where E_{stoi} and E_{Hdes} are total energies of stoichiometric slab and the slab with H desorbed, E_{H_2} is the total energy of a H_2 molecule and n shows the number of H_2 molecule formed. This expression gives the energy cost of forming *n* hydrogen molecules in gas phase by removing 2*n* hydrogen atoms from the slab and is closely correlated with the experimentally measured temperature and heats of hydrogen desorption. The calculated desportion energies with hydrogen atoms from different positions in $ScAl_3H_{12}$–$2AlH_4$ shown in Fig. 2 were given in Table 1. For comparison, the calculated hydrogen desorption energies from $TiAl_3H_{12}$ also were listed in Table 1 [12,13]. We stress that all the hydrogen desorption energies have been calculated with a periodic boundary condition using the VASP program.

As we can clearly see from Table 1, doping Sc or Ti in $NaAlH_4$ (0 0 1) leads to a similar effect to hydrogen desorption: many combinations having reduced hydrogen desorption energy as compared with that without Sc or Ti doping (1.383 eV). As Sc doping in $NaAlH_4$ (0 0 1) resulted in a more delocalized complex structure than Ti, this reduction in the hydrogen desorption energy was also extended. The extended effect is manifested by the fact that the hydrogen atom combinations of H1 and H14 or H2 and H17 between $ScAl_3H_{12}$ and the lower AlH_4^- units have an extremely low desorption energy of 0.058 eV. The combination of H1 and H13 (or H2 and H18) also has a low desorption energy of 0.335 eV. The lowered hydrogen desorption energy would make $NaAlH_4$ release hydrogen at a lower temperature. Desorption of H1 and H13 causes $ScAl_3H_x$ to link more tightly with the neighboring AlH_4^- groups by strengthening Al–Al and hydrogen bridge bonds. The Al–Al distance was reduced from 3.154 Å before desorbing these hydrogen to 2.708 Å. Furthermore, complete dehydrogenation from the complex structure may lead to formation of $ScAl_3$ or $ScAl_5$. The current results suggest that Sc may be more efficient as a catalyst for hydrogen

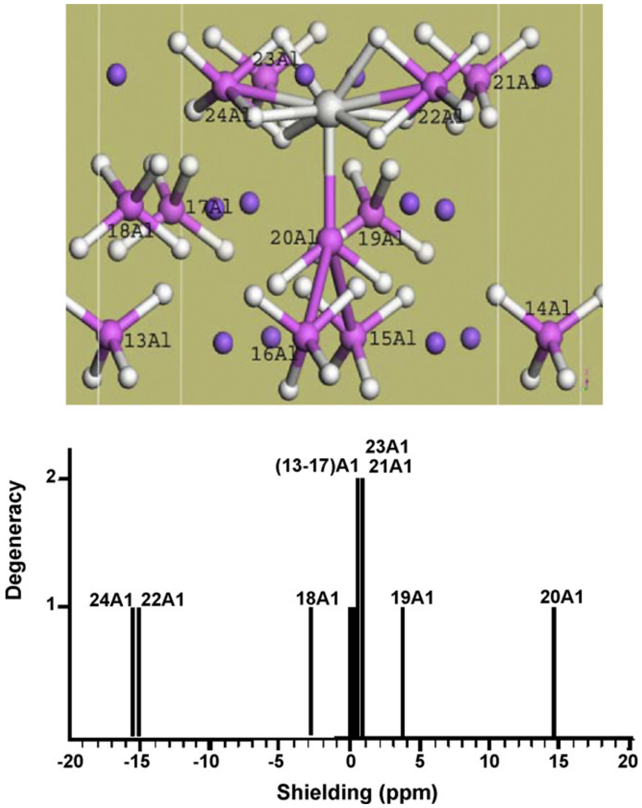

Fig. 3. DFT calculated ^{27}Al NMR chemical shielding in Sc-doped $NaAlH_4$ (0 0 1). The numbering of Al atoms is given in the upper panel.

desorption than Ti is. However, their overall performances as hydrogen storage catalysts have to be evaluated on basis of their abilities to catalyze both dehydrogenation and rehydrogenation reactions.

3.3. *NMR chemical shielding of Al in $ScAl_3H_{12}$–$2AlH_4$*

The unknown chemical shift peak at 20 ppm lower than the main Al peak in ^{27}Al MAS NMR spectra shown in the presentation by Bowman [11] stimulates our interests in the study of NMR properties of the complex structures isolated in our studies. On the basis of the most stable $ScAl_3H_{12}$–$2AlH_4$ structure, we calculated NMR chemical shielding by using the CPMD program. The calculated chemical shielding of Al NMR was plotted in Fig. 3 and the numbering of Al atoms was shown in the upper panel. As shown in Fig. 3, the chemical shielding of Al atoms in the H tetrahedral center lie at 0 ppm. We also note that there are small shifts for 18Al and 19Al (<5 ppm) although both are in the H tetrahedral center. Most notably, the chemical shieldings of the Al atoms directly bond to Sc have values of ∼15 ppm (20Al) and −15 ppm (22Al and 24Al). Detailed analysis of the shielding tensors revealed that the main component of the shielding tensor is parallel to the surface for 22Al and 24Al but perpendicular to the surface for 20Al. These features may correspond to the unknown peak in the experimental ^{27}Al MAS NMR spectra. The strong anisotropic nature of the NMR shielding tensor may affect the NMR spectra of chemical shifts measured experimentally. Further study will be needed to make a definitive assignment of the experimental NMR spectra.

4. Conclusion

In summary, we used first principles DFT calculations to characterize the energetics and structure of the Sc-doped $NaAlH_4$ (0 0 1) surface. Sc atom was found energetically favoring the interstitial site and connects with three neighboring AlH_4^- groups. In contrast to $TiAl_3H_x$ found in Ti-doped $NaAlH_4$, the complex formed by doping Sc extends to involve two neighboring AlH_4^- units with an effective formula of $ScAl_3H_{12}$–$2AlH_4$.

The formation of the $ScAl_3H_{12}$–$2AlH_4$ complex also lowers the hydrogen desorption energy from Sc-doped $NaAlH_4$ with respect to the clean, undoped surface. The NMR chemical shielding calculated on the basis of the complex structure embedded in the periodic slab may provide an explanation of the peak observed in ^{27}Al MAS NMR chemical shifts.

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