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PROJECT TITLE:

Understanding the Local Atomic-Level Effect of Dopants in Complex Metal Hydrides using Synchrotron X-ray Absorption Spectroscopy and Density Functional Theory Simulations

PRINCIPLE INVESTIGATOR:

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CO-INVESTIGATORS:

Yuri Lvov², Daniela Mainardi², Amitava Roy³

SUMMARY OF ACCOMPLISHMENTS

- Five peer reviewed journal publications (see below for full text):
 1. Dobbins T.A., Bruster E.B., Oteri E.U., Ilavsky J., “Ultrasmall-Angle X-ray Scattering (USAXS) Studies of Morphological Trends in High Energy Milled NaAlH₄ Powders”, *Journal of Alloys and Compounds*, **446-447** pp 248-254 (2007).
 2. Dathara G. K. P.; Mainardi D., “Structure and dynamics of Ti-Al-H compounds in Ti-doped NaAlH₄”, *Molecular Simulation*, **34**[2] pp. 201-210(10) (2008).
 3. Krishnan R., Agrawal D., Dobbins T.A., “Microwave Irradiation Effects on Reversible Hydrogen Desorption in Sodium Aluminum Hydrides (NaAlH₄)”, *Journal of Alloys and Compounds*, **470** [1-2] pp 250 (2009).
 4. Dathara G. K. P.; Mainardi D.S., “Thermodynamic Profiles of Ti-Doped Sodium Alanates”, *J. Phys. Chem. C*, **113** pp. 15051-15057 (2009).
 5. Dathara G. K. P.; Mainardi D.S., “Kinetics of Hydrogen Desorption in NaAlH₄ and Ti-Containing NaAlH₄”, *J. Phys. Chem. C*, **114** pp. 8026-8031 (2010).
- One Ph.D. Dissertation and Two M.S. Thesis completed
 1. Gopi K. Phani Dathara, Ph.D in Engineering completed March 2009, Dissertation Title: “Computational Study of Pristine and Ti-doped Sodium Alanates for Hydrogen Storage Applications”. Dissertation citation found at: <http://gradworks.umi.com/33/58/3358248.html>. Dissertation Advisor: D. Mainardi.
 2. Edward Bruster, M.S. in Physics completed May 2007, Thesis Title: “Structure Determination for Transition Metal Doped Sodium Aluminum Hydride Using X-ray Absorption Fine Structure (XAFS) and Ultra-small Angle X-ray Scattering (USAXS)”. Thesis citation found at: <http://www.worldcat.org/title/structure-determination-for-transition-metal-doped-sodium-aluminum-hydride-using-x-ray-absorption-fine-structure-xafs-and-ultrasmall-angle-x-ray-scattering-usaxs/oclc/162132442>. Thesis Advisor: T. Dobbins.
 3. Rahul Krishnan, M.S. in Molecular Science and Nanotechnology completed in August 2008, Thesis Title: “Effects of Microwave Irradiation, Particle Surface Area, and Species Diffusion on the Reversible Desorption of Hydrogen from Sodium Aluminum Hydride”. Thesis citation found at: http://www.worldcat.org/search?q=Effects+of+Microwave+Irradiation%2C+Particle+Surface+Area%2C+and+Species+Diffusion+on+the+Reversible+Desorption+of+Hydrogen+from+Sodium+Aluminum+Hydride&qt=owc_search. Thesis Advisor: T. Dobbins.

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LIST OF ALL PERSONNEL INVOLVED IN THE PROJECT

Name	Title	Capacity of Involvement
Tabbatha Dobbins (10%)	Assistant Professor	Leading x-ray scattering and x-ray absorption spectroscopy
Daniela Mainardi (10%)	Assistant Professor	Leading DFT simulations
Yuri Lvov (5%)	Professor	Leading dopant chemistry
Amitava Roy (5%)	CAMD Staff, Ph.D.	Beamline scientist for x-ray absorption spectroscopy at CAMD
Phani G. Dathara (Full Support)	Ph.D. Degree Completed March 2009 (Engineering)	In charge of conducting quantum mechanical DFT calculations of $M^{x+}(AlH_4)^{-x}$ complexes within the GGA approximation, and investigated the effects of vacancies and Ti^{x+} dopants in bulk $NaAlH_4$ hydrides using Ab Initio Molecular Dynamics calculations. He is expected to continue with extended calculations paying particular attention to the hydrogen adsorption/diffusion/desorption kinetics.
Edward Bruster (Full Support))	M.S. Degree Completed May 2007 (Physics)	Thesis Title: Structure Determination for Transition Metal Doped Sodium Aluminum Hydride Using X-ray Absorption Fine Structure (XAFS) and Ultrasmall-Angle X-ray Scattering (USAXS)
Rahul Krishnan (Full Support)	M.S. Degree Completed August 2008 (Molecular Science and Nanotechnology)	In charge of USAXS data collection and data analysis (Graduating August 2007); Involved in Microwave irradiation for H_2 desorption.
William Harrison (6 hours per week)	Undergraduate (Chemical Engineering)	Dedicated to conducting DFT calculations on $M^{x+}(AlH_4)^{-}$ complexes at the B3PW91/6-311+G** theory level, and used the GGA approximation on some of the larger systems and bulk materials.
Dominic Andrews (6 hours per week)	Undergraduate (Chemical Engineering)	Dedicated to conducting DFT calculations on $M^{x+}(AlH_4)^{-}$ complexes at the B3PW91/6-311+G** theory level, and used the GGA approximation on some of the larger systems and bulk materials.
Ejiroghene (Ej) Oteri (10 hours per week)	Undergraduate (Mechanical Engineering)	Dedicated to SEM of hydrides and aids in USAXS data reductions and data analysis on co-doped series of samples.

UPDATE LIST OF OTHER SUPPORT (CURRENT AND PENDING, FEDERAL AND NON-FEDERAL.). None Related.

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Ultrasmall-angle X-ray scattering (USAXS) studies of morphological trends in high energy milled NaAlH₄ powders

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Abstract

Transition metal dopants added to complex metal hydrides, specifically to sodium aluminum hydride (NaAlH₄), by high energy ball milling enhances dehydrogenation kinetics and induces dehydrogenation reaction reversibility. This study uses the power-law scattering parameter, p , gained from ultrasmall-angle X-ray scattering (USAXS) data to elucidate differences in NaAlH₄ particle morphology as dopant type and mill time is varied. Four dopant types were used. Two dopant types were used to represent the best kinetic enhancements having high desorption rates (e.g. TiCl₂, TiCl₃) and were compared with two dopant types which do not perform as well (e.g. ZrCl₃ and VCl₃). USAXS data for the doped hydrides were compared with undoped and milled NaAlH₄ powders. Mill times used were 0 min (blended), 1, 5, and 25 min. As indicated by the USAXS power-law scattering data, the undoped NaAlH₄ powders are comprised of primary particles each having a high surface area. The high particle surface area in the undoped NaAlH₄ particle system persists as mill time increases—with only the 25 min sample undergoing a marked decrease in primary particle surface area. Alternatively, the doped powders milled for 1, 5, and 25 min show uniformly decreasing hydride particle surface area. These decreases in particle surface area may be explained by either the colloidal particles increasing in surface smoothness or decreasing internal void space. TiCl₃-doped NaAlH₄ powders show the trend of maintaining particles having a morphology comprised of higher particle surface area during the high energy milling stage of powder processing compared with other dopants.

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Keywords: Metal hydrides; Ultrasmall-angle X-ray scattering (USAXS); High energy ball milling

1. Introduction

Since the discovery of catalytic effects in transition metal doped sodium alanate (NaAlH₄) powders by Bogdanovic and Schwickardi [1], dopant effects in these powders has been studied in an effort to understand and optimize doping strategies to control kinetic barriers to hydrogen release from alanate powders [2–9]. X-ray absorption spectroscopy has been used to characterize the local environment of dopant cations in efforts to elucidate dopant effects [2–9]. In addition to understanding chemical effects of dopants, understanding the effect of the

doping process on powder morphology, specifically, controlling powder particle surface area, may be one key aspect which could lead to better control of dehydriding kinetic performance in these systems.

High energy ball milling is typically used to introduce MCl_x catalytic dopants – where M = transition metals such as Ti²⁺, Ti³⁺, V³⁺, and Zr⁴⁺ – into sodium alanate (NaAlH₄) powders. However, high energy ball milling both with and without dopant additions, is known to have pronounced effects on powder particle morphology. Such change in powder morphology, when studied by scanning electron microscopy, is not easily tractable due to the stochastic nature of the high energy milling process. Decrease in powder particle size is expected to occur during the high energy milling process. Typically, decreasing particle size results in an increase in powder surface area per unit volume. Additionally, surface area changes occurring in each alanate powder particle (i.e. porous or rough particles versus smooth

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Fig. 1. SEM images of the surface of an undoped NaAlH₄ powder particle blended for 2 min in dry N₂ glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

particle surfaces) will also affect the efficiency of the gas/solid desorption reaction occurring at the hydride particle surface,

Ultrasmall-angle X-ray scattering (USAXS) makes possible the parameterization of colloidal particle systems using the surface fractal dimension (D_s) extracted from the power-law scattering regime of intensity (I) versus scattering wave vector (Q) scattering data, where $|Q| = (4\pi/\lambda)(\sin \theta)$ and 2θ is scattering angle [10–15]. Power-law scattering data from surface fractals (i.e. dense colloidal particles having a high surface area contributed by either surface roughness or by internal particle void space) are characterized by $\log |I|$ versus $\log |Q|$ slopes (called power-law slope, p) between -3 and -4 [15]. These power-law slopes are related to powder particle surface area, S , through the parameter surface fractal dimension, D_s —whereby $D_s = p + 2D$ (with D being mass fractal dimension and $D = 3$ for colloidal particles). The surface fractal dimension, D_s , relates powder particle surface area to particle size R by the relationship: $S \sim R^{D_s}$. For rough particles the parameter, D_s , varies between 2 and 3 (D_s approaches 3 for high surface area particles). By this formalism, colloidal particles having a low surface area (i.e. smooth particles with no internal voids) are characterized by the measured power-law slope $p = -4$ and those having high surface area (i.e. rough particles having internal voids) are characterized by $p = -3$ [15].

Electron microscopy of sodium alanate powders reveals primary particle structures which have both high surface roughness (i.e. each particle is comprised of a set of smaller particles) and

internal void space (i.e. each particle is not a fully dense colloid). Understanding those particle morphologies using only scanning electron microscopy is challenging—particularly when the most valuable contribution of morphological studies is made when those morphologies are well enough characterized to track the behavior of the powder system as milling occurs or as dopant type is varied. Parameterization of USAXS data into power-law slope (p) enables the effects of dopant type, concentration, and mill time on powder morphology to be tracked. It bears noting that USAXS data is collected from a statistically significant

Fig. 2. USAXS data: undoped NaAlH₄ powders blended for 2 min in dry N₂ glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

population of powder particles (on the order of mg of powder is contained in each measurement).

2. Experimental

2.1. Materials preparation

Commercial sodium alanate powders (NaAlH_4) (Sigma–Aldrich Corp.) was blended with 2 mol% each of TiCl_2 , VCl_3 , and ZrCl_4 and with 4 mol% each of TiCl_2 and TiCl_3 . The dopant powders were purchased from Sigma–Aldrich Corp. Samples were blended under a dry N_2 glovebox environment using an agate mortar and pestle for 2 min and subsequently milled (Certiprep SPEX 8000M high energy mill) using a tungsten carbide vial containing 3 g of WC milling media for times of 1, 5, and 25 min. For USAXS measurement, the milled powders were sealed between 3 mm thick kapton films. Some of the milled powders were reserved for scanning electron microscopy (AMRAY 1830 scanning electron microscope). For reference, undoped NaAlH_4 powders were blended, milled and prepared for USAXS and SEM analysis.

2.2. Ultrasmall-angle X-ray scattering (USAXS)

Ultrasmall-angle X-ray scattering (USAXS) uses single crystal optics to extend the dynamic $\mathbf{Q}$ -vector range to lower values compared to standard SAXS

instruments and makes it possible to measure features above $1\text{ }\mu\text{m}$ in size [10–12]. Using 1D-collimated USAXS instrument (with only vertically collimating crystals) the data are slit smeared. Numerical desmearing routines are available for isotropic microstructures—yielding pin-hole collimated USAXS data [13,14]. While it is possible to fit power-law scattering to slit-smeared data and correctly obtain the fractal dimension, this can be done reliably only for data at Q values significantly lower than slit length; or data at Q values significantly higher than slit length, when the data are effectively 2D colimated even when Bonse–Hart geometry is used. However, around slit length (around $0.04\text{ }\text{\AA}^{-1}$ for current experiment) the data transition from slit smeared into 2D collimated geometries and fractal dimension cannot be established by simple fitting of the power-law slope to the data. While it is possible to develop analytical fitting function which accounts for slit smearing and slit length, we opted to first desmear the data using well established and tested method used routinely and reliably at the USAXS instrument and then power-law can be fitted anywhere in the whole Q range to establish fractal dimension [12]. We have verified on selected data sets, that when selected fitted Q range is reliably within slit-smeared Q range (for $Q \ll$ slit length) the fractal dimensions are (within fitting errors) the same as when fitted to desmeared data. Absolute calibration of the intensity versus $\mathbf{Q}$ -vector data makes USAXS viable for yielding scattered intensity data normalized per gram of powder.

USAXS data were collected at Sector 33ID at the Advanced Photon Source, Argonne National Laboratory (Argonne, IL) using an X-ray energy of 11 keV. The USAXS instrument has a large dynamic $\mathbf{Q}$ range in slit-smeared configura-

Fig. 3. SEM images of M^{x+}Cl_x -doped NaAlH_4 powders milled for 1 min where M^{x+} is (a) 2 mol% TiCl_2 ; (b) 4 mol% TiCl_2 ; (c) 4 mol% TiCl_3 ; (d) 2 mol% VCl_3 and 2 mol% ZrCl_4 .

tion ($1.5 \times 10^{-4} \text{ \AA}^{-1} < |Q| < 1 \text{ \AA}^{-1}$). The USAXS data is measured with a high Q resolution of $\sim 1.5 \times 10^{-4} \text{ \AA}^{-1}$. Data reduction and analysis routines were performed with IGOR PRO 5.0.3 using Irena version 1 and Indra version 2 sub-routines [13,14]. The absolute intensity calibration of the data was corrected for multiple scattering where observed. Multiple scattering influences data at low Q values and with intensities close to peak values. Observed peak broadening (expressed as FWHM) in the current experiment were between no broadening (no multiple scattering) and up to three times broader as compared to empty beam peak profile. Therefore the data below $Q \sim 10^{-3} \text{ \AA}^{-1}$ (which generally represents over two decades of intensity from the peak value) were not used for establishing the fractal dimension. This minimizes the chance that the data in tables are contaminated by multiple scattering.

3. Results and discussion

3.1. Morphology of undoped sodium alanate (NaAlH_4) powders

The complex particle morphology of undoped NaAlH_4 powders can be seen in the scanning electron microscopy images of Fig. 1 showing high magnification images of powder particle surfaces before milling (Fig. 1(a)) and after milling for 1 min (Fig. 1(b)), 5 min (Fig. 1(c)), and 25 min (Fig. 1(d)). Both before and after milling, the powder particle is comprised of high surface roughness and internal porosity—both factors contribute to high particle surface area. Clear delineation of, and comparisons among, these complex microstructures is not achievable using SEM images alone. The USAXS data shown in Fig. 2 were obtained from undoped NaAlH_4 powders. USAXS power-law slopes, p , were measured from the scattering curves in the Q -range from 0.0035 to $0.016 \text{ \AA}^{-1}$. For the various mill times of 0, 1, 5, and 25 min, the USAXS power-law slope, p , is given by -3.00 , -3.34 , -3.29 , and -3.55 indicating colloidal particles with a rough surface (or spongy porous particles containing internal pores or groves) for the p near to -3.0 and lower particle surface area as p approaches -4 . High energy milling has the effect of decreasing surface area of colloidal NaAlH_4 particles. For chemically homogeneous distribution of the dopant species, milling for times between 5 and 25 min are needed.

The as-purchased NaAlH_4 powders are comprised of small colloidal particles corresponding to a Guinier region having a radius of gyration of around $2\pi/Q = 21 \text{ nm}$ [10]. These particles disappear from the microstructure – either by attaching to larger particles or fusing together – during high energy milling. With respect to the particle surface roughness obtained using USAXS power-law slope, p , the undoped NaAlH_4 powders are characterized by particles having high surface roughness—indicated by a USAXS power-law slope, p , between at nearly -3 (for the unmilled powders). As mill time increases to 1 and 5 min, the USAXS power-law slope, p , approaches -3.33 , indicating a structural transition toward powder particles containing less internal surface. At the maximum mill time used for these studies—25 min, the USAXS power-law had a maximum value of -3.55 , indicating that NaAlH_4 particle morphologies are comprised of colloidal particles containing fewer internal surfaces as a result of high energy milling.

Fig. 4. USAXS data: 2 mol% TiCl_2 doped NaAlH_4 powders blended for 2 min in dry N_2 glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

3.2. Morphology of the $y \text{ mol\% } \text{MCl}_x$ -doped NaAlH_4 powders

The remainder of this work addresses the variations in USAXS power-law slope, p , as a means for tracking the NaAlH_4 particle surface area in the doped sodium alanate systems. Fig. 3 shows SEM of the surface of unmilled M^{x+}Cl_x -doped NaAlH_4 , where $\text{M}^{x+} = \text{TiCl}_2$, TiCl_3 , VCl_3 , and ZrCl_4 . In each case, the NaAlH_4 particles appear to be comprised of both surface roughness and internal porosity. USAXS data in Figs. 4–6 were collected from 2 mol% TiCl_2 -doped, 4 mol% TiCl_2 -doped and 4 mol% TiCl_3 -doped NaAlH_4 powders, respectively. USAXS data in Fig. 7 were collected from 2 mol% VCl_3 -doped NaAlH_4 powders. USAXS data in Fig. 8 were collected from 2 mol%

Fig. 5. USAXS data: 4 mol% TiCl_2 doped NaAlH_4 powders blended for 2 min in dry N_2 glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

Table 1

USAXS power-law (p) given by the slope of $\log(I)$ vs. $\log(Q)$ or $I-Q^p$

USAXS power-law exponent (p)	NaAlH ₄	NaAlH ₄ + 2 mol% TiCl ₂	NaAlH ₄ + 4 mol% TiCl ₂	NaAlH ₄ + 4 mol% TiCl ₃	NaAlH ₄ + 2 mol% VCl ₃	NaAlH ₄ + 2 mol% ZrCl ₄
0 min mill	−3.00	−3.10	−3.07	−3.38	−3.23	−3.33
1 min mill	−3.34	−3.26	−3.15	−3.14	−3.22	−3.22
5 min mill	−3.29	−3.38	−3.43	−3.18	−3.40	−3.43
25 min mill	−3.55	−3.45	−3.29	−3.57	−3.45	−3.30

Power-law slope behavior yields particle morphology information. For rough colloids the power-law slope, p , has values between -3 and -4 (p closer to -4 for smooth colloids and p closer to -3 for rough colloids). Variance was less than ± 0.024 .

Fig. 6. USAXS data: 4 mol% TiCl₃-doped NaAlH₄ powders blended for 2 min in dry N₂ glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

Fig. 7. USAXS data: 2 mol% VCl₃ doped NaAlH₄ powders blended for 2 min in dry N₂ glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

ZrCl₄-doped NaAlH₄ powders. For each of the USAXS curves, power-law slopes, p , were measured from the scattering curves in the Q -range from 0.0035 to 0.016 Å^{−1}. The USAXS power-law slopes, p , measured from undoped and doped NaAlH₄ powders are presented in Table 1.

USAXS data reveals that key trends exist between alanate particle morphology, powder milling time and dopant type. Fig. 9(a)–(c) contains the absolute value of USAXS power-law slope, $|p|$, data versus mill time for each powder system studied. Compared with the undoped NaAlH₄ system, all MCl_x dopant systems led to an average lower surface area for the colloidal particles comprising the system immediately following dopant additions for the unmilled powders (as indicated by a higher $|p|$ in Fig. 9). The initial increase in $|p|$ is possibly due to the addition of smooth colloidal dopant particles. After 1 min mill time, the undoped NaAlH₄ powders measured higher values of $|p|$ than the doped powders for each dopant type. This indicates that the early stage of doping results in an increase powder particle surface area, possibly due to porosity introduced by dopant assisted desorption H₂ gases. The highest dopant content—i.e. 4 mol% TiCl₂ dopant and 4 mol% TiCl₃ realized the lowest value of $|p|$ corresponding to the highest average particle surface area. After

Fig. 8. USAXS data: 2 mol% ZrCl₄ doped NaAlH₄ powders blended for 2 min in dry N₂ glovebox and milled for (a) 0 min; (b) 1 min; (c) 5 min; (d) 25 min.

Fig. 9. USAXS power-law slopes, p , for the $M^{3+}Cl_x$ -doped $NaAlH_4$ powders (a) the $Ti^{3+}Cl_x$ -dopants; (b) 2 mol% VCl_3 -dopant; (c) 2 mol% $ZrCl_4$ -dopant. The 4 mol% $TiCl_3$ -doped $NaAlH_4$ powders have the lowest surface area during high energy milling times up to approximately 15 min.

5 min mill time, the each doped $NaAlH_4$ powder system was comprised of particles each having a higher average surface area than the undoped powders milled for 5 min—with the exception of $TiCl_3$. The $TiCl_3$ -doped $NaAlH_4$ powders realized very high surface area for each colloidal particle for much longer mill times

(excess of 5 min). Anton provided kinetic performance data for the dopants investigated in the form of desorption rate after 5 min of desorption time: $TiCl_3$ (6.57 wt.%/h), $TiCl_2$ (3.98 wt.%/h), VCl_3 (1.80 wt.%/h), and $ZrCl_4$ (1.50 wt.%/h) [2]. It may be concluded that the ability for the powder to homogeneously distribute the MCl_x dopant species in order for it to chemically catalyze the H_2 desorption reaction, while maintaining a low $|p|$ (rougher particle surface) may be a key indicator dopant kinetic performance.

4. Conclusions

USAXS data has provided a practical approach to parameterize stochastic microstructures produced during high energy ball milling of doped and undoped $NaAlH_4$ powders. This approach could be applied to a wide variety of hydrogen storage materials in efforts to correlate processing, de/rehydrogenation, and doping effects on powder morphology. Here, USAXS data parameterized, using surface fractal analysis, shows that doped alanate powders decrease particle surface roughness with longer mill times. Compared to other dopants, $TiCl_3$ provides the highest powder particle surface area—corresponding to the lowest value of $|p|$ for 1 and 5 min mill times (and linearly extrapolated up to 15 min mill time as shown in Fig. 9(a)). Since 5 min mill processing is expected to produce homogeneous distribution of dopant, it is concluded that the best dopants will maintain rougher colloidal hydride particle surfaces during homogeneous dopant distribution.

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Structure and dynamics of Ti-Al-H compounds in Ti-doped NaAlH₄

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Structure and dynamics of Ti–Al–H compounds in Ti-doped NaAlH₄

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Structure and stability of pristine and modified NaAlH₄ are first investigated using density functional theory (DFT) with plane-wave basis and PW91 functional. Vacancy and Ti-dopant effects in the sodium alanate bulk, (001) surface, and on-top (001) surface are then studied considering Na and interstitial lattice sites. Calculated substitution energies of Ti-doped (001) NaAlH₄ surfaces have shown almost equal probability of substitution at both lattice and interstitial sites. Ti–Al–H complexes are formed depending on the accessible AlH₄ groups around the Ti dopant. TiAl₂H₇ and TiAl₂H₂ complexes are found after geometry optimising doped-NaAlH₄ surface models. Their stability and dynamics over time at 423 and 448 K are investigated using periodic density functional molecular dynamics (DFT-MD) simulations. Results have shown increased association of Al and H with the complexes as time evolves. DFT-MD simulations show evolution from TiAl₂H₇ to TiAl₅H₇ as time and temperature increase in case of Ti dopant at Na surface site (Ti → S_{Na}), and evolution from TiAl₂H₂ to TiAl₃H₆ at 423 K and TiAl₃H₇ at 448 K in case of Ti dopant on-top of the interstitial surface site (Ti → T_i) with time.

Keywords: titanium; dopant; sodium alanate; metal hydrides; diffusion

1. Introduction

Targets set by the United States Department of Energy (DoE) for the development of on-board storage materials include systems able to achieve a gravimetric hydrogen density of about 9 wt% and volumetric density ~81 kg/m³ by 2015, including reversibility of hydrogen storage and release [1]. Complex metal hydrides are considered promising hydrogen storage materials due to their potential for achieving the gravimetric and volumetric hydrogen storage densities set by the DoE [2]. However, the practical use of complex metal hydrides in transportation applications is currently limited by their slow hydrogen absorption/desorption kinetics and high temperatures for hydrogen release.

Sodium aluminium hydride (sodium alanate, NaAlH₄) is one of the most investigated light metal hydrides due to its high hydrogen content and ability to speed up the reversible hydrogen absorption/desorption kinetics by addition of transition metal dopants, such as zirconium, vanadium and in particular titanium through the incorporation of Ti-containing compounds, such as TiCl₃ [3–7]. Two hypotheses have been drawn from those studies. Either titanium forms a catalytically active complex with components of NaAlH₄, or it performs lattice substitutions with Na [7–10] or Al [11] or both [12]. When the formation of NaCl due to the titanium salt used is possible, experiments show that Na

sites are preferred by Ti dopant over Al sites since the overall energy required to replace Na by Ti is less compared to the energy required to replace Al by Ti [13]. This observation is consistent with the experimental work by Fichtner et al. [10], who reported preference of Ti dopants for Na over Al sites. In a recent XANES and EXAFS work by Baldé et al. [14] interstitial sites and sites on the hydride surface are reported to be the preferred ones for titanium. In spite of these observations, the preferred sites for Ti dopant in the NaAlH₄ lattice are still debated in the literature.

Besides preferred sites for Ti dopants, resulting compounds from ball milling with titanium salts and cycling at various temperatures are also extensively investigated, since they are believed to be responsible for the improved hydrogen desorption kinetics by Ti-doped NaAlH₄. DFT studies by Lee et al. [15] suggested that Na and Al substitution by Ti in sodium alanates is unfavourable; however, the formation of TiAl₃ is thermodynamically favourable. Experimental EXAFS studies by Chaudhuri et al. [16] also showed the formation of stable intermetallic species resembling TiAl₃. Brinks et al. [17,18] have showed the formation of a solid Al_{1-x}Ti_x solution with $x \sim 0.07$ after cycling at 160°C. Haiduc et al. [19] found an hcp-Ti(Al) solid solution after doping with TiCl₃, and an XRD-amorphous phase when NaAlH₄ was doped with Ti(OBu)₄. These authors have

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Figure 1. (a) Calculated ground state structure of NaAlH_4 unit cell atom colours: purple-sodium, magenta-aluminium and grey-hydrogen. (b) Electron density maps of slices parallel to X and Y axes in NaAlH_4 unit cell. The highest (max) and lowest (min) electron densities are blue and red, respectively. (c) Total (TDOS) of NaAlH_4 and partial (PDOS) density of states of Na, Al and H in NaAlH_4 .

also observed that the composition of those Ti compounds is temperature dependent. At temperatures up to 175°C an amorphous Al–Ti alloy is formed, while at temperatures higher than 200°C intermetallic phases of the Al_xTi form are present. Baldé et al. [14] also observed the formation of crystalline TiAl_3 after heat treatment at 475°C and amorphous TiAl_3 at 225°C . From all these studies, the presence of one or more phases of Ti–Al compounds is expected to tune the thermodynamics and kinetics of Ti-doped sodium alanates. Moreover, the surface morphology of the doped particles may also affect the kinetics of hydrogen desorption [20,21]. In spite of all experimental and theoretical investigations on this topic, the basic role of titanium dopant in the formation of key intermetallics for improved hydrogen kinetics by sodium alanates is still unknown.

In this work, lattice structure and stability upon Ti doping at different bulk, surface and interstitial sites in NaAlH_4 are first investigated using DFT with plane-wave basis. Formation of Ti–Al–H compounds are then identified and their dynamics investigated using periodic density functional molecular dynamics (DFT-MD) simulations in order to understand the temperature effect on titanium atom diffusion in the doped- NaAlH_4 following chemisorption.

2. Methodology

Generalised gradient approximation (GGA) calculations within the DFT formalism is used in this paper for the study of structure and stability of pristine and modified sodium alanates. The Perdew and Wang (PW91) functional [22] and plane-wave basis (PW) set with valence electrons described by Vanderbilt ultra-soft pseudopotentials (USPP), is employed in all the calculations as implemented in the module CASTEP[®] [23] of the Materials Studio[®] software by Accelrys, Inc. [24]. DFT using plane wave basis set with valence electrons described using USPP or projector augmented wave are commonly used to determine the structure and energetics of NaAlH_4 and Ti doped NaAlH_4 [11,13,15,16,25–31]. All the geometry optimisation calculations performed are spin-unpolarised. The cutoff energy is 400 eV with convergence criteria set at 2.0×10^{-5} eV atom⁻¹, and a k-point separation of $0.05 \text{ \AA}^{-1}$ on unit cells and super cells. Electron density maps as well as total and partial density of states plots are calculated for the systems under investigation.

In order to study the temperature effect on titanium atom diffusion in Ti doped- NaAlH_4 following chemisorption, DFT-MD simulations are conducted as implemented in CASTEP at 423 and 448 K. In DFT-MD, each step performs a classical molecular dynamics step with forces computed at the aforementioned GGA/PW91/PW-USPP theory level. NVT ensemble dynamics is used in this calculations considering a Nose–Hoover thermostat with a chain length of 7 (number of thermostats coupled to maintain the target temperature in the ensemble). With the wavefunction extrapolation scheme implemented in CASTEP[®], usually time steps in the order of 1 femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) provide good numerical stability and conservation of the constant of motion comparable to force field based molecular dynamics methods [32]. The time-step used for the simulations is 2 fs, and results from 2-ps simulations are reported here. The mean signed deviation in the constant of motion observed in our calculations is in the order of 4.5 kJ/mol.

3. Results

3.1 Structure of pristine NaAlH_4

A sodium alanate unit cell (Figure 1(a)) is built according to its tetragonal structure, which belongs to the $I41/a$ space group (#88) with sodium, aluminium and hydrogen atoms occupying the 4(a), 4(b) and 16(f) Wyckoff positions, respectively, with $x_{\text{H}} = 0.2662$, $y_{\text{H}} = 0.6084$ and $z_{\text{H}} = 0.0442$ [31]. Calculated DFT ground state NaAlH_4 lattice parameters and bond lengths (Table 1) are well in agreement with the values reported by Hauback et al. [33] from their neutron diffraction experiments.

Table 1. Calculated structural parameters of NaAlH₄ unit cell.

	Calc. (Å)	Expt. ^a (Å)
Lattice parameters	$a = b = 4.982$ $c = 11.149$	$a = b = 4.98$ $c = 11.15$
Na–Al	3.523	3.52
Al–H	1.612	1.63

^aFrom [32].

The NaAlH₄ electron density maps are shown in Figure 1b, where a coloured scale is used to quantify the electron density within the lattice (highest, blue and lowest, red). According to this scale, not only valence but also core electrons densities are represented and therefore, all atomic species are coloured blue. Figure 1(b) shows higher electron density within the AlH₄ groups than between Na atoms and AlH₄ complexes as expected for this crystal. From the NaAlH₄ total (TDOS) and partial (PDOS) density of states plots (Figure 1c), it can be noticed that the valence band of NaAlH₄ is mainly formed by contributions from the *s* orbital of hydrogen and the *p* orbital of aluminium, while the electronic states containing the *s* orbital of sodium are in the conduction band. The calculated band gap of the NaAlH₄ cell is 4.9 eV, which compares well with the value of 4.8 eV reported by Ozolins et al. [31].

3.2 Structure of modified NaAlH₄

In this section, vacancy and Ti-dopant effects in the sodium alanate bulk (Figure 2(a)), (001) surface (Figure 2(b)) and on-top (001) surface (Figure 2(c)) are studied considering Na and interstitial sites. Structure and energetics of pristine and modified NaAlH₄ models are presented and discussed in terms of bond lengths, TDOS, PDOS and cohesive (E_{coh}), substitution (ΔE_{subst}) and titanium-addition (ΔE_{add}) energies. Cohesive energy is defined as the difference between the energy of the total system and the sum of the individual atomic energies. The substitution energy per atom of Na by X (= vacancy

or Ti), ΔE_{subst} , is defined by Equation (1)

$$\Delta E_{\text{subst}} = \frac{E_{\text{coh}}(X\text{Na}_{n-1}\text{Al}_n\text{H}_{4n}) - E_{\text{coh}}(\text{Na}_n\text{Al}_n\text{H}_{4n})}{N}, \quad (1)$$

where N is the total number of atoms in the model, $n = 16$ for bulk substitution and $n = 8$ for surface substitution, respectively, according to the lattice models used. The energies per atom resulting from titanium-addition to interstitial and on-top surface sites, ΔE_{add} , is defined by Equation (2).

$$\Delta E_{\text{add}} = \frac{E_{\text{coh}}(\text{TiNa}_8\text{Al}_8\text{H}_{32}) - E_{\text{coh}}(\text{Na}_8\text{Al}_8\text{H}_{32})}{N}. \quad (2)$$

3.2.1 Bulk models

A $(2 \times 2 \times 1)$ supercell consisting of 16 NaAlH₄ units (Na₁₆Al₁₆H₆₄) with $N = 96$ atoms is built by extending the tetragonal $I4_1/a$ sodium alanate cell twice along the ‘*a*’ and ‘*b*’ lattice dimensions. A Na atom inside the NaAlH₄ bulk occupying the B_{Na} site (Figure 2(a)) is chosen to be removed (vacancy creation) or substituted by a Ti dopant. Hence, lattice models representing a vacancy at this Na bulk site ($0 \rightarrow \text{B}_{\text{Na}}$) and Ti in B_{Na} site ($\text{Ti} \rightarrow \text{B}_{\text{Na}}$) are constructed and geometry optimised using plane wave DFT techniques. Changes in structure and energetics due to vacancy ($0 \rightarrow \text{B}_{\text{Na}}$) and Ti dopant in NaAlH₄ bulk ($\text{Ti} \rightarrow \text{B}_{\text{Na}}$) are discussed in detail in our earlier paper [34]; however, the main conclusions are summarised here.

Calculations show that the lattice structure is preserved in both cases ($0 \rightarrow \text{B}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{B}_{\text{Na}}$), however, changes in bond lengths are seen mainly in the $\text{Ti} \rightarrow \text{B}_{\text{Na}}$ case (Table 2). The first row in Table 2 represents the average B_{Na} nearest neighbouring Al–X bond lengths, where X = Na (pristine), 0 ($0 \rightarrow \text{B}_{\text{Na}}$) and Ti ($\text{Ti} \rightarrow \text{B}_{\text{Na}}$); that is either the B_{Na} site is occupied by Na, left vacant or replaced by the Ti dopant. The native

Figure 2. Models of NaAlH₄ with different sites tested for Ti dopants. (a) Bulk: Na lattice site “B_{Na}” (b) Surface: Na lattice site “S_{Na}” and interstitial site “S_I” in the surface of NaAlH₄ and (c) sites “T_{Na}” and “T_I” on the NaAlH₄ surface. Purple, magenta and white/grey represent Na, Al and H atoms, respectively.

Table 2. Bond distances between Al and H with vacancy (0) and Ti dopant in bulk Na site (B_{Na}).

Bond lengths (Å)	Species in B_{Na} site		
	Na	0	Ti
Al	3.523	–	3.219
H	2.410	–	2.028
Al–H (nearest neighbours)	1.612	1.583–1.626	1.599–1.671
Na–Al (nearest neighbours)	3.523	3.477	3.400
Al–H (average, other than nearest neighbours)	1.612	1.611	1.606

Al–Na bond length 3.523 Å; however, when Na is substituted by Ti dopant the new bond length, Al–Ti, is decreased by ~ 0.3 Å. The second row in Table 2 represents the average B_{Na} nearest neighbouring H–X bond lengths ($X = Na, 0, Ti$). The calculated H–Ti bond length is ~ 2 Å, which is 0.4 Å shorter than the corresponding Na–H in pristine sodium alanate.

The third and fourth rows in Table 2 show values for the B_{Na} nearest neighbouring Al–H and Na–Al bond lengths. These Al–H bond lengths increased in the order of 0.06 Å for $Ti \rightarrow B_{Na}$, whereas a slight increase in this distance (by 0.014 Å) is found when $0 \rightarrow B_{Na}$. Significant decrease in the Na–Al bond lengths (~ 0.12 Å) compared to the Al–H distances is found when titanium substitutes Na in B_{Na} , where as the decrease in Na–Al distance when Na is substituted by a vacancy is in the order of 0.05 Å when compared to the pristine lattice. Finally, the fifth row in Table 2 represents the average Al–H bond lengths other than the B_{Na} nearest neighbouring distances in the AlH_4 groups. Relative to the Al–H bond lengths in pristine $NaAlH_4$, the corresponding distances decrease by 0.005 Å in the $Ti \rightarrow B_{Na}$ case and remain almost the same when $0 \rightarrow B_{Na}$.

All the structural differences found mainly when $Ti \rightarrow B_{Na}$ can be attributed to the difference in atomic radii of sodium (1.86 Å) and titanium (1.47 Å) atoms. The presence of titanium dopants replacing the native sodium sites B_{Na} results in a decrease of the lattice parameters, and shows changes in the distances between sodium and hydrogen as well as aluminium and hydrogen. Elongation and therefore weakening of

Al–H bond in the presence of a Ti at B_{Na} is observed and supported by calculations of density of states and electron density maps from the changes in the overall electronic structure [34]. Change in the electronic structure indicates possible formation of intermetallics such as Ti–Al and Ti–H compounds. From the cohesive energy calculations (Table 3) is seen that $Ti \rightarrow B_{Na}$ is 1.88 eV more stable than the pristine $NaAlH_4$, and the later is 6.85 eV more stable than the case in which a vacancy is created at B_{Na} ($0 \rightarrow B_{Na}$).

In order to get insights on Ti diffusion into the $NaAlH_4$ bulk, surface models of sodium alanate are built and Ti-substituted surface Na as well as Ti addition in surface interstitial sites, and on-top Na and interstitial surface site models are investigated and discussed in the next section.

3.2.2 Surface and on-top surface models

The (001) $NaAlH_4$ surface is investigated in this work. This surface is found to be closely packed and has the least surface energy compared to the $NaAlH_4$ (100), (101) and higher order crystallographic planes such as (110) and (112) [13]. In order to facilitate modelling of Ti doping on and above the (001) $NaAlH_4$ surface, a two-layer slab exposing the (001) $NaAlH_4$ crystallographic surface with a vacuum thickness of 5 Å is built by cleaving the $(2 \times 2 \times 1)$ supercell to expose the (001) crystal surface (Figure 3). The total system then consists of 8 $NaAlH_4$ units ($Na_8Al_8H_{32}$) containing $N = 48$ atoms.

Table 3. Cohesive energy relative to pristine system, E_{coh}^* , Ti-addition energy, ΔE_{Ti} and substitution (vacancy (0) $\rightarrow$ Na and $Ti \rightarrow Na$) ΔE_{subst} energy.

Site	Species in site	System	E_{coh}^* (eV)	ΔE_{Ti} (eV atom $^{-1}$)	ΔE_{subst} (eV atom $^{-1}$)
B_{Na}	Na	$Na_{16}Al_{16}H_{64}$	0.00		
	0	$Na_{15}Al_{16}H_{64}$	– 6.85		– 0.07
	Ti	$TiNa_{15}Al_{16}H_{64}$	1.88		0.02
S_{Na}	Na	$Na_8Al_8H_{32}$	0.00		
	0	$Na_7Al_8H_{32}$	– 6.68		– 0.14
	Ti	$TiNa_7Al_8H_{32}$	3.23		0.07
S_I	Ti	$TiNa_8Al_8H_{32}$	6.58	0.13	
T_{Na}	Ti	$TiNa_8Al_8H_{32}$	3.89	0.08	
T_I	Ti	$TiNa_8Al_8H_{32}$	3.46	0.07

Figure 3. Representative model for (001) NaAlH_4 surface with atoms labelled for reference. Test sites on surface (S_{Na} and S_{I}) as well as on top surface (T_{Na} and T_{I}) are shown.

Six different models are constructed to investigate vacancy creation and effects of Ti dopants. Test sites for substitution/addition of point defects (vacancy, Ti dopant) are designated as ' S_{Na} ' (Na lattice site in top layer) (Figure 2(b)), ' S_{I} ' (interstitial site between two Na lattice sites and two Al lattice sites in top layer) (Figure 2(b)), ' T_{Na} ' (site on top of S_{Na}) and ' T_{I} ' (site on top of S_{I}) (Figure 2(c)). Hence, the six models considered are $\text{Na} \rightarrow \text{S}_{\text{Na}}$ (pristine), $0 \rightarrow \text{S}_{\text{Na}}$ (vacancy creation on the surface at S_{Na} site), $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ (Ti-substituted Na at S_{Na}), $\text{Ti} \rightarrow \text{S}_{\text{I}}$ (Ti added to the interstitial surface S_{I} site), $\text{Ti} \rightarrow \text{T}_{\text{Na}}$ (Ti placed on-top the surface S_{Na} site), and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ (Ti placed on-top the surface interstitial S_{I} site).

Constructed models are geometry optimised and ground state conformations are shown in Figure 4 for the models considering titanium. The Ti dopant (red) at S_{Na} , $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ model (Figure 4(a)), settles between the surface and sub-surface layers forming bonds with hydrogen and aluminium atoms in surrounding accessible AlH_4 groups. This creates a distortion in the crystal lattice mainly due to the difference between ionic radii of titanium and sodium atoms. From the Ti local environment in the $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ model it is observed that the Ti atom coordinates to seven H atoms at distances in the 1.81–1.97 Å range, and two aluminium atoms at distances in the 2.6–2.7 Å range. Up to eight hydrogen and five aluminium atoms have been found at distances from the Ti dopant in the 1.84–2.00 Å and 2.61–3.40 Å ranges, respectively, in this case [13]. Since typical Ti–Al and Ti–H bond lengths in TiAl and TiH compounds such as TiAl_3 and TiH_2 are in the 2.7–2.9 Å [35] and in the order of 1.92 Å [35], respectively, the possible formation of a Ti–Al–H complex (TiAl_2H_7) is predicted

Figure 4. Optimised models of Ti doped NaAlH_4 surfaces with Ti dopant occupying different test sites ((a) S_{Na} , (b) S_{I} , (c) T_{Na} and (d) T_{I}).

in our calculations. In such complex, the calculated average distance between Ti dopant and the two nearest neighbouring Al atoms (Al2 and Al8) is 2.65 Å, and the seven nearest neighbouring hydrogen atoms is 1.9 Å in very good agreement with bond lengths in typical TiAl and TiH compounds.

The optimised $\text{Ti} \rightarrow \text{S}_{\text{I}}$ model (Figure 4(b)) shows that Ti dopant resides in the interstitial space right below the surface and forms a Ti–Al–H complex with neighbouring lattice Al and H atoms. From the Ti dopant local environment in this model it is observed that the Ti coordinates to five H and three aluminium atoms at distances in the 1.81–1.90 and 2.51–2.93 Å (average 2.75 Å) ranges, respectively. Hence, the possible formation of a TiAl_3H_5 complex is seen in the $\text{Ti} \rightarrow \text{S}_{\text{I}}$ case.

After placing the Ti dopant on-top the surface Na site, T_{Na} , ($\text{Ti} \rightarrow \text{T}_{\text{Na}}$ model, Figure 4(c)), it migrates to the T_{I} site during the geometry optimisation calculation. After optimisation is complete, the Ti dopant resides above the crystal surface and therefore, little distortion is introduced in the NaAlH_4 lattice structure. In this case, a more localised Ti–Al–H complex is formed. The Ti atom is coordinated to three hydrogen and two aluminium atoms at distances in the 1.74–1.86 and 2.50–2.75 Å ranges, suggesting the possible formation of a TiAl_2H_3 compound. Similarly in the case of $\text{Ti} \rightarrow \text{T}_{\text{I}}$ model (Figure 4(d)), the Ti dopant resides above the crystal surface and therefore, little distortion is introduced in the NaAlH_4 lattice structure. A TiAl_2H_2

Figure 5. TDOS and PDOS plots from optimised (a) pristine, (b) $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and (c) $\text{Ti} \rightarrow \text{T}_{\text{I}}$ models.

compound seems to form with Ti–H bond length of 1.73 Å and Ti–Al bond lengths in the 2.74–2.77 Å range.

From the cohesive energy calculations (Table 3), the cohesive energies of models $\text{Ti} \rightarrow \text{S}_{\text{Na}}$, $\text{Ti} \rightarrow \text{S}_{\text{I}}$, $\text{Ti} \rightarrow \text{T}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ are higher than to corresponding to pristine NaAlH_4 surface model, and therefore possible. In order to analyse the preferred sites for titanium dopants on the (001) NaAlH_4 surface, the energy required to perform $\text{Ti} \rightarrow \text{S}_{\text{Na}}$, $\text{Ti} \rightarrow \text{S}_{\text{I}}$, $\text{Ti} \rightarrow \text{T}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ with respect to the pristine case is calculated. Hence, the substitution energy Equation (1) for the $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ model and titanium-addition energies Equation (2) for the $\text{Ti} \rightarrow \text{S}_{\text{I}}$, $\text{Ti} \rightarrow \text{T}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ models are computed. Calculations show that the energy required for such substitution/addition is $\text{Ti} \rightarrow \text{S}_{\text{Na}} \approx \text{Ti} \rightarrow \text{T}_{\text{I}} < \text{Ti} \rightarrow \text{T}_{\text{Na}} < \text{Ti} \rightarrow \text{S}_{\text{I}}$ (Table 3). The difference between the energy required for $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ is 0.003 eV atom⁻¹, while the energy required for $\text{Ti} \rightarrow \text{S}_{\text{I}}$ is substantially higher than the corresponding one in the other three cases. Since the energy required for $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ is less compared to others, these two sites (S_{Na} and T_{I}) and probably T_{Na} would be preferred by the Ti dopants over S_{I} . However, occupation of the S_{I} sites by Ti dopant would be also possible at elevated temperatures due to increased supplied energy as well as diffusion of the dopants on the surface and/or into the lattice.

3.2.3 Density of states

Similar DOS plots are obtained for the optimised $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ models (Figure 5). Looking at the contributions from different atomic orbitals of Ti, Al and H species in doped- NaAlH_4 it is possible to elucidate the

particular Ti–Al–H complexes that form when $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ in NaAlH_4 take place. A shift in the Fermi level towards the conduction band is seen with introduction of Ti dopant in the lattice at both, S_{Na} and T_{I} sites. The calculated band gaps are, respectively, 1.00 and 0.93 eV in the $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_{\text{I}}$ models. The pristine NaAlH_4 TDOS plot (Figure 5(a)) shows contributions from the *s* orbital of hydrogen and the *p* orbital of aluminium. The TDOS and PDOS of the $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ model (Figure 5(b)) show that the energy states found right below the Fermi level are mainly formed by contributions from the *d* orbital of titanium, while in the case of $\text{Ti} \rightarrow \text{T}_{\text{I}}$ (Figure 5(c)), they are formed by contributions from the *d* orbital of Titanium and *p* orbital of aluminium.

In $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ model, Ti is coordinated to two aluminium and seven hydrogen atoms. Moreover, since the individual Al–H bond lengths increase with respect to the bonds in the pristine lattice (bond lengths in the AlH_4 groups are increased by 0.03–0.20 Å), the possible formation of a TiAl_2H_7 complex is suggested.

In the case of $\text{Ti} \rightarrow \text{T}_{\text{I}}$, Ti is coordinated to two aluminium and two hydrogen atoms, and since the individual Al–H bond lengths in the AlH_4 groups are increased (by 0.20 Å), the possible formation of a TiAl_2H_2 complex is predicted. Hydrogen atoms H3 and H8 (Figure 3) that were previously bonded to aluminium in pristine NaAlH_4 , have shown no significant interaction with Al after optimisation of the $\text{Ti} \rightarrow \text{T}_{\text{I}}$ model; Al–Ti and Al–H average bond distances are 2.75 and 1.77 Å in the TiAl_2H_2 complex, respectively.

From these studies we can conclude that the energy required to free the hydrogen atoms bound to AlH_4 groups in pristine NaAlH_4 is decreased due to introduction of titanium, resulting in the possible

Figure 6. Snapshots showing the time evolution of TiAl_2H_7 complexes in $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ model at two time steps from DFT-MD simulations at 423 and 448 K. Atom colours: Red (Ti), magenta (Al) and grey/white (H). Hydrogen atoms encircled in black represent number of hydrogen atoms associated with the complex as a result of hydrogen hopping from AlH_4 groups other than that are shown in the picture.

formation of TiAl_2H_7 and TiAl_2H_2 complexes with hydrogen atoms shared between Al and Ti. DOS of Ti doped NaAlH_4 of Ti–Al–H complexes, illustrates a possible catalytic role of Ti, i.e. lowering the formation energy of AlH_3 -type species and therefore, the barrier for H_2 desorption.

Our DFT results show that the complex observed in $\text{Ti} \rightarrow \text{T}_1$ model is a precursor to the complexes observed

in $\text{Ti} \rightarrow \text{S}_1$ and $\text{Ti} \rightarrow \text{T}_{\text{Na}}$ models when subjected to elevated temperatures. Hence, further analysis is concentrated on the Ti–Al–H complexes that are believed to form in the $\text{Ti} \rightarrow \text{S}_{\text{Na}}$ and $\text{Ti} \rightarrow \text{T}_1$ models. Thus, in next section, the dynamics of TiAl_2H_7 and TiAl_2H_2 complexes over time at different temperatures is discussed and insights into the diffusion of Ti dopants in the NaAlH_4 lattice are presented.

Figure 7. Same as Figure 6 for TiAl_2H_2 in $\text{Ti} \rightarrow \text{T}_1$ model.

3.3 Dynamics of Ti-doped NaAlH₄

The time evolution of TiAl₂H₇ (Figure 6) and TiAl₂H₂ (Figure 7) complexes after formed in Ti → S_{Na} and Ti → T_I models at 423 and 448 K are investigated with DFT-MD simulations. Initial total environment around dopant is shown in Figure 4a (TiAl₂H₇) and 4b (TiAl₂H₂), and subsequent pictures show the local complex environments at three different time intervals (0, 1 and 2 ps) at both temperatures in Figures 6 and 7, respectively. Different views are taken in Figures 6 and 7 with respect to Figure 4 for better visualisation of the complexes and association of aluminium atoms. In Figure 7 the atoms circled black represent hydrogen atoms that hop from neighbouring AlH₄ groups to dopant accessible AlH₄ groups.

From the results of DFT-MD simulations of Ti → S_{Na} model at 423 and 448 K, it is noticed that the Ti dopant settles between surface and subsurface layers and no further diffusion into the lattice is seen. The neighbouring six AlH₄ groups are drawn towards the Ti dopant, and increased association of aluminium atoms as well as hydrogen atoms with Ti is found after dynamics (Figures 6 and 7).

After 1 ps at 423 K, the number of aluminium atoms coordinating with titanium in the complex increase from two (at distances in the 2.6–2.7 Å range) to five (at distances in the 2.6–2.7 Å range). The number of hydrogen atoms (seven) coordinating with titanium are at distances in the 1.76–2.02 Å range, resulting in the possible formation of TiAl₅H₇ complex at 423 K after 1 ps. Besides the formation of a Ti–Al–H complex, Al–Al association (with a 2.97 Å bond length) is also seen from the DFT-MD results at this temperature. After 2 ps, no significant changes are observed in the complex except for the rearrangement of the Ti–Al–H complex with a Al2–Al8 bond length of 2.62 Å. All the other bond lengths remain unaltered.

When temperature is set to 448 K, no significant changes in the TiAl₅H₇ complex is seen over time. Rearrangement of Al and H atoms in this complex is however observed, but the number of hydrogen and aluminium atoms associated with the complex remains unaltered. The Al–Al distance reduces to 2.78 and 2.46 Å after 1 and 2 ps, respectively, at this temperature.

In the case of Ti → T_I model where the TiAl₂H₂ complex is formed, diffusion of dopant into the NaAlH₄ lattice is seen with temperature (Figure 7) through the top layer with final settling between surface and sub-surface layers. At 423 K and after 1 ps (Figure 7), the number of aluminium atoms coordinating with Ti dopant (at distances in the 2.57–2.76 Å range) increases from two to three and the number of coordinating hydrogen atoms (at distances in the 1.74–2.00 Å range) increase from two to six, resulting in the formation of a TiAl₃H₆

complex. After 2 ps at 423 K, the complex remains unchanged with rearrangement of associated aluminium and hydrogen atoms. Hydrogen hopping from one AlH₄ group to another is seen after 2 ps at 423 K.

At 448 K and after 1 ps, the Ti–Al–H complex is the same as the one found after 2 ps at 423 K (TiAl₃H₆). After 2 ps at this temperature, the coordinating aluminium atoms remain the same (at an average distance of 2.73 Å from Ti), and coordinating hydrogen atoms increased from six to seven (at distances from Ti in the 1.69–1.97 Å range), resulting in the formation of a TiAl₃H₇ complex.

The results on Ti → T_I at different temperatures suggest that the formed complexes are possible after diffusion of Ti dopants from the surface into the lattice, penetrating through the interstitial site on the surface (S_I). From this result it is expected that the Ti dopant placed initially at a T_{Na} site would diffuse on the surface and penetrate through the interstitial site based on aforementioned discussions.

4. Discussion

When compared to the presence of dopants in bulk and surface, NaAlH₄ with Ti dopants in bulk tends to be less stable than the case of NaAlH₄ with Ti dopants on its surface, as observed from the differences in cohesive energies of the different models presented here. From the cohesive energy point of view, Ti → S_I is the most stable conformation possible. Looking at the energy required to introduce dopants in the NaAlH₄ lattice through titanium substitution and titanium addition energies (ΔE_{subst} and ΔE_{add}), bulk substitution is favourable followed by Ti → S_{Na} and Ti → T_I. The first step for the dopant before substitution at the lattice site would be to adsorb on the surface and diffuse into the lattice. Hence, the preferred sites for Ti dopants to adsorb after initial mechanochemical milling process may be estimated by comparing the possible sites for surface substitution. From the constructed models to simulate the (001) NaAlH₄ surface doping, two possibilities of substitution at Na lattice site (Ti → S_{Na}) as well as substitution on top of interstitial site between two Na and two Al atoms (Ti → T_I) have equal probability since the energy required to do that is similar in both cases.

From DFT simulations it is found that the Ti dopant prefers to settle between the surface and subsurface layers in case of Ti → S_{Na} and Ti → S_I models, and on the surface in case of Ti → T_{Na} and Ti → T_I models. Optimised configurations with the Ti dopant placed at possible sites on the NaAlH₄ surface (T_{Na}, S_I and T_I) result in the same model after simulating dynamics at elevated temperatures. Formation of TiAl₂H₇ and

TiAl₂H₂ depend upon the accessible AlH₄ groups from the Ti local environment. These complexes are shown to weaken the Al–H bonds in AlH₄ complexes since the hydrogen atoms that were previously bonded only to an aluminium atom are now shared between the Ti dopant and aluminium atom. This effect would help in lowering the required energy for hydrogen desorption from the doped-NaAlH₄ lattice, facilitating hydrogen desorption by forming a multi-atomic complex.

Ti dopants replacing Na atoms would result in a complex with Ti surrounded by all the adjacent six AlH₄ groups in case of the NaAlH₄ lattice structure. This Ti dopant surrounded by six Al atoms can be interpreted as the reported Ti–Al solid solution observed after mechanochemical milling of NaAlH₄ and TiCl₃ [19]. Since the Ti dopants on the (001) NaAlH₄ surface also have equal probability, a more localised complex is seen in Ti → T₁, since Ti dopant has access to only two AlH₄ groups.

From the dynamics of the formed Ti–Al–H complexes at different temperatures, it is seen that Ti dopant prefers to reside between surface and subsurface layers with no further diffusion into the lattice irrespective of the surface model under consideration. After that diffusion process, mobility of AlH₄ groups is observed towards the Ti dopant, resulting in association of more Al atoms with Ti dopants over time at different temperatures. After 2 ps simulation, Ti forming bonds with five Al atoms and six hydrogen atoms in case of Ti → S_{Na} and three aluminiums and six hydrogen atoms in case of Ti → T₁ is seen. The Ti–Al–H complex in the case of Ti → S_{Na} model seems like a precursor to the phase with atomic Ti dispersed in aluminium. Complex observed in case of Ti → T₁ model seems like a precursor to the TiAl₃ phase, since association of Ti with three Al atoms is seen with a high covalent character in the formed Ti–Al bonds.

5. Conclusions

In this work, the role of titanium dopant in the formation of key intermetallics for improved hydrogen kinetics of sodium alanates is investigated using DFT with plane-wave basis and PW91 functional. The NaAlH₄ lattice structure and stability upon Ti-substituted bulk and surface Na sites, as well as Ti addition in surface interstitial sites and Ti on-top Na and interstitial surface sites are investigated. Equal probability of Ti dopant substitution at both lattice and interstitial Na sites in the (001) NaAlH₄ surface is found from substitution energies calculations. The composition of Al and H in the observed Ti–Al–H complexes depends on the accessible AlH₄ groups around the Ti dopant, and TiAl₂H₇ and TiAl₂H₂ are found to form after geometry

optimisation calculations. Periodic DFT-MD simulations are then conducted in order to understand the temperature effect on titanium atom diffusion on the doped-NaAlH₄ following chemisorption at 423 and 448 K. Results have shown the existence of the observed Ti–Al–H complexes as well as increased association of Al and H with the complexes as time evolves at both temperatures. The complexes observed after geometry optimisation represent the TiAl solid solution observed after ball milling of TiCl₃-doped NaAlH₄, and the complexes at elevated temperatures represent precursors to amorphous TiAl₃ and atomic Ti dispersed in aluminium, making this study consistent with experimental observations.

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Microwave irradiation effects on reversible hydrogen desorption in sodium aluminum hydrides (NaAlH₄)

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ABSTRACT

The effect of microwave irradiation on the reversible desorption reaction in sodium aluminum hydride (NaAlH₄) is explored. NaAlH₄ is doped with 2 mol% TiCl₂ and pre-activated by high energy ball milling and aging to show the presence of metallic aluminum phase. As a catalyst, Ti²⁺ has been used to improve desorption kinetics in sodium alanate. X-ray diffraction was performed on the samples exposed to microwave irradiation for 10, 20, 30, 40 and 50 min. Results show that when the powders show the presence of aluminum, a steady increase in the formation of the hexahydride (Na₃AlH₆) phase and Al occurs during microwave irradiation; and is accompanied by a steady reduction in the NaAlH₄ phase XRD peak (*hkl*) intensities. This data suggests that microwave irradiation drives the reversible H₂ desorption reaction in NaAlH₄. NaAlH₄ doped with 2 mol% TiCl₂ which does not show the presence of Al phase, undergoes a reduction in NaAlH₄ peak intensities with increasing microwave exposure (and no reversible product phases are detected in this case). Dielectric studies on NaAlH₄ indicate that microwave penetration is low. Therefore, it is proposed that microwave irradiation heating of the Al particulate phase is responsible for the hydrogen desorption reaction pathway which is similar to that of conventional heating.

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1. Introduction

Sodium aluminum hydride (NaAlH₄) has a crystalline structure wherein Al³⁺ is tetrahedrally coordinated by H[−] anions. Upon heating (to ~186 °C), H₂ gas is liberated in a reversible reaction making NaAlH₄ a viable candidate for on-board hydrogen storage [1–4]. The reversible hydrogen storage reaction has been well studied since its discovery by Bogdanovic and Schwickardi [1] in 1997. The desorption of H₂ from NaAlH₄ occurs by the two step reaction as follows:

In past few years, microwave processing of materials has realized many successes due to its rapid heating characteristics and non-thermal effects. Roy et al. have shown the advantage of microwaves over conventional heating in several studies, and have demonstrated the decrystallization of oxides under the effect of electric and magnetic microwave fields [5]. Microwaves can heat different states of matter to high temperatures in less time and pro-

duce superior sintered products, with higher densities and smaller grain sizes, compared to those processed by conventional heating. Presently, microwave processing is the most viable option for sintering of powders into highly dense bodies within minutes [6]. Additionally, researchers in the area of microwave processing of materials project efficient heating profiles with lower energy cost [7]. Sato et al. calculated the energy consumption for sintering traditional ceramics to 100% theoretical density using a microwave furnace and compared those values to the energy consumption for performing the same operations in a conventional furnace. Table 1 compares processing time and energy consumption of microwave versus conventional gas kilns. The microwave furnace achieved 100% theoretical density using one-fifth of the energy (kWh) relative to the conventional furnace. The main reason for the reduction in energy consumption in microwave furnaces is the reduced processing time [8]. The reaction pathways under microwave irradiation may be dramatically different compared to those driven by conventional processes. The rapid heating caused by microwave irradiation could also result in bypassing of certain intermediate product phases [9].

Recently, Nakamori et al. published a study of the dehydrogenation of some metal hydrides (LiH, NaH, MgH₂, CaH₂ and TiH₂) and alkali borohydrides (LiBH₄, NaBH₄ and KBH₄) via microwave irradiation [10]. It has been shown that microwave processing

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Table 1

Comparison between processing time and energy consumption of microwave and conventional furnaces for traditional ceramics

Performance comparison	Microwave (MW)	Conventional (CV)	Ratio (MW/CV)
Processing time (h)	2	8	1/4
Energy consumption (kWh)	63	335	1/5

These values were calculated by Sato et al. [8].

does drive the dehydrogenation process. However, in those experiments, microwave treatment tends to drive the metal hydrides into an amorphous state [10]. Fang et al. have reported a higher degree of microwave enhancement on the sintering properties of amorphous phases in alumina above enhancements observed in stable crystalline phases [11]. The Fang et al. study would suggest that microwaves couple more readily to disordered structures relative to ordered structures. In fact, microwaves may drive order-to-disorder reactions due to this coupling. For metal hydrides, loss of crystallinity under microwave treatment will affect the reversible nature of the desorption reaction, which is highly essential for on-board vehicular hydrogen storage applications. The work presented here reveals the processing conditions for the formation of reversible product phases after first step of the desorption reaction in NaAlH₄ driven using microwave irradiation.

2. Experimental procedure

For this study, sodium aluminum hydride (Sigma–Aldrich 90% technical grade) and titanium(II) chloride (Sigma–Aldrich 99.98% pure) were used. Mixtures of NaAlH₄ and 2 mol% TiCl₂ were prepared by high energy ball milling (HEBM) (SPEX Certiprep 8000M Miller) for 25 min, using tungsten carbide (WC) milling media and mill jar. One batch of the TiCl₂ catalyzed NaAlH₄ starting powder was prepared by HEBM only (called Batch 1), while the other was aged for 2 weeks in a dry N₂ glove box after HEBM until it showed the presence of metallic Al. The sample containing the metallic Al is said to be ‘pre-activated’ (and is called Batch 2). The ratio of the mass of the milling media to the mass of the powder was maintained at 1.25. For microwave experiments, 0.2 g of the starting mixture was loaded into small vials within a glove box and the vials were sealed under dry nitrogen atmosphere to prevent exposure of powders to air. Samples from Batch 1 and Batch 2 were processed using a 2 kW/2.45 GHz multi mode microwave furnace. Batch 1 was microwave treated for 30 and 60 min. Batch 2, the Al pre-activated NaAlH₄, was microwave treated for 10, 20, 30, 40 and 50 min. After microwave irradiation, the samples were characterized by X-ray diffraction (Rigaku Miniflex) to determine the product phases. Cu Kα₁ (1.54 Å) radiation was used. The step size for the scans was fixed at 0.1° (2θ) while the scan rate was 4°/min. MDI Jade (Version: 6.5.23) was used to analyze the X-ray diffraction data. Dielectric measurements were conducted on non-catalyzed, inactivated NaAlH₄ using HP 8510 Network Analyzer (Materials Research Laboratory, Pennsylvania State University). NaAlH₄ was packed into a coaxial cable. The input port (Port 1) of the network analyzer was connected at one end of the coaxial cable while the output port (Port 2) at the other end. In transmission mode, input is given at Port 1 and is output measured at Port 2 (S₂₁). In reflection mode, input is given at Port 1 and the output is also measured at Port 1 (S₁₁). Both modes were used for this study. Residual gas analysis (RGA) was performed on the microwave treated samples at 10, 20, 30, 40 and 50 min using a Stanford Research Systems QMS 200 Gas Analyzer.

3. Results and discussion

The dielectric loss of pure NaAlH₄ in a 2.45 GHz microwave field is not sufficient to drive the dehydrogenation reaction. Measurements show that the real permittivity of undoped NaAlH₄ is 4.077 while the loss factor is very low (1.16×10^{-3}). Fig. 1 gives the transmission and reflection losses on a logarithmic scale as a function of frequency ranging from 0 to 18 GHz. Negligible transmission losses indicate that microwave range frequencies can pass from Port 1 straight through NaAlH₄ to Port 2 without being absorbed by NaAlH₄. Reflection losses are relatively higher because of surface conduction in NaAlH₄ which is responsible for losses in the signal measured at Port 1. From these results, it is clear that the penetration of microwaves into pure NaAlH₄ is poor. When samples of pure

Fig. 1. (a) Negligible transmission losses due to low absorption of microwave frequencies in NaAlH₄ and (b) high reflection losses due to surface conduction in NaAlH₄.

NaAlH₄ are exposed to microwave radiation, no measurable weight loss was observed, i.e. no hydrogen is desorbed after the exposure. Therefore, the metal hydride samples were catalyzed with TiCl₂, a known catalyst for the dehydrogenation reaction [1–4,12] and, also, a material with moderate dielectric loss properties.

As mentioned earlier, one batch of catalyzed NaAlH₄ did not contain metallic Al phase in the precursor material (Batch 1). The X-ray diffraction patterns collected from Batch 1 powders are given in Fig. 2 for untreated, microwave treated for 30 min and microwave treated for 60 min samples. On exposure to microwaves for 30 and 60 min, no peaks corresponding to Na₃AlH₆ or Al are observed. However, the NaAlH₄ peak intensities steadily decrease with increasing microwave exposure time. This decrease in NaAlH₄ peak intensity is likely due to amorphization of the NaAlH₄ lattice. The NaAlH₄ peak at $2\theta = 29.7^\circ$, which is the strongest intensity NaAlH₄ peak, reduces in intensity with increasing microwave exposure time. The less intense peaks ranging between $2\theta = 74^\circ$ and $2\theta = 79^\circ$ nearly disappear completely after microwave exposure. These results are consistent with data reported by Nakamori et al. [10] wherein the amorphization of LiBH₄ is observed. Microwave treatment tends to cause loss in long range periodicity thus making the hydrides amorphous. This amorphization is a disadvantage to the deployment of microwave desorption from hydrides for systems where reversibility is a requirement. A strategy where a susceptor material, which heats readily upon microwave exposure, is included may improve the outlook for reversibility after microwave exposure. This is the case for Batch 2 powders (which contain metallic Al).

In order for microwave processing to impact hydrogen storage, it is imperative to identify reversible dehydrogenation compounds, such as Na₃AlH₆ and Al, to confirm that microwave exposure is facilitating the reversible desorption reaction first reported by Bogdanovic and Schwickardi [1]. Fig. 3 shows the phase progression in Batch 2 after different irradiation times—0, 10, 20, 30, 40 and 50 min. The samples are labeled as UnMW, MW_10, MW_20, MW_30, MW_40 and MW_50, respectively. Batch 2 powders were comprised of NaAlH₄ pre-activated with metallic Al. XRD analysis of the untreated sample (i.e. UnMW) (Batch 2) shows NaAlH₄

Fig. 2. X-ray diffraction pattern for Batch 1 powders (NaAlH_4 not activated with metallic Al). Shown inset is the intensity reduction in the NaAlH_4 peak at $2\theta \sim 29.6^\circ$ with microwave exposure times of 30 and 60 min. This peak intensity undergoes reduction with more time of microwave exposure.

and Al (Fig. 3). Na_3AlH_6 is also a decomposition product of NaAlH_4 . However, in trace amounts it is not detected by XRD. In general, a minimum of 1 vol.% of a phase is required for its detection by XRD. Trace amounts of Al are detected while Na_3AlH_6 are not detected by XRD because Na has a lower electron density than Al and since Na is the primary constituent in the hexahydride phase, the diffraction peak intensity from this phase is diminished below background. The work of Anton [12] showed that ball milling of as-received NaAlH_4 activates or partially dehydrogenates it. Gross et al. [4] showed that NaAlH_4 doped with 9 mol% of TiCl_3 , when milled for

3 h, results in the partial (%) decomposition of NaAlH_4 into Na_3AlH_6 and Al. HEBM and aging for 2 weeks activates our samples leading to the appearance of the Al decomposition phase. XRD data for the untreated sample (called UnMW) contains peaks that correspond to NaAlH_4 and two peaks at 2θ values of 38.602° and 44.811° corresponding to metallic Al. Ball milling also reduces the particle size in most powder systems and these particle size effects may also have an effect on the ability of materials to couple with microwaves. Lorensen and co-workers [13] studied the effect of particle size on the ability of carbon to absorb microwave heat and demonstrated

Fig. 3. X-ray diffraction patterns for Batch 2 powders which were pre-activated with metallic Al. XRD patterns are arranged in order of increasing time of microwave exposure. The symbols in the last pattern indicate presence of Na_3AlH_6 and Al phases only. At longer microwave exposure times, (40 and 50 min) Na_3AlH_6 and Al product phases exist while NaAlH_4 peaks are absent.

that the heating rate decreases with an increase in particle size. The Maxwell–Wagner model [14] describes the relaxation time in a capacitor with a two-layer dielectric. The relaxation time (τ) is a function of the permittivities (ϵ_1 , ϵ_2), conductivities (σ_1 , σ_2) and the dimensions (d_1 , d_2) of the two layers and is given by

$$\tau = \frac{\epsilon_1 d_2 + \epsilon_2 d_1}{\sigma_1 d_2 + \sigma_2 d_1} \quad (2)$$

Based on the Maxwell–Wagner model, we can infer that for a given material with given permittivity, conductivity and dimensions, penetration will be best at lower microwave frequencies. Otherwise, it may be possible to achieve good penetration at higher frequencies by reducing the particle size i.e. affecting d_1 and d_2 . Thus, in the case of hydrides, it is expected that reduction of the particle size will result in greater polarizability, higher dielectric constant and thus more microwave penetration into the bulk of particles.

To quantify phases driven by the reaction, we have performed a relative peak intensity analysis (reported in Table 2). Two NaAlH_4 peaks ($2\theta \sim 30^\circ$ and $2\theta \sim 60^\circ$), two Na_3AlH_6 peaks ($2\theta \sim 32^\circ$ and $2\theta \sim 58^\circ$) and two Al peaks ($2\theta \sim 39^\circ$ and $2\theta \sim 45^\circ$) were chosen

for this analysis. The ratios of the peak intensities of Na_3AlH_6 to NaAlH_4 and Al to NaAlH_4 were calculated for each pattern. As the reaction proceeds, it is expected that the intensity ratios should increase because Na_3AlH_6 and Al should increase in quantity and NaAlH_4 should decrease as the reaction proceeds with microwave exposure. These ratios increase with increasing microwave time showing that the desorption process continues over the duration of microwave exposure. NaAlH_4 peaks at $2\theta \sim 30^\circ$ and $2\theta \sim 60^\circ$ vary from 100% to 28.1% intensities, respectively, in the untreated sample (UnMW) pattern to 0% in MW.40 and MW.50. Na_3AlH_6 ($2\theta \sim 58^\circ$ and $2\theta \sim 32^\circ$) has 0% intensity in UnMW, but its intensity increases progressively with irradiation time to reach 93.9% and 27.6%, respectively in MW.50. Al peaks ($2\theta \sim 39^\circ$ and $2\theta \sim 45^\circ$) vary from 34.5% to 15.4% intensity in control sample (i.e. UnMW) to 100% and 50.5% in MW.50. Whenever the NaAlH_4 peaks diminish to zero intensity, the peak intensity ratio goes to infinity, as indicated by ∞ in Table 2. This data confirms that NaAlH_4 is gradually converted into Na_3AlH_6 and Al releasing hydrogen by the reversible dehydrogenation reaction of step 1 in Eq. (1). Relatively small NaAlH_4 peaks at $2\theta = 51.6^\circ$, 55° , 60.5° , 61.8° , 75.8° have all diminished in successive diffraction patterns with increasing irra-

Table 2
Ratio of product to reactant XRD peak intensities

Ratio of product: reactant X-ray diffraction intensities	Na ₃ AlH ₆ ($2\theta \sim 32^\circ$): NaAlH ₄ ($2\theta \sim 30^\circ$)	Na ₃ AlH ₆ ($2\theta \sim 58^\circ$): NaAlH ₄ ($2\theta \sim 60^\circ$)	Al ($2\theta \sim 45^\circ$): NaAlH ₄ ($2\theta \sim 30^\circ$)	Al ($2\theta \sim 39^\circ$): NaAlH ₄ ($2\theta \sim 30^\circ$)	Sample weight loss (g)
UnMW	0	0	0.154	0.345	0
MW_10	0.433	0.332	0.175	0.349	0.0020
MW_20	2.198	1.484	1.205	2.311	0.0030
MW_30	14.206	∞	7.897	14.706	0.0037
MW_40	∞	∞	∞	∞	0.0024
MW_50	∞	∞	∞	∞	0.0033

These ratios are increasing with increasing microwave exposure time due to formation of Na₃AlH₆, Al and consumption of NaAlH₄. Also indicated is the weight loss in each sample. The initial weight of all samples was 0.2 g. The theoretical weight loss for H₂ liberated from the 0.2 g samples in step 1 of the NaAlH₄ decomposition reaction is 0.0074 g.

diation time. At $2\theta = 77.9^\circ$, a line marker for Na₃AlH₆ falls between the two NaAlH₄ peaks in the UnMW pattern. At close inspection, the MW_20, MW_30, MW_40 and MW_50 samples contain a very low intensity X-ray peak at $2\theta = 77.9^\circ$ corresponding to this line. At the longest exposure times, the NaAlH₄ peaks all disappear and the sample exhibits peaks corresponding to only Na₃AlH₆ and Al phases.

Table 2 contains gravimetric analysis data (weight loss) for Batch 2 powders microwave treated for 10, 20, 30, 40 and 50 min. In all cases, the initial sample weight was 0.2 g. An increase in weight loss during microwave exposure is observed. Fig. 4 shows this trend graphically (in terms of hydrogen loss). Fig. 5 shows residual gas analysis (RGA) for hydrogen desorbed from the sample during microwave exposure. The hydrogen composition (in %) is relative to the hydrogen content in the gas stream of the measurement assembly apparatus feed lines, which included N₂ and H₂O. Hydrogen was the third most abundant gas detected by the RGA (with N₂ most abundant $\sim 80\%$, followed by H₂O and CH₄). The presence of other gases in the RGA measurement is indicative that the 0.2 g NaAlH₄ sample releases a H₂ volume which is relatively low (maximum content 9.3%) compared to the volume of the apparatus feedlines. The low content of O₂ (approximately 1%) indicates that desorbed H₂ reacted with O₂ in air to form H₂O (maximum content 13%). Data which reveals an upward trend in weight loss with microwave exposure time occurs from 0 to 30 min (Fig. 4). This is an important observation along with XRD data, because gravimetric and RGA data specify hydrogen gas losses. The presence of only Na₃AlH₆ and Al

decomposition phases in the XRD patterns of the microwave treated samples shows that hydrogen is desorbed during the first step in the reaction in Eq. (1). The hydrogen weight loss calculated based on 3.7 wt% [3] hydrogen release during step 1 in the desorption reaction (Eq. (1)) is 0.0074 g (for the 0.2 g samples). The sample which was microwave heated for 30 min lost 0.0037 g (approximately, 50% of the theoretical hydrogen loss). Fig. 5 shows that the amount of H₂ desorbed decreases with increasing microwave exposure time. This data is entirely consistent with the 0 to 30 min gravimetric data (Fig. 4) which shows a decreasing desorption rate with increasing microwave exposure time. The departure of the 40 min sample from the general trend of weight loss with increasing microwave exposure time (Fig. 4) cannot be explained at this time.

Two phenomena are observed during the exposure of TiCl₂ doped NaAlH₄ to microwave irradiation. In Batch 1 powders, metallic Al phase is absent from the starting powders or the untreated sample. These samples show a tendency to lose crystalline nature (amorphize) on exposure to microwave radiation. The electromagnetic field in the microwave furnace tends to transform the metal hydride from a stable crystalline phase to a thermodynamically unstable amorphous phase [11]. This is consistent with results shown by Nakamori et al. [10] wherein hydride powders become amorphous upon microwave exposure. In those studies, the desorption reaction efficiency is increased after microwave driven dehydrogenation [10]. Batch 2 on the contrary shows the presence of metallic Al phase in the untreated sample. Here, we clearly detect the reversible product phases of Na₃AlH₆ and Al. Amounts of those phases increase with increasing microwave exposure time.

Fig. 4. Samples weight loss as a function of increasing microwave exposure time. An upward trend in weight loss is seen. The horizontal at 0.0074 g indicates the theoretical hydrogen weight loss for the 0.2 g samples used in this study. Standard deviation on the measurement process is ± 0.00014 g (determined using 2X repeated measurements).

Fig. 5. Residual gas analysis (RGA) showing the composition (%) of liberated H₂ at 10, 20, 30, 40 and 50 min relative to other gases (e.g. N₂, H₂O, CH₄ and O₂) in the measurement assembly.

Possibly, under the microwave irradiation, the metallic Al phase couples to microwave irradiation to produce sample heat up resulting in increased atom mobility in the NaAlH₄ phase—an effect that would tend to counter a microwave driven amorphization reaction in the NaAlH₄ phase. This, in turn, could drive the desorption reaction of NaAlH₄ with a reaction pathway similar to that observed under conventional heating conditions. Detection of reversible product phases in a microwave driven reactions is key to ensuring reversibility in microwave irradiation driven desorption processes.

Another interesting phenomenon observed in these studies is the splitting of NaAlH₄ peaks after microwave treatment. This possibly indicates strain in the NaAlH₄ lattice structure. This lattice strain may be related to the diffusion of hydrogen out of the lattice. This residual strain may also indicate onset of amorphization of the NaAlH₄ crystalline phase by microwave irradiation. Doublet peaks or splitting of the peaks [15] in the NaAlH₄ phase are a common phenomenon observed among the microwave treated samples from Batch 2. This could be attributed to residual stress in the crystallographic structure of NaAlH₄ due to atom vibrations influenced by microwave irradiation. The second peak in the NaAlH₄ structure reveals at a decreased lattice parameter, indicating that the crystal may have undergone loss of interstitial H[−] (i.e. H₂ desorption) without structure transformation to Na₃AlH₆ and Al.

4. Conclusions

Microwave assisted dehydrogenation of NaAlH₄ doped with 2 mol% TiCl₂ has been carried out in the absence (Batch 1) and presence (Batch 2) of metallic Al phase in the starting material. Microwave exposure of Batch 1 resulted in NaAlH₄ becoming amorphous. Presence of metallic Al in the untreated sample (Batch 2) shows the reversible product phases, Na₃AlH₆ and Al on microwave exposure. The presence of these phases confirms the reversible nature of sodium aluminum hydride under microwave assisted dehydrogenation. Further research is needed to understand the thermodynamics and kinetics of the microwave assisted dehydrogenation reactions. The condition for retention of crystalline nature of other metal hydrides under microwave irradiation is

also worth exploring in future studies. This will determine the conditions for which microwave irradiation can be used as a dehydrogenation/processing technique to achieve higher levels of energy efficiency for on-board hydrogen storage systems. Ultimately, energy efficiency through the use of microwaves may be addressed and may result in a new technology for on-board vehicle hydrogen storage applications. Future work will also include microwave assisted hydrogen absorption on NaAlH₄ to further test the viability of these systems in cyclic applications.

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Thermodynamic Profiles of Ti-Doped Sodium Alanates

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Pathways leading to TiAl_3 or intermediate phase formations that result and take part in dehydrogenation by Ti-doped NaAlH_4 are not completely understood. Hence, six possible thermodynamic reaction pathways in Ti-doped sodium alanates for the formation of Ti–Al alloys and release of hydrogen are studied in this work at the generalized gradient approximation level within the density functional theory formalism. From all the possible reaction pathways, the one suggesting the formation of the aluminum hydride, TiAl , and metallic Ti phases as intermediates with hydrogen evolution after each intermediate step is found to be the most favorable thermodynamic path for hydrogen desorption in Ti-doped sodium alanates. Results from this work suggest a three-step reaction pathway to the formation of TiAl_3 and aluminum in its +3 oxidation state present in aluminum hydride species responsible for the formation of Ti–Al alloys.

Introduction

Sodium aluminum hydride (sodium alanate, NaAlH_4) is one of the most investigated light metal hydrides since the pioneering work by Bogdanovic et al.¹ The decomposition of sodium alanate to release hydrogen is known to proceed through a two-step reaction mechanism, resulting in the formation of Na_3AlH_6 and aluminum phases in the first step (eq 1) and NaH and aluminum phases in the second step (eq 2). As a result, the total hydrogen desorbed from the undoped sodium alanate adds up to 5.6 wt %.

Bogdanovic et al.¹ and Gross et al.² have demonstrated reversible hydrogen storage in sodium alanates with the ability to accelerate the reversible hydrogen adsorption/desorption kinetics by the addition of transition-metal compounds, such as titanium. Furthermore, the temperature required for hydrogen desorption from Ti-doped sodium alanates was found to be reduced to near room temperatures ($\sim 33^\circ\text{C}$).^{1–3} Anton⁴ has demonstrated that, particularly, titanium salts, such as TiCl_3 , are the best catalysts/doping agents compared to other transition-metal salts. Since then, extensive experimental^{4–20} and theoretical^{6,21–29} studies are done that shed light on various phenomena, including formation of solid Ti–Al, TiAl_3 alloy, as well as Ti–Al–H compounds, along with Al clustering; however, a clear understanding of the thermodynamic profiles of hydrogen desorption in Ti-doped sodium alanates is still lacking.

In situ X-ray diffraction studies by Gross et al. in 2000² and 2002¹⁹ have shown the formation of the metallic Al phase after ball milling NaAlH_4 with TiCl_3 . These authors also reported the presence of the metallic Al and Ti phases accompanied by the partial dehydrogenation after high-energy ball milling of Ti salts with NaAlH_4 , a fact that was not observed during ball

milling of NaAlH_4 alone.^{2,19} Mazjoub et al.¹³ have found, from their X-ray diffraction (XRD) experiments, the products NaCl , TiAl_3 , and gaseous hydrogen upon heating Ti-doped sodium alanates. Weidenthaler et al.,¹² from XRD studies, also reported the formation of TiAl_3 alloy at elevated temperatures succeeding the product phases of metallic Ti and Al. Leon et al.⁷ and Dobbins et al.³⁰ have also shown the reduction of Ti^{3+} to Ti^0 after the high-energy ball milling of NaAlH_4 with TiCl_3 . From all the aforementioned experimental findings, the following two conclusions can be drawn. The TiAl_3 formation seems to be preceded by the metallic Ti and Al phases, and the source of aluminum for the formation of TiAl_3 is Al in its metallic state.

Brinks et al.¹⁰ have showed the formation of a solid $\text{Al}_{1-x}\text{Ti}_x$ solution with $x \sim 0.07$, ultimately leading to the formation of TiAl_3 at elevated temperatures. This observation is further supported by Haiduc et al.,⁸ reporting an hcp $\text{Ti}(\text{Al})$ solid solution after doping with TiCl_3 and an XRD-amorphous phase after doping with $\text{Ti}(\text{OBu})_4$. These authors have also found that the composition of those Ti compounds is temperature-dependent. At temperatures up to 175°C , an amorphous Al–Ti alloy is formed, whereas at temperatures higher than 200°C , intermetallic phases of the Al_xTi form are present. Balde et al.⁵ also observed amorphous TiAl_3 alloys at temperatures below 225°C and crystalline TiAl_3 after heat treatment at 425°C . These observations report metallic Ti and Al and solid TiAl phases to precede the formation of TiAl_3 .

Titanium nanoclusters as doping agents have been also used by Fitchner et al.¹⁶ to investigate the thermodynamic profiles of hydrogen desorption by titanium-doped sodium alanates. The authors have shown no intermediate phases related to TiAl or TiAl_3 but reported reduced temperatures of hydrogen desorption from sodium alanates in the presence of those Ti nanoclusters. Recent XPEEM studies by Dobbins et al.³¹ reported Al in its +3 oxidation state in the vicinity of Ti^0 regions after ball milling for 5 min, resembling the aluminum in NaAlH_4 rather than a metallic aluminum phase. These authors³¹ reported that the Al in its +3 oxidation state is responsible for the formation of Ti–Al alloys. Our previous theoretical calculations²¹ suggested that species resembling alanes (AlH_3) and TiAl compounds

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precede the formation of TiAl_3 and that Al in its +3 oxidation state present in AlH_3 seems to react with Ti to form TiAl and TiAl_3 .

The current state of knowledge, therefore, suggests that the formation of TiAl_3 species is evident and stoichiometrically favorable from the atomic compositions of titanium and aluminum in Ti-doped NaAlH_4 . However, the pathways leading to TiAl_3 formation or the intermediate phases that result and take part in dehydrogenation reactions are not completely understood. Despite all experimental and theoretical investigations on this topic, the basic role of titanium dopant in the formation of key intermetallics is unknown, and the source of aluminum responsible for the TiAl alloy formation is still unidentified.

Two sets of thermodynamic pathways for hydrogen desorption from undoped and Ti-doped sodium alanates are investigated in this paper. The first set of pathways (eqs 6 and 9) follows the reported two-step decomposition reaction¹ to yield hydrogen from undoped NaAlH_4 . The enthalpy of the reactions and the temperature for transition from reactants to products (reaction temperature where the change in free energy is equal to zero) are predicted from our calculations and compared with the reported experimental values. The second set of reaction pathways (eqs 10a and 11a) proposed in this paper includes the resulting phases that are observed to be possible upon doping sodium alanates with TiCl_3 or titanium nanoparticles. On the basis of the various explored thermodynamic reaction pathways, the most favorable one is identified, explained, and suggested in this paper.

Computational Details

The generalized gradient approximation (GGA) within the density functional theory (DFT) formalism is used for the investigation of thermodynamic reaction pathways for hydrogen desorption in Ti-doped sodium alanates. Solid structures in this study are optimized using the Perdew and Wang (PW91) functional³² and plane wave (PW) basis set. The valence electrons are described by Vanderbilt ultrasoft pseudopotentials (USPP) or norm-conserving pseudopotentials, and all calculations are performed as implemented in the CASTEP³³ module in the Materials Studio software by Accelrys, Inc.³⁴ DFT using plane wave basis set or projector-augmented waves is commonly used to determine the structure and to study the electronic as well as material properties of NaAlH_4 and Ti-doped NaAlH_4 .^{6,22–25,28,35–39}

Evaluation of the vibrational properties for estimating the thermodynamic properties at different temperatures using the direct force constant approach is reported for the pure crystal structures of NaAlH_4 and Na_3AlH_6 , as well as their corresponding decomposition reactions.²⁶ The direct force constant approach⁴¹ (also known as finite displacement/supercell method) calculates the forces on atoms by inducing small displacements from their mean positions. A force constant cutoff is, therefore, used in the calculations beyond which the forces on the atoms are assumed to be zero. Limitations in the direct force constant method include artificial increase in supercell dimensions to accommodate the decay of the potential to near zero.⁴² The limitations in this method often result in a significant deviation in the calculated versus experimental properties, such as the temperature of hydrogen desorption.²⁶ As an effort to provide more realistic predictions of observable properties at the macro scale, in this paper, the thermodynamic relations explaining the two-step decomposition of sodium alanate resulting in hydrogen desorption are studied using the density functional perturbation

theory (DFPT) or linear response.⁴² The lattice dynamics using the DFPT formalism is calculated by minimizing the second-order perturbation in the total electronic energy of the system. The force constant matrix thus depends on the ground-state electron charge density and on its linear response to a distortion of atomic positions, which is calculated by differentiating the Hellmann–Feynman forces on atoms, with respect to the ionic coordinates.⁴²

Calculation of the vibrational properties of crystalline structures is performed by computing the phonon density of states (DOS) using the linear response and the finite displacement/supercell methods as implemented in CASTEP. In CASTEP, the linear response method is only implemented for the insulators and with a restriction of using norm-conserving pseudopotentials. For calculation of phonons using the linear response method, compounds with band gaps greater than 1 eV are optimized using norm-conserving pseudopotentials with the energy cutoff set at 900 eV. The electronic parameters for phonon calculations are consistent with the geometry optimization calculations. In the linear response method, the phonon dispersion relations and the phonon density of states are evaluated on a coarse/medium k-point grid and are interpolated onto a finer grid with a k-point grid spacing of $0.04 \text{ \AA}^{-1}$. In the case of metals (band gaps less than 1 eV), the USPP and direct force constant approach are used. The supercells sized greater than $10 \times 10 \times 10 \text{ \AA}$ are constructed from the optimized unit cell models, and the phonon DOS is evaluated at the Γ point only. To be consistent in evaluation of the enthalpies and free energies, the electronic energy is taken from the geometry optimization calculations using norm-conserving pseudopotentials at 900 eV cutoff (for all compounds), and free energy contributions are taken from the appropriate calculated models. The vibrational properties are estimated by applying the appropriate technique (linear response or direct force constant). The linear response method is used for the models with a band gap greater than 1 eV (NaAlH_4 , Na_3AlH_6 , NaH , NaCl , and AlH_3), and the direct force constant approach is applied for the models that are metallic with no band gaps or band gaps less than 1 eV (Ti^0 , TiAl , TiAl_3 , and Al^0).

Results

1. Decomposition of Sodium Alanate. To estimate the macroscopic thermodynamic observables of the decomposition reactions of sodium alanate, such as the enthalpy, the Gibbs free energy, and the desorption temperature, the structures of the reactants and products are geometry-optimized and electronic and vibrational properties are calculated, as explained in the Computational Details. The Gibbs free energy of the reaction (ΔG°) and the enthalpy of the reaction (ΔH°) are calculated by taking the difference between the respective properties of products and reactants (weighted by their stoichiometric coefficients) when each is in its standard-state pressure, but at the system temperature. The thermodynamic properties of each compound are computed from the simulation outputs according to the eqs 3–5.

$$G(T) = H(T) - TS \quad (3)$$

$$H(T) = U(T) + PV \quad (4)$$

$$U(T) = U_0 + U_{\text{ZPE}} + U_{\text{VIB}} + U_{\text{TRANS}} + U_{\text{ROT}} \quad (5)$$

where G , H , and S are the free energy, enthalpy, and entropy, respectively. The total internal energy, U , is obtained by adding

TABLE 1: Calculated Lattice Parameters of NaAlH₄, Na₃AlH₆, and Al. DFT (GGA) Calculations of NaAlH₄ and Na₃AlH₆ from ref 39, Single-Crystal X-ray Diffraction Values for NaAlH₄ from ref 40, X-ray Refinement and Neutron Powder Diffraction Values for Na₃AlH₆ from ref 39, and Experimental Values for Aluminum from ref 43 are Shown for Comparison

unit cell	ultrasoft pseudopotentials	norm-conserving pseudopotentials	DFT ³⁹ (GGA)	exptl (refs 39, 40, 43)
NaAlH ₄	$a = b = 4.99$ $c = 11.08$ $\alpha = \beta = \gamma = 90$	$a = b = 4.99$ $c = 11.35$ $\alpha = \beta = \gamma = 90$	$a = b = 4.99$ $c = 11.07$ $\alpha = \beta = \gamma = 90$	$a = b = 5.02$ $c = 11.33$ $\alpha = \beta = \gamma = 90$
Na ₃ AlH ₆	$a = 5.36$ $b = 5.54$ $c = 7.72$ $\alpha = \gamma = 90$ $\beta = 89.90$	$a = 5.37$ $b = 5.56$ $c = 7.75$ $\alpha = \gamma = 90$ $\beta = 89.89$	$a = 5.32$ $b = 5.56$ $c = 7.72$ $\alpha = \gamma = 90$ $\beta = 89.72$	$a = 5.40$ $b = 5.51$ $c = 7.73$ $\alpha = \gamma = 90$ $\beta = 89.72$
Al	$a = b = c = 4.05$ $\alpha = \beta = \gamma = 90$	$a = b = c = 4.01$ $\alpha = \beta = \gamma = 90$		$a = b = c = 4.06$ $\alpha = \beta = \gamma = 90$

the energies related to the electronic (U_0), including its zero-point energy correction (U_{ZPE}) at 0 K, and the translational (U_{TRANS}), rotational (U_{ROT}), and vibrational (U_{VIB}) degrees of freedom at temperature T . The product of the pressure P and the molar volume, V , is equal to the contribution to enthalpy from the total volume changes. In the case of solids, because changes in volume are negligible, the enthalpy is practically equal to the total internal energy. The electronic energies of the solids are obtained from our electronic structure calculations. The zero-point energy corrections, along with the other contributions to obtain the enthalpy and entropy at different temperatures, are obtained from the phonon density of states calculations. The electronic energy of hydrogen is obtained from the plane wave calculations using norm-conserving pseudopotentials and the other contributions from statistical mechanics evaluations of hydrogen under the ideal gas approximation. In the case of hydrogen, P is equal to 1 atm and V is the molar volume of hydrogen. The desorption (or reaction) temperature is equal to the temperature at which ΔG° is equal to zero.

The lattice parameters of the NaAlH₄ (tetragonal), Na₃AlH₆ (monoclinic), and Al (cubic) unit cells are obtained from our geometry optimization calculations. Calculated structural parameters agree well with the reported experimental values from NaAlH₄ single-crystal X-ray diffraction by Laughner et al.,⁴⁰ X-ray refinement and powder diffraction of Na₃AlH₆ by Ozolins et al.,³⁹ and crystal structure of aluminum reported by Tougaït et al.⁴³ (Table 1). To further validate our calculations, the IR vibrational frequencies of sodium alanate are also compared with the reported values.⁴⁴ The normal modes in the IR spectrum of NaAlH₄, corresponding to the Al–H symmetric stretching in the AlH₄ tetrahedra, are found to be 1808 cm⁻¹ and asymmetric stretching modes at 1737 and 1704 cm⁻¹. These modes agree well with the reported experimental values of 1850 cm⁻¹ for the Al–H symmetric stretch and 1670 cm⁻¹ for the peak assigned to asymmetric stretch.⁴⁴ The four calculated peaks at 865, 735, 705, and 601 cm⁻¹, corresponding to the Al–H bending region, are found in the IR spectrum and are also seen at 900, 800, 735, and 695 cm⁻¹ in the experimentally reported IR spectrum by Gomes et al.⁴⁴

The evaluated free energies and the enthalpies of the decomposition reactions (eqs 1 and 2) are plotted as functions of temperature in Figure 1. The temperature associated with the point at which $\Delta G^\circ = 0$ is calculated and compared with the reported experimental values. This temperature signifies the start of the decomposition of the sodium alanate phase and evolution of hydrogen, according to the first reaction (eq 1), and decomposition of sodium aluminum hexahydride and evolution of hydrogen in the second reaction (eq 2). The solid, dotted, and dashed lines represent the temperature-dependent free energies and enthalpies of the reactions and the zero

reference energy, respectively. From Figure 1a, it is shown that the first reaction is predicted to take place at 308 K and that the enthalpy of the reaction at the reaction temperature is found to be 37 kJ/mol using a polynomial fit. The calculated enthalpy of dehydrogenation compares well with the reported values of 37 kJ/mol³ determined from the liquid-state dehydriding and 40.9 kJ/mol⁴⁵ determined from the solid-state dehydriding of NaAlH₄. In Figure 1b, the free energy line crosses the zero reference line (i.e., the free energy of reactants is equal to the free energy of products) at 413 K, and the enthalpy of the reaction is predicted to be 23 kJ/mol, which overestimates by 7 kJ/mol the experimental reported one of 16 kJ/mol.⁴⁵

The dehydrogenation in undoped NaAlH₄, Ti-doped NaAlH₄, and Na₃AlH₆ is reported to occur at $T > 423$ K, 306 K (1 atm of hydrogen plateau pressure)³ $< T < 353$ K (7 atm of hydrogen plateau pressure),² and $T = 423$ K, respectively. Our calculated values of 308 and 413 K for the first and second reactions,

Figure 1. Thermodynamics of hydrogen-desorption reactions in NaAlH₄. (a) The first step of desorption reactions (eq 1) and (b) the second step (eq 2). The red solid lines in both figures represent free energy changes, the red dots represent enthalpies as a function of temperature, and the dotted line represents the zero reference. Experimental values in (a) are from ref 3. The experimental value for the transition temperature in (b) is from ref 2 and the enthalpy value from ref 44.

respectively, compare well with the transition temperatures of Ti-doped sodium alanates. These observations indicate that the high decomposition temperatures in undoped sodium alanates result from high activation barriers for hydrogen desorption rather than unfavorable thermodynamics.

On the basis of the agreement of the calculated versus reported experimental values for the dehydrogenation temperature, we conclude that the theory levels used in our calculations are justified for the prediction of the thermodynamics of hydrogen desorption in sodium alanates. Upon introduction of titanium salts, the temperature for hydrogen desorption is expected to be reduced and the kinetics of hydrogen desorption is reported to be improved,¹ which may be due to the formation of Ti–Al phases or Ti–Al–H phases that could directly or indirectly help the transition from one anionic species to other, thereby improving the kinetics of hydrogen desorption at reduced temperatures. The next section discusses the possible phases that could result after the introduction of Ti dopants in sodium alanates. TiCl_3 salt is used in our studies as reacting species with NaAlH_4 , as TiCl_3 is reported as the best dopant until date.⁴

2. Ti-Doped Sodium Alanates. In this section, thermodynamic reaction pathways resulting in Ti–Al complexes, followed by dehydrogenation of sodium alanate, are presented. Out of the total six thermodynamic reaction pathways of TiCl_3 -doped NaAlH_4 studied in this paper, the first four reaction pathways (eqs 6–9) are deduced from observations reported in the literature, as explained in the Introduction.

Pathway I:

Pathway II:

Pathway III:

Pathway IV:

For the formation of TiAl_3 , the source of aluminum is not clearly defined, as there are two sources of aluminum present in the doped system: Al in its zero oxidation state (Al^0), resulting from partial desorption of hydrogen, and Al in its +3 oxidation state (Al^{3+}), as present in sodium alanate. Hence, in this study, reactions 6–9 represent the formation of TiAl_3 alloy from each source separately in the first two reaction paths, followed by the combination of both available sources of aluminum in the third one.

The first reaction path (eq 6) indicates that aluminum in its +3 oxidation state present in NaAlH_4 reacts with Ti^0 , forming TiAl_3 without forming any intermediate phases. The second path (eqs 7a and 7b) shows the formation of metallic Ti and Al and titanium reacting with the metallic aluminum to form TiAl_3 . The third path suggests the formation of TiAl when Ti reacts with Al present in NaAlH_4 , along with the metallic aluminum (eq 8a), and TiAl further reacts with the metallic Al, resulting in TiAl_3 (eq 8b). The fourth reaction path (eq 9) considers the formation of a sodium aluminum hexahydride phase and TiAl_3 when the reactants used are metallic titanium and sodium aluminum hydride. This reaction (eq 9) is possible when Ti nanoparticles are used as doping agents instead of TiCl_3 . The fifth (eq 10a) and the sixth (eq 11a) proposed reaction paths are based on the observations from recent XPEEM results by our collaborators³¹ and results from our previous paper on structure and dynamics of Ti–Al–H compounds.²¹

Pathway V:

Pathway VI:

The fifth reaction path (eqs 10a and 10b) considers the formation of alane hydride and metallic Ti intermediates that further combine to give TiAl_3 . The sixth reaction path (eqs 11a, 11b, and 11c) suggests the formation of the alane hydride, TiAl , and metallic Ti phases as intermediates with hydrogen evolution after each intermediate step. From all the possibilities explained through the listed reactions (eqs 6–11a), the most favorable thermodynamic path for hydrogen desorption in Ti-doped sodium alanates is determined in this work.

Initial structures of all the compounds are imported from the ICSD database⁴⁶ and are reoptimized to obtain the geometry-optimized unit cells. The phonon DOS is evaluated, as explained in the Computational Details, using the optimized compound configurations. The vibrational contributions to the free energy are then derived from phonon DOS. The enthalpies of reactions at 303 K (25 °C) evaluated from our calculations are compared across the reactions to find the most favorable reaction path. The enthalpy of each compound is calculated by adding the vibrational, translational, and rotational contributions to the sum of its electronic and zero-point energies. The enthalpies of the reactions are calculated by taking the difference between the sum of enthalpies of products and sum of enthalpies of reactants. All the calculated values are listed in Table 2.

From the calculated values of the enthalpies of reactions, the products are favored in all the cases. Based on the values from Table 2, reaction path VI is the most favorable among all the

TABLE 2: Enthalpies and Free Energies of Reactions and Pathways (Total) at 303K. All the Energies are in kJ/mol of H₂

pathway	reaction	ΔH°	ΔG°	$\Delta H_{\text{PATHWAY}}$	$\Delta G_{\text{PATHWAY}}$
I	eq 6	-59	-92	-59	-92
II	eq 7a	-29	-62	-208	-237
	eq 7b	-179	-175		
III	eq 8a	-46	-80	-123	-151
	eq 8b	-77	-71		
IV	eq 9	-3	-38	-3	-38
V	eq 10a	-123	-166	-160	-233
	eq 10b	-37	-67		
VI	eq 11a	-123	-166	-212	-315
	eq 11b	-66	-97		
	eq 11c	-23	-52		

reaction paths proposed. This reaction path predicts aluminum hydride and TiAl intermediates and indicates the source for aluminum as the aluminum present in its +3 oxidation state in AlH₄ groups of sodium alanate. However, ΔH_{II} is only 4 kJ/mol of H₂ greater than that of reaction path VI, which predicts TiAl₃ from metallic aluminum and titanium intermediates (as observed by Gross et al.¹⁹ and Weidenthaler et al.¹²). Reaction path II indicates that the source of Al for the formation of Al₃Ti alloy is from the metallic Al that is formed after partial desorption of hydrogen rather than aluminum in sodium alanate. Among the other reaction paths, reaction path I that predicts the reaction of Ti⁰ with Al³⁺ present in sodium alanate, forming TiAl₃ directly without any intermediate phases, is less favorable by 153 kJ/mol of H₂ compared with reaction path VI. Reaction paths III and V are less favorable by 89 and 52 kJ/mol of H₂, respectively, compared with reaction path VI. Reaction path IV is the least favorable one among all the studied reaction paths.

Limitations in available methodologies for evaluating all the values (vibrational, translational, rotational and zero-point energies) that are needed to compute the enthalpies of the reactions induce errors in the calculations. A clear estimate of errors cannot be made here, as the experimental values are not available for the reactions proposed in this paper. For that matter, a comparison is made between the calculated enthalpy of reaction in reaction path IV with the experimental value of 6 kJ/mol of H₂ by Dobbins et al.,³¹ which resulted in a mean unsigned error of 3 kJ/mol of H₂. Besides this observation, calculated enthalpies of formation of TiAl₃ from metallic Al and Ti species are also compared with the experimental value of -146 kJ/mol,⁴⁷ which resulted in a mean unsigned error of 33 kJ/mol. Hence, our calculations over predict the formation enthalpy of TiAl₃ from the metallic Ti and Al phases by 33 kJ/mol, and the error observed in our calculations falls in the range of 3–33 kJ/mol. The difference between the most favorable path (reaction path VI) and reaction path II is 4 kJ/mol, which is significantly less than the possible error in our calculations. Hence, evaluating the most favorable path only from enthalpies of reactions is not sufficient and calls for further investigation. The next step in this paper is to include entropic contributions and look at the Gibbs free energies of reactions to decide the most probable reaction path.

Free energies of the reactions are calculated by subtracting the temperature-dependent entropies from the calculated enthalpies of the reactions. Upon inclusion of entropies and after calculating free energies (Table 2), reaction path VI is the most favorable one in which the products are favored by 315 kJ/mol of H₂. The Gibbs free energy of reaction path II is 78 kJ/mol of H₂ less compared with that of reaction path VI. Despite the error in our calculations, reaction path VI holds out among all

the proposed reaction paths in which the products are favored by 315 kJ/mol of H₂.

In an attempt to reduce the error in our calculations, in all metal reactions, such as $\text{Ti}^0 + 3\text{Al}^0 \rightarrow \text{TiAl}_3$ and $\text{TiAl} + 2\text{Al}^0 \rightarrow \text{TiAl}_3$, enthalpies of the reactions are calculated using the finite difference/supercell method, as explained in the Computational Details. To validate this approach, the formation enthalpy of TiAl₃ is compared with reported experimental information. The calculated value of -145 kJ/mol differs by 1 kJ/mol from the experimental reported value of -146 kJ/mol.⁴⁷ Recalculating using the new enthalpy of formation of TiAl₃, the enthalpies of reaction paths II and III are -174 and -119 kJ/mol of H₂ and the free energies are -207 and -147 kJ/mol of H₂, respectively (Table 2). After considering the corrected values of enthalpies and free energies of the reactions, reaction path VI is still the most favorable one among all the proposed thermodynamic pathways in Ti-doped sodium alanates.

Discussion

Decomposition reactions of undoped sodium alanates have been widely studied using experiments and theoretical methods. They are repeated in this study to provide better predictions, validate our methodology, and to precede further investigations on the thermodynamics of Ti-doped sodium alanates. Evaluating the phonon DOS to calculate the zero-point energies and vibrational, translational, and rotational contributions to the total free energy is one of the most computationally complex and expensive tasks. DFPT formalism has obvious advantages over the finite displacement/supercell approach in terms of size of the cell and the value of the force constant. In the case of Coulombic attractions between ionic species in crystals, the force constant matrix decays to zero, typically, in the 8–10 Å range.⁴¹ Specifying a smaller number as a force constant cutoff may introduce some wrap-around errors that may manifest as imaginary frequencies. Hence, this requires the supercells with cell edges ranging in lengths from 16–20 Å, which, in turn, increases the memory requirements for the tasks to be computed. For metals, the force constant matrix decays to zero sooner than that for insulators, which can be evaluated fairly easily using finite displacement/supercell methods. DFPT calculations are accurate but computationally expensive, as well as complex, to be implemented for metals. Hence, DFPT is implemented only for insulators in CASTEP. On the basis of the above reasons, a combination of both methods is employed in this study.

Temperatures of the desorption reactions predicted from Gibbs free energy of reactions give a temperature of 306 K for the first reaction (eq 1), and the enthalpy of the reaction is found to be positive (~37 kJ/mol) over the range of temperatures from 0 to 600 K, indicating it as an endothermic reaction. The entropy difference between the products and reactants in the first reaction (eq 1) is equal to the change in entropy of hydrogen from condensed to gas phase. In the 300–400 K range, the calculated entropy of gaseous hydrogen from our DFT calculations is 136–144 J mol⁻¹ K⁻¹ and the entropy change in the reaction is equal to 120–123 J mol⁻¹ K⁻¹. From this data, we can conclude that the total entropy change in the reaction is equal to the entropy change due to the transformation of hydrogen from condensed to gas phase because the contributions from solids are negligible. This calculated entropy is also in agreement with the reported value of 130 J mol⁻¹ K⁻¹ for the condensed to gas phase change in hydrogen.⁴⁸ In the second reaction (eq 2), the predicted values of reaction temperature and enthalpy of the reaction are 413 K and 23 kJ/mol, respectively. The discrepancies in calculated values at higher temperatures are

due to the anharmonicity introduced in the vibrations, which is not very accurately predicted by the harmonic approximation used in the methodology. However, the calculated values closely approximate the macroscopic observables.

In the case of the Ti-doped sodium aluminates, we investigated the various thermodynamic pathways to answer the long-standing questions related to various resulting phases from doping NaAlH₄ with TiCl₃. The formation of TiAl₃ is stoichiometrically possible from the composition of titanium and aluminum present in TiCl₃-doped sodium aluminates. However, two of the unanswered questions are (i) whether this formation is direct with no intermediates or a multistep reaction pathway with other intermediates and (ii) what is the source of aluminum that corresponds to the formation of the TiAl₃ alloy. From the first four pathways studied in this paper, reaction paths I and IV show the formation of TiAl₃ without any intermediates, but it is shown that the formation of metallic aluminum and titanium species that further leads to formation of TiAl₃ (pathway II, eq 7a), is deemed favorable and follows the experimental observations.^{12,19} The formation of amorphous TiAl before the final product, TiAl₃, observed in some experiments,^{8,10} is also studied (pathway III, eq 8a). However, the suggested pathways (eqs 6–9) have not shown the possibility that reaction path III (eq 8a) is favored over reaction path II (eq 7a). This observation suggests the formation of amorphous TiAl is not possible from metallic Ti and Al, as shown in eq 8a, which calls for further investigation. Recent XPEEM studies³¹ show that aluminum is present as Al³⁺ around metallic titanium after 5 min of ball milling, which suggested two other possible reaction pathways, V and VI (eqs 10a and 11a). Further investigation, based on enthalpy and free energy of the reactions, shows that reaction pathway VI is the most favorable among all the possible ones presented in this paper.

Conclusions

Thermodynamics of hydrogen desorption through the two-step decomposition reaction of undoped sodium aluminates is studied in this paper at the generalized gradient approximation within the density functional theory formalism. On the basis of the excellent agreement between predicted and observed values, further studies on various thermodynamic pathways leading to formation of TiAl₃, the source of aluminum for the formation of TiAl₃, and evolution of hydrogen from Ti-doped sodium aluminates are presented and discussed.

Two sets of thermodynamic pathways for hydrogen desorption from undoped and Ti-doped sodium aluminates are investigated in this paper. The first set of pathways (eqs 6–9) follows the reported two-step decomposition reaction to yield hydrogen from pristine NaAlH₄. The enthalpy of the reactions and the temperature for transition from reactants to products are predicted from our calculations and compared with the reported experimental values. The second set of reaction pathways (eqs 10a–11a) proposed in this paper includes the resulting phases that are observed to be possible upon doping pristine sodium aluminates with TiCl₃ or titanium nanoparticles. On the basis of the various explored thermodynamic reaction pathways, the most favorable one is identified, explained, and suggested in this paper. The results suggest a three-step reaction pathway (VI) to the formation of TiAl₃ (Ti and AlH₃ after the first reaction, TiAl after the second, and finally resulting in TiAl₃) and aluminum in its +3 oxidation state present in aluminum hydride species is responsible in the formation of Ti–Al alloys.

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Kinetics of Hydrogen Desorption in NaAlH₄ and Ti-Containing NaAlH₄

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Understanding the fundamental reaction path and identifying the rate-limiting steps in the decomposition of materials evolving hydrogen are two challenging tasks when studying complex metal hydrides as viable onboard hydrogen storage materials. In this work, we use computational techniques to study the free-energy barriers associated with the reactions involved in the evolution of hydrogen via the first step of sodium alanate decomposition ($\text{NaAlH}_4 \rightarrow \frac{1}{3}\text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2$). Results from our calculations suggest a four-step reaction that includes the transition from AlH_4^- to AlH_6^{3-} anions, Al clustering, and H_2 evolution. The calculated free-energy barrier and enthalpy of activation associated with one molecule of H_2 release are on the order of 80 and 82 kJ/mol H_2 , respectively. The rate-determining step for this mechanism is found to be the hydrogen evolution from associated AlH_3 species. The role of titanium in the improved kinetics of Ti-containing sodium alanates is elucidated from our coupled density functional theory/molecular dynamics calculations. Ti stays on the hydride surface and serves as both the catalytic species in splitting hydrogen from $\text{AlH}_4^-/\text{AlH}_3$ groups as well as the initiator for Al nucleation sites in Ti-doped NaAlH_4 .

Introduction

Pioneering research by Bogdanovic et al.¹ demonstrated sodium aluminum hydride (sodium alanate, NaAlH_4) as a potential complex metal hydride for onboard hydrogen storage. The decomposition of NaAlH_4 is well known to proceed through a two-step reaction resulting in Na_3AlH_6 and aluminum phases in the first step (eq 1) and NaH and aluminum phases in the second step (eq 2). The total hydrogen desorbed from the native material adds up to 5.6 wt %.

Sodium alanates suffer from inherent limitations related to unfavorable thermodynamics (high temperature required to release hydrogen) and slow kinetics of hydrogen desorption.¹ Moreover, the reversibility of hydrogen storage was also not demonstrated by NaAlH_4 . Results from further research on sodium alanates have shown reversibility and improvement in thermodynamics and kinetics by doping/catalyzing with transition-metal compounds,^{1,2} particularly titanium.³ Numerous research studies including experimental^{2–16} and theoretical^{9,10,17–24} investigations have been reported to date to elucidate the role of titanium in the improved kinetics of hydrogen de/absorption in sodium alanates. Great progress has been achieved in understanding the role of titanium in improved hydrogen kinetics by sodium alanates; however, no conclusive results have been drawn regarding the kinetic pathway and the rate-limiting steps in the pathway of sodium alanate decomposition. To elucidate the role of Ti, a solid understanding of the kinetics of hydrogen desorption from sodium alanates is still needed.

This article aims at understanding the fundamental reaction path involved in the decomposition of sodium alanates for hydrogen desorption and identifying the rate-limiting steps in the reaction path using computational techniques. Important conclusions forming the basis of the reactions studied in this article (eqs 1 and 2) are provided here. Suggested progress in the first reaction (eq 1) is by transition from AlH_4^- to AlH_6^{3-} combined with the nucleation and growth of the Al phase.¹ Early studies by Gross et al.¹⁶ using in situ X-ray diffraction have shown the possibility of transition through the long-range diffusion of mass species that are heavier than hydrogen. This observation was further supported by recent isotope-scrambling experimental studies, indicating that the diffusion of hydrogen as the atomic or molecular species is unlikely to precede the diffusion of mass species that are heavier than hydrogen.⁵ Recent computational studies by Gunaydin et al.¹⁸ have shown the possibility of AlH_3 vacancy-assisted hydrogen desorption, which is favorable over the NaH vacancy-assisted hydrogen desorption proposed by Walters et al.¹⁰

Followed by the prediction of the kinetic limitations and the rate-limiting step in the decomposition path, the effect of titanium addition to the NaAlH_4 lattice is drawn from the various results (DFT and DFT-MD) obtained in this study. To the best of our knowledge, an extensive investigation of the reaction paths in sodium alanate decomposition leading to hydrogen evolution has not yet been reported. Hence, first in this article, reaction progress leading to the formation of various phases is studied from a kinetic point of view using transition-state theory. During the decomposition of sodium alanate, the transition from AlH_4^- to AlH_6^{3-} is not clearly understood (eq 1). Possible reactions leading to the transition of AlH_4^- to AlH_6^{3-} studied in this article agree with the reported computational^{10,18,22,24} and experimental observations.¹⁶ Second, and followed by the predictions of the kinetic path for the transition of AlH_4^- to AlH_6^{3-} , the role of titanium from optimized conformations and time-dependent dynamics at elevated temperatures of Ti-containing sodium alanate models is investigated in this work using a combined density functional theory and molecular

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dynamics (DFT-MD) approach. Hence, this article provides detailed insight into the rate-limiting steps in hydrogen desorption and the role of Ti in reversible hydrogen storage in sodium alanates, which can later be applied to engineering other viable, light complex metal hydrides as onboard storage materials.

Methodology

The generalized gradient approximation (GGA) within the density functional theory (DFT) formalism is used in this article for the study of sodium alanate structures. DFT calculations using a plane wave basis set with valence electrons described using Vanderbilt ultrasoft pseudopotentials (USPP) or the projector augmented wave (PAW) are commonly used to determine the structure and to accurately study the electronic as well as material properties of NaAlH₄ and Ti-containing NaAlH₄.^{17–23,25–30} Therefore, in this work, optimization calculations of the sodium alanate unit cell are performed using the Perdew and Wang (PW91) functional³¹ and plane-wave basis set with valence electrons described by USPP, as implemented in the CASTEP³² module in Materials Studio software by Accelrys, Inc.³³ Geometry optimization calculations of the sodium alanate unit cell are spin-unpolarized with a 500 eV kinetic energy cutoff and a *k*-point mesh with a grid spacing of 0.04 Å^{−1}. The optimized structure of sodium alanate is then used to construct NaAlH₄ surfaces. Two-layered slabs are considered to identify the rate-limiting steps in studying the kinetics of hydrogen desorption in sodium alanates, and four-layered slabs are used in investigating Ti-containing NaAlH₄ using DFT-MD calculations.

Transition-state theory calculations are conducted as implemented in the DMol³ module in Materials Studio software by Accelrys, Inc.³³ Initial structures of the reactants and products are geometry optimized using the GGA (PW91) method, and DNP (double numerical plus polarization and diffuse functions) numerical basis functions. The reaction path connecting the reactant and product is predicted using the linear synchronous transit (LST) tools by Halgren and Lipscomb.³⁴ Then, the transition state along the reaction path is found using the combined linear and quadratic synchronous transit (LST/QST) methods. First, the maximum along the reaction path is found using LST search, and the resulting configuration is minimized using conjugate gradients.³⁵ The obtained transition state is then used to find a maximum using QST followed by minimization using conjugate gradients. This process is iterated until the true transition state is obtained, which is verified by confirming one imaginary frequency related to the maximum along the reaction coordinate and the minimum along all other directions. Vibrational analysis is then performed on all of the optimized configurations of reactants, products, and transition states. From the vibrational analysis, enthalpic and entropic contributions to the total free energy are obtained. The total free energy of each configuration is calculated by the difference between the enthalpy (including the electronic energy) and temperature multiplied by entropy. All of the free energies reported in this work are divided by the number of formula units in the reactant model.

Molecular dynamics calculations of NaAlH₄ and Ti-containing NaAlH₄ models are performed as implemented in CASTEP. Electronic parameters are consistent with the geometry optimization parameters using plane-wave DFT methods. The time step used in those calculations is 2 fs, and equilibration runs using canonical ensemble are set for 2 ps, followed by production runs for 2 ps using the microcanonical ensemble.

Results and Discussion

The desorption of hydrogen in complex metal hydrides includes solid–solid and solid–gas phase transformations.

Providing algorithmic solutions to define the solid–solid transitions is difficult because the problems encountered are less general and more research-specific. In the case of solid–solid transitions, most of the material transformations include the variation in the cell vectors and the rearrangement of the atomic/molecular species. Hence, the complete description of the phase transformation requires the full construction of the potential energy surface of the material described by all of the relevant internal and/or molecular coordinates. To construct the full potential energy surface, one needs to know the low-energy barrier jumps that correspond to the various configurations of the material due to the rearrangement of atomic/molecular species as well as the high-energy barrier jumps that correspond to the diffusion of those species. To study the processes that are responsible for the material transformations, transition states that connect the various minima on the potential energy surface need to be determined. Thus, the global transformation from the reactant to product phases is too difficult to model. The problem of hydrogen desorption from NaAlH₄ is more research-specific and requires a strategy to model the important transformations rather than providing an algorithmic solution to determine the activation barriers. Important transformations correspond to the distinct phases observed in the experiments during the desorption of hydrogen from NaAlH₄.

The desorption of hydrogen from sodium alanates results in the transition of the tetragonal phase of sodium alanate to a monoclinic sodium aluminum hexahydride, fcc Al phases, and gaseous hydrogen.¹⁶ In this article, local deformations in the reactant model to represent the seed for the nucleation and growth of the resulting product phases are considered, and the activation energy for the initiation of the product phase is calculated. Calculations in this article require a slab model constructed on the basis of the symmetry of the reactant phase. A local region in the slab, with sufficient atomic/molecular species that can transform into a seed for the product phase, is then selected. This selected region is well isolated from its symmetric images in the adjacent cells. Different types of transformations are modeled in this work, and transition states connecting various local deformations are identified using synchronous search transition-state methods as explained in the Methodology section. Thus, from our calculations, we predict the activation enthalpy and activation energy for the transition from AlH₄[−] anionic species present in tetragonal NaAlH₄ to AlH₆^{3−} anionic species present in monoclinic Na₃AlH₆.

Reactant and Product Models. In this section, we identify and study the possible reactions leading to hydrogen desorption mediated by the diffusion of AlH₃ species in NaAlH₄. The transition from AlH₄[−] anionic species to AlH₆^{3−} anionic species in the first step of the decomposition reaction (eq 1) is proposed to follow the following reaction path:

The initial model to represent NaAlH₄ is built by cleaving the optimized unit cell (using the plane wave basis set and

Figure 1. Models representing reactants and products in reactions listed in eqs 3–6. AlH₄ groups are shown as polyhedrons, and Na ions are shown as balls: magenta, aluminum, gray, hydrogen, and purple, sodium. (a) (Reactant1) Sodium alanate, (b) (Product1/Reactant2) the first intermediate showing AlH₃ and the AlH₅²⁻ ion, (c) (Product2/Reactant3) AlH₆³⁻ ion and two desorbed AlH₃ species, (d) (Product3/Reactant4) association of desorbed AlH₃ species, and (e) (Product4) final product showing the evolution of one hydrogen molecule. AlH₄ groups involved in reactions are represented by a ball-and-stick model (magenta, aluminum and red, hydrogen).

USPP) to expose the 001 surface termination. This model is two layers thick and has been extended along the *a* and *b* lattice directions to build a slab containing eight formula units of NaAlH₄. To model the reactions (eqs 3–6) to obtain the free-energy (activation) barriers and heats of the reactions, models representing the reactants and products are built and optimized using DFT combined with numerical basis sets and all electron relativistic pseudopotentials as described in the methodology section.

In the first reaction (eq 3), the reactant is the NaAlH₄ slab (Figure 1a, Reactant1), and the product is built by dragging an AlH₃ unit from one of the AlH₄⁻ groups on the surface, leaving the hydride ion in the lattice. Aluminum is constrained (zero degrees of freedom) in its position; however, the hydrogen atoms bonded to aluminum and the other groups in the slab are left unconstrained. Optimization calculations follow to obtain the relaxed geometry with optimized electron density and forces between the atoms (Figure 1b, Product1/Reactant2).

The product from the first reaction shown in eq 3 (Figure 1b, Product1/Reactant2) is taken as the reactant for the second reaction, and the product from the second reaction (eq 4) is modeled to represent the transition from AlH₅²⁻ to AlH₆³⁻ as shown in Figure 1c (Product2/Reactant3). In Figure 1c, aluminum atoms in created AlH₃ species are constrained, and the remaining groups in the lattice are unconstrained. The third reaction (eq 5) represents the association of aluminum as in Figure 1d (Product3/Reactant4). In this product model, the lattice with NaAlH₄ groups is constrained, and aluminum atoms in AlH₃ species are left unconstrained. The final step leading to the evolution of hydrogen is the model in Figure 1d (Product3/Reactant4), and the product (Figure 1e, Product4) is modeled by dragging two hydrogen atoms to form molecular hydrogen from the associated AlH₃ species in the aluminum phase.

Kinetics of Hydrogen Desorption. The first reaction (eq 3) indicates that one AlH₄⁻ group, highlighted in Figure 1a, possibly on the surface loses one hydride species and forms an AlH₃ group that diffuses toward the NaAl₃H₆–Al interface. The

extra hydride ion is shared by one of the nearest diagonally located AlH₄⁻ groups (Figure 1b), forming AlH₅²⁻ species along with the rearrangement of two Na ions to satisfy the charge neutrality in the lattice. Further transition from AlH₅²⁻ to AlH₆³⁻ (eq 4) is possible by the similar loss of a hydride ion from one of the nearest diagonally located AlH₄⁻ groups and diffusion toward the formed AlH₅²⁻ ion (Figure 1c). This transition creates another AlH₃ species that diffuses toward the NaAl₃H₆–Al interface. The single hydride ion diffuses toward the formed AlH₅²⁻ ion, transforming it into the AlH₆³⁻ ion (Figure 1c) combined with the rearrangement of Na ions to satisfy charge neutrality. The movement of the hydride ion from one AlH₄⁻ group can be termed reorientation and hopping from one AlH₄ tetrahedra to the other rather than diffusion of the hydride species. The diffused AlH₃ species associate (eq 5) and further decompose to evolve hydrogen, leaving Al in its crystalline phase (eq 6). As indicated in the first decomposition reaction (eq 1), three NaAlH₄ groups participate in the formation of one Na₃AlH₆ group, two Al species, and three molecules of hydrogen. By combining all of the AlH₄ groups that are involved in the transition and evolution of hydrogen, the stoichiometry of the first decomposition reaction (three AlH₄ groups react, resulting in one AlH₆³⁻ anion, two metallic Al atoms, and three H₂ molecules) is well detailed in the proposed reaction path of this study.

Various states resulting from the preceding reactions are also present in the succeeding reactions to provide a realistic environment. These modeled reactions can be explained from a computational point of view by saying that all eight formula units that are present in the reactant are still present in the product phase. This presence enables the calculation of energies of all further phases resulting from the reactant relative to the energy of the reactant, providing not only a reference to all the barriers but also the possible cancellation of systematic errors. The reaction path is predicted using the LST tool, and the transition state connecting the reactants and products is found using the combined LST/QST tool as explained in the Meth-

Figure 2. Forward free-energy barriers at 298.15 K for the reactions (eqs 3–6) leading to the transition from AlH_4^- to AlH_6^{3-} combined with the nucleation of aluminum and the evolution of one H_2 molecule.

odology section. The free-energy barriers from reactants are computed by taking the differences between the free energies of the transition states and those of the reactants.

Free-Energy Barriers. Free energies of the reactants, transition states, and products at finite temperatures are calculated by adding the free-energy contributions to the electronic energies of the respective models and dividing by the number of formula units in the model. Figure 2 shows the calculated free-energy barriers for the proposed set of reactions (eqs 3–6).

It is observed that after optimizing the modeled product of the first reaction in the proposed reaction path (eq 3) the hydride ion left in the lattice in place of the AlH_4^- group and the nearest diagonally located AlH_4^- group move toward each other to form the AlH_5^{2-} ion (Figure 1b). Na^+ ions surrounding the vacant space left by the AlH_4^- group on the surface are displaced from their lattice positions and rearrange to bind with the formed AlH_5^{2-} ion. The calculated forward free-energy barrier at 298.15 K for the first reaction (eq 3; formation of one AlH_3 species and transition from AlH_4^- to AlH_5^{2-}) is 32 kJ/mol. The reverse barrier in the first step is on the order of 4 kJ/mol, indicating a metastable phase of AlH_5^{2-} . In the second (eq 4) reaction, leading to the transition from AlH_5^{2-} to AlH_6^{3-} , the forward and reverse free-energy barriers are 36 and 21 kJ/mol, respectively. The total barrier for the transition from the AlH_4^- anion to the AlH_6^{3-} anion, mediated by AlH_5^{2-} , in the first decomposition reaction totaled 63 kJ/mol. In the third (eq 5) reaction, Al nucleation from the association of created AlH_3 species, the forward free-energy barriers is equal to 5 kJ/mol. The fourth reaction (eq 6) resulting in the release of one H_2 molecule from the associated AlH_3 species has a forward free-energy barrier of 51 kJ/mol. We observe the two kinetic limitations that correspond to the formation of the Na_3AlH_6 phase from NaAlH_4 and metallic Al from the associated AlH_3 species. From our calculations, the minimum energy required to release one H_2 molecule is equal to the energy required to cross the free-energy barrier associated with the fourth reaction leading to gaseous hydrogen from AlH_3 . Hence, it can be concluded that our calculations predict that the free-energy barrier and the enthalpy of activation associated with one molecule of H_2 release are on the order of 80 and 82 kJ/mol H_2 , respectively.

The reported value of the activation energy required to release one mole of hydrogen is on the order of $\sim 118.1(120.7)$ kJ/mol H_2 for the first decomposition reaction of sodium alanates (Na_3AlH_6) (eq 1) and between 72 and 80 kJ/mol H_2 in Ti-doped sodium alanates.¹⁴ The difference between the calculated and observed values is due to the model selected in our calculations. The models do not take into account the rearrangement of the AlH_4^- anions remaining in the lattice or the growth of the Na_3AlH_6 phase. For example, the diffusion barrier for AlH_3 species is reported to be 12 kJ/mol by Gunaydin et al.¹⁸ These reactions may not form any additional steps in the proposed

reaction pathway; however, they may be responsible for increasing the height of the barriers. Despite the discrepancies between the calculated and observed values, the calculations provide a qualitative picture of the kinetic limitations in the first decomposition reaction and point to the issues that need to be addressed.

The free energy of the first decomposition reaction (eq 1) at 298.15 K is equal to 44 kJ/mol. By summing heats of reactions to determine the enthalpy of the reaction for the first decomposition reaction (eq 1), a value of 49 kJ/mol H_2 is found from our calculations. The experimentally reported enthalpy of the first decomposition reaction to yield hydrogen is equal to 38.5 kJ/mol H_2 .² This deviation from the experimental observation is due to the calculation from intermediate transition phases instead of from the final fully grown sodium aluminum hexahydride and aluminum phases.

In this article, studied kinetic reaction paths leading to gaseous hydrogen revealed a four-step reaction for the transition from the AlH_4^- anion to the AlH_6^{3-} anion that completes one of the two proposed hydrogen desorption reactions in sodium alanates. The kinetic limitations in the first decomposition step that needs to be addressed are the initiation of the Na_3AlH_6 phase (AlH_6^{3-}) and hydrogen evolution from the associated AlH_3 species nucleating the aluminum phase. The initiation of the Na_3AlH_6 phase requires the formation of AlH_3 species from AlH_4^- anions, preferably at one of the surfaces, that in turn leads to the formation of AlH_6^{3-} anions. This transition process is associated with a barrier of 63 kJ/mol. The high activation barrier of eq 4 is due to the diffusion of AlH_3 toward the Al nucleation site and its association with the other aluminum atoms present at that site. The formation of the Al nucleation site is also a hurdle in the case of sodium alanates that needs to be addressed. In the case of the rate-limiting step in the proposed eq 6, the energy required to remove hydrogen from the AlH_3 species is high, which leads to a high activation barrier. These issues call for the need for a catalytic species that could lower the barrier.

Role of Titanium

To understand the role of titanium in sodium alanates, the local environment of titanium in ball-milled mixtures of Ti salts and NaAlH_4 should be studied. Besides the position of titanium species, intermediate compounds that result from ball milling or solid-state doping should also be identified. Some of the conclusions from our previous study¹⁷ and the published literature are summarized here. From our calculations, we observe that the titanium dopants remain on the surface during the entire simulation time, eliminating the possibility of bulk doping that agrees well with the reported literature.^{7,36} It is also observed in the literature that the barriers for hydrogen desorption decreased by 36–46 kJ/mol H_2 upon doping with titanium salts.¹⁴ Researchers also reported a significant decrease in the energy required to detach hydrogen from AlH_4 species as a result of shared hydrogen between Ti and Al.^{22,24} The current state of knowledge suggests that the formation of Ti–Al alloys is evident and stoichiometrically favorable from the atomic compositions of Ti and aluminum in Ti-doped NaAlH_4 . Furthermore, Ti–Al alloys in the form of amorphous TiAl and amorphous/crystalline TiAl_3 are observed that depend on the amount of doping, ball-milling times, temperature, and so forth.^{13,16,36–44}

The questions related to the position of dopants and the local environment around titanium dopants were addressed and reported in our previous paper,¹⁷ which is related to the structure

Figure 3. Models representing optimized configurations of (a) Ti placed on top of the interstitial site and (b) Ti replacing the Na lattice site on the surface model of sodium alanate. AlH_4 groups are shown as polyhedrons, and Na ions are shown as balls. Colors are used as follows: magenta, aluminum; gray, hydrogen; and purple, sodium. AlH_4 groups involved in reactions are represented by ball-and-stick models (magenta, aluminum; blue, titanium; and red, hydrogen).

and dynamics of Ti–Al–H compounds in Ti-containing sodium alanates. In our previous work,¹⁷ various accessible sites for titanium on the 001 surface of a sodium alanate lattice were chosen and the models with Ti placed at the chosen sites were investigated to obtain the most probable configurations of Ti-containing sodium alanates. Furthermore, intermediate compounds resulting from the interactions between Ti and AlH_4 groups (Ti–Al and Ti–Al–H compounds) were also reported. Results from geometry optimization and DFT-coupled molecular dynamics (DFT-MD) of two-layer slabs were also reported in our previous paper.¹⁷ We studied six thermodynamic pathways to understand the favorable reaction pathway that ultimately leads to the formation of TiAl_3 . The most favorable pathway reported in our paper related to thermodynamic profiles of hydrogen desorption is a three-step reaction mediated by AlH_3 .⁴⁵

In this article, the identified most probable configurations of Ti-containing sodium alanates are studied and analyzed in order to understand the role of titanium in hydrogen evolution from NaAlH_4 . Geometry optimization and DFT-MD calculations are performed in this study using four-layer slabs of NaAlH_4 . The top two layers represent the surface and the subsurface layers, and the bottom two layers represent the bulk of the NaAlH_4 lattice. Two accessible sites—the interstitial site on top of the surface (between the two AlH_4 units and two Na ions) and the Na surface lattice site—are chosen because they are reported to be the most probable sites for Ti.¹⁷ Figure 3a,b shows the optimized configurations of Ti placed on top of the interstitial site and Ti replacing the sodium lattice site on the surface, respectively. In both cases, the identified TiAl_xH_y compounds

are similar to the ones that are observed in the two-layer slab models reported in our previous paper.¹⁷ Values of x and y depend on the accessible AlH_4 groups around Ti.¹⁷

From the optimized configurations, the hydrogen atoms that are previously bonded to aluminum alone are now shared between titanium and aluminum and also the bond between aluminums and titanium. In the case of titanium on top of the interstitial site (Figure 3a), Ti is seen to form bonds with two hydrogens from the accessible AlH_4 groups, and in the case of Ti replacing the sodium lattice site, Ti is seen to form bonds with six hydrogens from surrounding AlH_4 groups. These configurations can be compared to the ball-milled samples of Ti-containing NaAlH_4 . After the optimization of Ti-containing sodium alanates, some of the hydrogens are detached completely from aluminum, bonding only with titanium. Similar theoretical studies by Liu et al.²² have also shown that the energy required to remove hydrogens that are bound to titanium is lower by 0.6–0.7 eV compared to the energy required to remove hydrogens that are attached to aluminum in AlH_4 groups in pure sodium alanates. This predicts the role of titanium as a catalyst, facilitating the breaking of hydrogens that are covalently bound to the aluminum in $\text{AlH}_4/\text{AlH}_3$ groups.

The next step in this work is to study the stability and dynamics of the formed titanium-containing intermediates at elevated temperatures. DFT-MD simulations run for a very long time (seconds timescale) ideally should reproduce the proposed reaction paths and the phase separations as seen in experiments. Our simulations span a very short time (4 to 5 ps) and predict the precursors to the actual reaction path, and the reaction mechanisms are predicted on the basis of our results from MD simulations. In this study, DFT-coupled MD is used to study the dynamics at 423 K (150 °C) of both sodium alanates and Ti-containing sodium alanates. In the DFT-MD approach, after each MD step, the electron density is minimized and the forces between the atoms are calculated using DFT. Optimized models from DFT calculations are taken, and molecular dynamics calculations are run for 2 ps in the canonical ensemble (constant number of molecules, constant volume, and constant temperature) to equilibrate the structure at 423 K. Following equilibration, another molecular dynamics calculation is run for 2 ps in the microcanonical ensemble (constant number of molecules, constant volume, and constant energy) to investigate the behavior of atomic/molecular species at the elevated temperature of 423 K.

From the DFT-MD simulations of sodium alanates, the reorientation and movement of AlH_4 groups around the lattice sites is seen with time evolution. No sites for aluminum nucleation or the breaking of bonds with AlH_4 groups are observed. The movement of all the AlH_4 groups in the four layers of the slab is random in three dimensions, representing the natural diffusion in the lattice. This indicates that the kinetics of the transitions from AlH_4^- to AlH_5^{2-} and from AlH_5^{2-} to AlH_6^{3-} are not happening on the pico/nanosecond timescale, which complements reported slow kinetics of hydrogen desorption in sodium alanates.

An improvement in the kinetics, however, is observed in Ti-containing sodium alanates. MD simulations of Ti-containing sodium alanates have shown that the formed Ti–Al–H compounds after optimization are still in existence at elevated temperatures. An increased number of aluminum atoms are seen to be associating with titanium, indicating a probable site for the nucleation of the aluminum phase. An increased number of hydrogen atoms from the surrounding groups are also seen to be associating with titanium as a function of time and temperature. In both of the Ti-containing models, titanium is not seen

to be diffusing into the lattice, which eliminates the possibility of bulk doping of titanium in the NaAlH₄ lattice.

In the case of Ti replacing a Na lattice site (Figure 3b), the AlH₄ groups in the top two layers are seen to be diffusing toward titanium, forming hybrid complexes of Ti–Al–H compounds, whereas the movement of AlH₄ groups in the bottom two layers indicates random movement in the lattice. Hydrogens that were previously bonded to aluminum are now transferred to titanium in the Ti–Al–H complexes, exhibiting no bonding character with aluminum. In the case of titanium on top of the interstitial site, hydrogens from the AlH₄ groups in the subsurface layer are seen to be hopping from one lattice site to the other toward the aluminum atoms that are bonded to titanium. This can be termed reorientation and hopping rather than the diffusion of hydrogen species in the lattice. The hydrogens that hop from AlH₄ groups in the subsurface layer are expected to transfer to titanium, thereby detaching from aluminum and forming molecular hydrogen.

Therefore, the role of Ti can be explained from our DFT/DFT-MD calculations. Titanium is present on the surface of the sodium alanate during the entire simulation time and exhibits a catalytic role in splitting hydrogen from the surrounding AlH₄/AlH₃ groups. Ti draws hydrogens from accessible AlH₄/AlH₃ groups, and the newly formed bonds between Ti and H are easily broken compared to Al–H bonds in AlH₄ or AlH₃ groups. This explains the lowered kinetic barrier for the evolution of hydrogen from AlH₄ or AlH₃ species in Ti-containing sodium alanates compared to that for pure NaAlH₄ compounds. Besides the catalytic role, Ti also forms bonds with Al and we also see that the AlH₄ groups on the surface and the ones that are present in the subsurface layers are drawn toward Ti, indicating the initiation of the Al nucleation site facilitated by Ti.

Conclusions

A reaction path for hydrogen desorption through the first step of sodium alanate decomposition is proposed and investigated. The reaction path studied here leading to gaseous hydrogen revealed a four-step reaction for transition from the AlH₄[−] anion to the AlH₆^{3−} anion, Al clustering, and hydrogen release. The rate-limiting step in the decomposition of sodium alanates is associated with hydrogen evolution from associated AlH₃ species that forms a seed for the nucleation of an aluminum phase. Though the barrier for aluminum association is very low compared to the other steps in the reaction pathway, the seed for nucleation is not seen from the DFT-MD calculations on sodium alanates at elevated temperatures. Ti, from our studies and as suggested in other studies, plays a role in the catalytic scission of hydrogen atoms from AlH₄ groups and initiates a nucleation site for Al by reducing the barriers in hydrogen desorption.

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