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Proposed Mechanisms for the Catalytic Activity of Ti in $NaAlH_4$

Terry J. Frankcombe*

Research School of Chemistry, Australian National University, ACT 0200, Australia

CONTENTS

1. INTRODUCTION

Using hydrogen as an energy carrier is a widely anticipated alternative to the current global dependence on hydrocarbon-based liquid and gaseous fuels, particularly for mobile applications. However, physical storage of pure hydrogen on board passenger cars is challenging from an engineering point of view, primarily due to the low density of hydrogen gas and the effort required to compress it to a reasonable density or liquefy it for cryogenic storage at 20 K.[1−3] As a result, there is a strong worldwide push to develop high hydrogen density materials suitable for use in convenient hydrogen storage systems.[3−5]

The essential capabilities of hydrogen storage systems are often taken to be the targets laid down by the United States Department of Energy (DoE), as part of a partnership with automobile manufacturers called "FreedomCAR". The DoE specified targets for 2005 for hydrogen storage densities and hydrogen delivery and refuelling rates. These targets were not met. Subsequently, the targets for 2010 and 2015 were revised toward more conservative values. The revised targets for 2010 were hydrogen densities of 4.5 wt % and 28 kg H_2 m^{-3}. When considering these US-specific targets, it is important to realize that these are system targets, which necessitate consideration of tanks and control equipment, etc. A hydrogen storage material of a particular density can thus only be used in a hydrogen storage system of significantly lower hydrogen density.

A range of storage materials have been proposed. These include complex metal hydrides comprised of an ionic lattice of s-block cations and hydrides of p-block elements as polyatomic anions, such as alanates and borohydrides. While the accessible hydrogen content of complex metal hydrides is reasonable (often in the 3−12 wt % range), storage reversibility, high hydrogen release temperatures, and slow kinetics of the pure hydrides are problematic.

That complex metal hydrides contained a high density of hydrogen that could be released on heating has been known for a long time. However, it was thought that various properties of these materials made them at best inconvenient for mobile hydrogen storage applications. A breakthrough came in the mid-1990s, when Bogdanović and Schwickardi demonstrated that doping the complex metal hydride $NaAlH_4$ with a few mol % of Ti lowered the decomposition temperature, improved the kinetics, and, importantly, allowed rehydrogenation of the decomposition products.[6] It had been known since at least the 1950s that Ti was catalytically active for alanates in solution,[5,7,8] but this was the first indication that Ti worked catalytically for the dry material. Interest in using complex metal hydrides as hydrogen storage materials was dramatically reawakened.

The catalysis by Ti was observed to be unusual from early on. Surprisingly, it was found that Ti as a catalyst was a little bit special; a number of other transition metals that have traditionally been used to catalyze hydrogen reactions were found to be not nearly as effective for reversible dehydrogenation of $NaAlH_4$ as Ti. Some marked differences were observed between the catalytic behavior of Ti and other d-block elements in the $NaAlH_4$ system and in other complex metal hydrides, such as $LiAlH_4$ and $LiBH_4$. Naturally, this lead many investigators to probe the mechanism of action of the Ti catalysis. For more than a decade, Ti-doped $NaAlH_4$ has been subject to intense scrutiny. While phenomenological models describing (de)hydrogenation of the Ti-doped sodium alanate system have recently had some success,[9,10] no clear consensus picture of the nature of the role of Ti in $NaAlH_4$ has emerged.

Quite a number of proposals for the mode of action of Ti have been published in the literature. A few authors have briefly summarized some of the published work and proposals on doping methods and the mechanism of action of Ti-based catalysts,[11−19] but the coverage is patchy. The purpose of this review is to survey and summarize these proposals into a single comprehensive reference, something that does not currently exist in this form.

This review deals specifically with Ti-based doping in sodium alanate. Thus, as a general rule, mechanisms proposed for other catalysts in sodium alanate, or for similar catalysis in other complex metal hydrides,[20−26] are not specifically included. This is a reflection

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of the special place Ti catalysis has in sodium alanate hydrogen storage research and the often surprising lack of catalytic effect observed for many other types of dopants.

In this review, proposed mechanisms for Ti catalysis are arranged into a number of broad themes, with individual proposals described in turn. In order to definitively establish the context for the mechanistic proposals in the literature, a brief overview of the decomposition of sodium alanate, the nature of the additives investigated for catalyzing hydrogen storage in sodium alanate, and what happens to the Ti on doping into the material is also presented.

2. OVERVIEW OF $NAALH_4$ DECOMPOSITION

$NaAlH_4$ is known to release hydrogen in a number of distinct steps, with Na_3AlH_6 and NaH as partially dehydrogenated phases appearing as the dehydrogenation progresses. This decomposition is usually described by the three reaction steps

$$NaAlH_4 \rightarrow {}^{1}/_{3}\,Na_3AlH_6 + {}^{2}/_{3}\,Al + H_2 \qquad (1)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + {}^{3}/_{2}\,H_2 \qquad (2)$$

$$NaH \rightarrow Na + {}^{1}/_{2}\,H_2 \qquad (3)$$

which correspond to 3.8 wt % hydrogen storage for eq 1 and 1.9 wt % (relative to the original $NaAlH_4$) for each of eqs 2 and 3. The final decomposition of NaH (step 3) is usually considered unobtainable for mobile applications, requiring too high temperatures at useful pressures. Thus, decomposition to NaH, Al, and H_2 (via reactions 1 and 2) corresponds to an accessible hydrogen density of 5.6 wt %. While this is above the 2010 DoE weight density target, the non-$NaAlH_4$ components of a practical storage system usually bring the achievable system hydrogen density below the DoE target. The first two decomposition steps occur at temperatures of around 480 and 525 K, respectively,[27] though lower temperatures are also reported.[28,29] Recent *in situ* microscopy has revealed that during the decomposition of undoped $NaAlH_4$ the product material becomes porous, with grains of product phases appearing irregularly distributed throughout dehydrogenated material.[28,29] Porous dehydrogenation products had been observed previously.[30]

Describing the decomposition of $NaAlH_4$ by the three steps above is not universally accepted. Based largely on the absence of observations of a hexahydride phase in many lightweight complex metal hydride systems, Balema and Balema[31] have proposed that the main decomposition reaction is the direct decomposition of the tetrahydride, *viz.*

$$NaAlH_4 \rightarrow NaH + Al + {}^{3}/_{2}\,H_2 \qquad (4)$$

In this picture, the hexahydride is produced as a side reaction

$$NaAlH_4 + 2NaH \rightarrow Na_3AlH_6 \qquad (5)$$

which competes with reaction 4. However, it is difficult to reconcile this picture with the observed broad agreement of dehydrogenation profiles with the 3.9 wt % and 1.9 wt % hydrogen release predicted by steps 1 and 2. Gross et al.[32] had earlier explicitly concluded that reaction steps 1 and 2 were independent and sequential (termed “interdependent” in ref 32, meaning reaction 2 can only commence after reaction 1 has produced Na_3AlH_6). Nonetheless, this direct decomposition picture has recently received some support from the study of the energetics of alanate nanoparticles, which predicts that small $NaAlH_4$ nanoparticles do indeed decompose in a single step to produce NaH.[33]

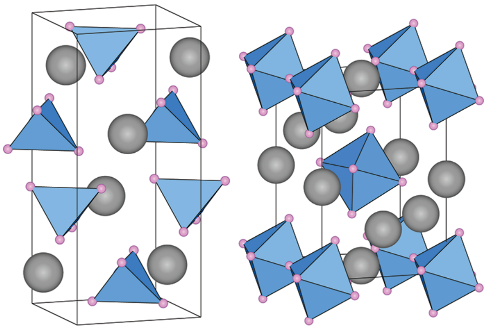

Figure 1. Structures of the $NaAlH_4$ (left, ref 41) and α-Na_3AlH_6 (right, ref 39) crystals: large solid balls, Na^+ cations; solid polyhedra, $[AlH_x]^{3-x}$ anions.

The structures of the pure alanate phases, illustrated in Figure 1, have been elucidated from X-ray[32,34−40] and neutron[39−41] diffraction experiments. There is widespread agreement on the $I4_1/a$ structure of $NaAlH_4$ under ambient conditions, though there is evidence of at least one more polymorph appearing on heating.[42−45] In contrast, a number of space group symmetries have been suggested for Na_3AlH_6,[34,46−49] which exists in at least α and β forms.[27,38,49] For α-Na_3AlH_6 most investigators agree on a space group usually expressed as $P2_1/n$ (space group number 14, expressible in the standard setting $P2_1/c$ using standard techniques[50]).

Periodic density functional theory (DFT) calculations by Vajeeston et al.[46] suggest that alternate $NaAlH_4$ phases may exist at very high pressures. A high pressure phase transition was later confirmed experimentally by Kumar et al.[37] However, the experimentally realized phase has a different structure from that proposed by Vajeeston et al., exhibiting monoclinic rather than the proposed orthorhombic symmetry.

DFT calculations consistent with the experimentally derived ambient pressure structures have been published too frequently to give a comprehensive list here, but for a sampling see refs 40, 46, 49, and 51−58. These electronic structure theory calculations reveal that these materials conform to the bonding motif that has come to be expected from complex metal hydrides: an ionic lattice of s-block element cations (Na^+) and complex p-block hydride anions ($[AlH_4]^-$ and $[AlH_6]^{3-}$). This multifaceted bonding has made complex metal hydrides such as $NaAlH_4$ a strenuous testing ground for new solid state modeling methodologies.[52] Cleavage/surface energies of the perfect $NaAlH_4$ crystals have also been calculated,[53,59] which can be used to estimate preferred crystallite shapes in the nanocrystalline material.[33]

$NaAlH_4$ can be re-formed by recombining the NaH and Al decomposition products under hydrogen pressure. This is an extremely attractive route for on-board refueling. Without a catalyst, this process is slow and requires high pressures and temperatures. Over the past 15 years it has repeatedly been shown that adding a few mol % Ti (or a small number of other catalysts) allows $NaAlH_4$ to decompose to NaH and metallic Al, with H_2 released on heating, and that applying H_2 pressure to the products spontaneously re-forms the crystalline $NaAlH_4$ without requiring very high temperatures. Cycling studies have shown that the reaction can be cycled hundreds of times, hydriding and dehydriding the same material repeatedly, with only slow loss of hydrogen capacity. Such properties are highly desirable in a hydrogen storage system, though the kinetics of hydrogen release at the convenient temperatures at which mainstream PEM fuel cells operate remains disappointingly low. Recent developments in high temperature PEM fuel cells[60,61] somewhat alleviate the latter problem, potentially simplifying operational heat management engineering.

Per unit Ti, improvements in the kinetics of hydrogen release/uptake slow with increasing amounts of added Ti. This is accompanied by the obvious decrease in the by-weight hydrogen storage capacity of the overall material, meaning there is an optimum window of a few wt % Ti for mobile hydrogen storage. However, analysis of the Arrhenius parameters of the hydrogen release[62,63] indicates that there is a large drop in the decomposition reaction activation energy on addition of *any* Ti, which then remains approximately constant for higher doping levels. Only the Arrhenius pre-exponential factor is Ti concentration dependent. This suggests that the presence of Ti opens a different (de)hydrogenation reaction path to that of the undoped material but offers no real enlightenment as to the mode of action of the Ti catalyst.

3. PRELIMINARIES: TI DOPANTS

3.1. What's the Best Way To Dope with Ti?

In their seminal work, Bogdanović and Schwickardi[6] used β-$TiCl_3$ as the Ti-containing starting material that was added as dopant. Subsequently, $TiCl_3$ has been a common Ti-source material for studies of Ti-doped sodium alanates.[64−74] Other Ti salts and Ti compounds, such as $TiCl_4$, TiF_3, $Ti(OBu)_4$, TiH_2, and TiO_2, have been used with varying levels of success.[71−77] Titanium metal powder has been shown to be an effective catalyst,[78−80] as have Ti and TiN nanoparticles and colloids.[65,81−84]

Not all Ti-containing materials are effective catalysts, however. Resan et al.[71] have demonstrated that $TiAl_3$ and Ti_3Al alloys are not effective dopants. This raises interesting questions about the role of Ti−Al phases commonly observed forming in the doped system. It has also been observed that adding extra metallic Al to the doped system goes a long way toward mitigating the hydrogen capacity loss that is associated with doping.[66,75] The role of Ti−Al alloys shall be discussed in more detail in section 3.2.

The doping conditions, such as the temperature of the materials during doping and whether wet or dry techniques are used, appear to be important.[85−89] There have been contradictory reports on whether the system retains a "memory" of the doping conditions on cycling.[16,86,90,91]

Many transition metals that are commonly effective in catalyzing a wide range of chemical processes have been tested as an alternative to Ti. Most do not provide the improved kinetics and reversibility that Ti-based dopants do.[92] However, in 2006 Bogdanović et al.[93] found that doping with $CeCl_3$, $PrCl_3$, or $ScCl_3$ yielded better catalytic activity than $TiCl_3$. In the same year, Pukazhselvan et al.[94] similarly concluded that a mischmetal containing Ce, La, Nd, and Pr was more effective than Ti-based dopants. Very recently, Wang et al.[95] have shown that a CoB catalyst works very well.

Codopants have been demonstrated to be effective, in the sense that when doping with both Ti-containing dopants and another metal, the system kinetics are superior to using Ti (or the codopant) alone. Codopants such as Zr,[11,96−99] $HfCl_4$,[77] KH,[100] and Fe[11,97,101,102] have been shown to be effective. Indeed, it may be that Fe as a codopant may unintentionally present in many experiments, as doped sodium alanate is very often prepared using high-energy ball milling using steel balls, a potential source of Fe ions.[21,103] It has been suggested that when codoping with Ti and Zr, the individual reactions 1 and 2 are each enhanced by one of the dopants.[96,104] (Such suggestions are not limited to advocates of codoping, as others[105,106] have suggested that the mode of Ti catalysis may be different for the decomposition of $NaAlH_4$ and Na_3AlH_6.)

A number of authors have demonstrated enhanced kinetics using only carbons as a dopant.[107−109] Cento et al.[109] have reported that using carbons alone as a dopant results in a substantially increased dehydrogenation rate but no lowering of the temperatures required for dehydrogenation. Furthermore, using carbons of various types as a codopant with a traditional dopant (usually Ti-based, but also $HfCl_3$) has been reported to be very successful.[77,110−112] However, others have indicated that codoping with $Ti(OBu)_4$ and high surface area carbon actually *increased* the dehydrogenation temperature of the doped alanate.[109] Taken together, these results suggest that the role of carbons as dopants is more likely to be physical than chemical. The presence of the carbon structures is likely to be influencing the grain size and porosity of the doped material, altering the rate at which gaseous hydrogen can move in and out of the bulk material.

3.2. Where Is the Ti, and in What State?

An obvious question to ask when trying to determine the mechanism of the catalytic activity of titanium is: Where is the Ti in the doped material? A related question is: What is the oxidation state of the Ti after doping?

Just like many other aspects of Ti-doped alanates, there are many contradictory claims on the fate of Ti dopants in the doped material. It has been conclusively demonstrated that adding the titanium in either oxidized (Ti^{3+} or Ti^{4+} compounds) or metallic form (metallic powders and Ti colloidal particles or nanoparticles) works as a dehydrogenation/rehydrogenation catalyst and yields a cyclable hydrogen storage material without a significant induction period. Achieving similar catalysis results suggests a similar mechanism irrespective of the dopant. It is then reasonable to assume that, on or shortly after doping, either the Ti ions get reduced to Ti^0 or the Ti^0 atoms get oxidized to Ti^{3+}/Ti^{4+}. There are plenty of authors who claim the former, that Ti ions get reduced to Ti^0, often presumed to be catalytic.[16,65,80,101,113−121] Some authors argue that there is not complete reduction or oxidation, but they favor the intermediate Ti^+ as the catalytically active species.[119,122] Quite a few authors have been more specific than this, observing TiH_x species ($x = 1,2$) present in the doped material, or even as the active catalytic species.[66,80,89,113,123−126] Certainly there is ample evidence that using TiH_2 as the dopant provides effective catalysis.[76,80,89,127] On the other hand, Léon et al.[115] specifically state that their EXAFS results shows no evidence of TiH_2 formation in $TiCl_3$-doped $NaAlH_4$. It has also been suggested that both oxidized and reduced Ti are present after doping with different methods and that these species catalyze (de)hydrogenation through different mechanisms.[78,79] Łodziana and Züttel argue for different Ti oxidation states in different regions within the alanate material.[128]

It is regularly observed that Ti−Al phases form within the doped system. These are usually Al-dominant phases, ranging from $TiAl_3$ crystallites to Ti_xAl_{1-x} alloys with reported values of x as low as 0.07. Ti_xAl_{1-x} particles with x estimated in the range 0.13−0.18 have recently been directly observed on the surface of hydrogen-cycled $TiCl_3$-doped $NaAlH_4$ powder using high resolution microscopy.[129] The frequency of observing Ti−Al phases has led to many suggestions that they are the catalytically active species.[76,119,121,123,127,130−134] This idea has been repudiated by the observations that doping the sodium alanate system with Ti−Al does not yield effective catalysis,[71] that the formation of Ti−Al phases correlates with a reduction in the effective hydrogen capacity of the material,[65,133,135] and that adding additional Al powder on doping (to act as an excess Ti "sponge") counteracts this capacity loss.[66,75] Furthermore, large changes in the presence of Ti−Al phases do not correlate with large changes in the observed kinetics.[47,136] The contradiction between the Ti−Al phases being major Ti-containing elements of the doped systems and the apparent inactivity of these Ti−Al phases leads to the speculation that the active species is a minor, distinct Ti component. This would suggest that the 2−4% Ti content observed to produce optimum hydrogen storage properties may be only required in order to achieve a much lower concentration of active Ti, in equilibrium with this major Ti−Al component as a Ti reservoir.

Proposals of a Ti−Al reservoir phase in conjunction with a more dispersed active Ti-containing species do not always paint the Ti−Al alloy as inactive. For example, Gross et al.[76] proposed that while Ti in the alanate lattice may offer the major catalytic effect, the presence of a Ti−Al alloy phase may have an effect on the kinetics in a secondary manner, once the primary catalysis channel is opened by the dispersed Ti.

It is worth noting that the ineffectiveness of doping with Ti−Al phases puts Ti-doped $NaAlH_4$ at odds with other closely related systems. For example, $TiAl_3$ catalyzes $LiAlH_4$,[23] and $CeAl_4$ catalyzes $NaAlH_4$.[137] The latter serves to emphasize once more the unique nature of Ti catalysis in the $NaAlH_4$ system.

Separate from pure Ti−Al phases, a number of authors have suggested that an important location of the Ti is in a Ti−Al−H species, either as an isolated unit or a condensed phase.[138−141] Specific Ti−Al nanoclusters have also been suggested.[142]

A substantial amount of work has been done looking at whether monodispersed Ti atoms or ions are more stable in substituted or interstitial locations in the $NaAlH_4$ crystal.[12,47,51,125,128,132,133,138,143−149] Most of these studies have been computational, and they generally favor substitution over interstitial sites. An early issue was what was a reasonable competing state against which to measure stability, as the obvious efficient approach for assessing the substitutional stability in a bulk system—replacing various atoms by Ti and calculating the energies—does not maintain a constant energy zero to which to compare the calculated energies. What to consider an appropriate reference state for relative stability calculations has been shown to depend strongly on the physical situation being modeled, with respect to the availability of nearby condensed Al phases, etc.[18,51,144,154] A recent experimental study looking specifically at this issue saw no evidence of Na substitution in EXAFS spectra.[133] One must also question the relevance of looking at states such as Ti perfectly substituted for Al in the alanate lattice. It seems unlikely that any relevant process would replace, for example, $[AlH_4]^-$ with $[TiH_4]^-$, particularly as Ti atoms and ions are well-known for their propensity to form strong Ti−H bonds with substantially more than four hydrogen atoms/two hydrogen molecules at a time.

4. WHAT IS THE MECHANISM?

Probably the simplest explanation of how Ti might work as a catalyst for the sodium alanate system is as a "hydrogen pump".[150] It is well-known that Ti, along with many other transition metal elements, will barrierlessly adsorb H_2 to produce two chemisorbed hydrogen atoms (see Figure 2). Thus, Ti on or in a surface can act as a conduit for the breaking and forming of H−H bonds with a substantially lower activation energy than at other sites. If the H atoms can migrate to and from the Ti site without too-high energy barriers, a catalytic dehydrogenation and hydrogenation pathway results.

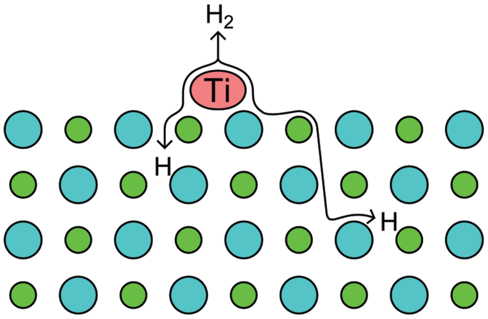

Figure 2. Schematic representation of the hydrogen pump/spillover mechanism. Ti species on the surface provide a barrierless path for the $H_2 \rightleftharpoons 2H$ reaction. Hydrogen atoms diffuse to and from the reaction center independently.

Such a role for Ti in the sodium alanate system has been suggested by quite a number of authors, either in isolation[16,32,67,110,119,151,152] or in conjunction with some other mechanism.[15,18,98,108,111,121,123,153−155] However, a substantial difficulty with the idea that a primary role for Ti is providing a (near) barrierless H_2 dissociation/association pathway is that there are many other metals that should act in a similar manner. Yet it has been demonstrated over and over again that usually these other potential catalysts generally do not perform nearly as well as Ti as a catalyst for hydrogen storage in the sodium alanate system. Furthermore, both early papers[82] and more recent work[156] indicate that the kinetics of hydrogen release from the doped alanate are not consistent with H_2 dissociation/association being the rate limiting step.

Bellosta von Colbe et al.[157] and Brinks et al.[66] performed explicit tests of the enhanced H_2 dissociation/association pathway mechanism. Bellosta von Colbe et al. used isotopic labeling, placing Ti-doped $NaAlH_4$ under a D_2 atmosphere. Hydrogen exchange with the solid was observed through the presence and growth in concentration of gaseous HD. No HD was observed for undoped controls, indicating that the Ti dopant was indeed active in providing low energy routes between molecular hydrogen and the hydride. However, Bellosta von Colbe et al. made the important observation that their experiment was "static" from the point of view of the hydrogen content of the hydride. The H/D exchange was observed to occur much faster than re-formation of the alanate from the dehydrogenation products. Thus, while Ti-containing species are indeed active on the surface of the hydride, this does not imply that this is the primary mechanism for dehydrogenation/rehydrogenation catalysis.

Brinks et al.[66] added $TbNiAlH_{1.33}$ in place of a Ti catalyst. $TbNiAlH_{1.33}$ is an interstitial hydride with very fast kinetics, meaning it should work as an excellent $H_2 \rightleftharpoons 2H$ bridge. $TbNiAlH_{1.33}$ produced only a slight improvement in the alanate dehydrogenation kinetics, implying once more that Ti catalyzes $NaAlH_4$ through some other mechanism.

Overall, it is clear that the hydrogen pump/spillover mechanism is active in the doped alanate but is not sufficient to explain the catalytic effect.

4.1. Mechanisms in Terms of Mobile Species

For the reactions in eqs 1 and 2 to occur in the solid state, there must be long-range transport of various species to facilitate phase separation of the products. With this in mind, a number of mechanisms have been proposed that focus on the identity of the mobile species. The action of Ti is then often proposed to be to promote the mobility of the mobile species, usually in some unspecified manner.

A number of mobile species have been detected during the alanate decomposition. The most important of these seem to be AlH_3-like species. Consensus is growing that AlH_3 or a closely related species is mobile in the reacting alanate system. This had been an early suggestion by, for example, such authors as Gross et al.[32] More recently, Fu et al.[158] studied the decomposing alanate using inelastic neutron spectroscopy and DFT, concluding that $(AlH_3)_n$ species, $n = 1, ..., 4$, were present and mobile in their samples. Walters and Scogin proposed a model in which the mobile species were both AlH_3 and NaH.[159] Chaudhuri et al.[67] presented Car−Parrinello molecular dynamics of AlH_x migration ($x \leq 3$) on Al surfaces, suggesting that these small species are responsible for long-range hydrogen migration in the reacting alanate system. Fang et al.[121] have proposed a loose catalysis mechanism in which "Al−H species" are mobile, with their mobility somehow being enhanced by being formed through hydrogen attachment to Ti−Al clusters. Dathar and Mainardi[155] have proposed a model for the first decomposition step from tetrahydride to hexahydride based on DFT-MD simulations of alanate slabs. This model, and the subsequent Ti catalysis mechanism, is based on AlH_3 (and a few other AlH_x ions) being the main mobile species, and it shall be discussed in more detail in section 4.7. Ivancic et al.[160] observed a highly mobile species carrying both Al and H atoms, suggesting a highly AlH_3-defective phase.

A number of other results are consistent with mobile AlH_3 or similar, but they do not rule out other species larger than hydrogen being mobile. For instance, Lohstroh and Fichtner studied the H−D kinetic isotope effect of the decomposition of sodium alanate.[156] On the basis of the observed isotope effect, they concluded that the rate limiting step is diffusion of a hydrogen-containing species. Furthermore, the isotope effect was not consistent with hydrogen atom migration but was consistent with a migrating AlH_3, other Al_xH_y, or NaH. Sakaki et al.[161] observed mobile vacancies larger than H-vacancies with a concentration that tracked the (reversible) progress of the dehydrogenation reaction. Ojwang et al.[162] have studied a series of solid state reactions describing $NaAlH_4$ dehydrogenation, based on the mechanism proposed by Walters and Scogin,[159] in which crystalline Na_2AlH_5 and $Na_5Al_3H_{14}$ are intermediate products that are formed without H_2 release. The calculated energetics are consistent with AlH_3 as an intermediate, which then decomposes to release H_2.

4.2. Role of Mobile Vacancies

As alluded to above, some decomposition and catalysis mechanisms based on mobile vacancies (as distinct from mobile interstitial species) have been proposed.

On the basis of DFT calculations of the potential energy of various crystal structures, Araújo et al.[146] proposed a Na vacancy mediated model. They found that removing hydrogen from AlH_4 tetrahedra adjacent to a Na vacancy was actually exothermic. AlH_3 units remaining after hydrogen removal were found to be more tightly bound and more closely resembled the gas phase AlH_3 geometry when the structure was modeled as being Na-deficient. Their proposed role of the Ti catalyst was therefore an indirect one, promoting the formation and migration of Na vacancies within the sodium alanate crystal.

A detailed vacancy-mediated model has been proposed by Palumbo, Paolone, Cantelli, and Jensen.[163−167] Using anelastic spectroscopy, a highly mobile species with characteristics consistent with a point defect was identified. Experiments with isotopically substituted crystals indicated that this point defect was hydrogen-based. Furthermore, it was found that the presence of Ti dopants strongly affected the elastic moduli of the alanate material, implying changes to the potential energy profiles of migration processes throughout the material. These investigations eventually led these authors to propose a mechanism involving hydrogen vacancies in AlH_6 clusters undergoing rapid rearrangement, with the vacancies hopping from one hydrogen site to another within these nominally octahedral structures. It is proposed that the overall alanate decomposition mechanism starts with AlH_4 clusters reacting at elevated temperatures to form a combination of perfect AlH_6 and defective AlH_{6-x} units, segregated Al, and interstitial H. The H atoms migrate to the surface, via interstitial sites and vacancy hopping, to recombine and evolve H_2.

In this model the role of Ti is multifaceted. First, Ti aids the initial reaction of the AlH_4 tetrahedra by destabilizing the Al−H bonds (for which there is ample evidence; see section 4.5). Second, the Ti atoms dispersed through the alanate act as intermediate hydrogen traps, acting as an intermediate site between the very stable positions, with H bound to Al, and the most unstable interstitial positions. Such an intermediate trap can enhance the migration kinetics, essentially giving the H atoms a place to acquire additional thermal energy and take advantage of a substantially higher Boltzmann factor to jump up each intermediate level. Third, the effect of the Ti dopants softening the elastic moduli of the whole structure reduces the span of energies covered by the various sites within the reacting material. All of these effects increase the proportion of defective, vacancy-containing AlH_{6-x} units compared to the case of the perfect AlH_6. Additionally, the presence of Ti trapping sites hinders H−H recombination on rehydrogenation, allowing the mechanism to proceed in reverse. The potential felt by migrating H as it moves through the undoped and doped crystal under this model is indicated schematically in Figure 3. This model is presented in terms of largely undetermined energies, the relative magnitudes of which are critical to the plausibility of the proposed mechanism.

In contrast with the above work, Voss et al.[168] claim that the presence of Ti dopants does *not* substantially increase the long-range diffusivity of hydrogen, despite creating some low energy $AlH_6 + AlH_5 \rightarrow AlH_5 + AlH_6$ paths. On the strength of DFT modeling and quasielastic neutron scattering measurements, they conclude that the fast hydrogen dynamics and hydrogen vacancy migration remains distinctly localized. Rather, they propose that the Na^+ ion is the most important migrating species. From DFT calculations and vibrational analysis of stationary points, it is shown that, counterintuitively, Na^+ ion migration can explain the differences observed by Palumbo and co-workers on deuteration. Just like in a gas phase diatomic, the mean Al−H distance is affected by anharmonicity in the Al−H stretching potential. This dynamical effect, and the average bond length that results, is mass dependent. To take this into account, Voss et al. held the Al−H distance at the experimentally observed Al−D mean distances and probed the potential energy changes on Na vibrational motion. It was found that the vibrational frequencies

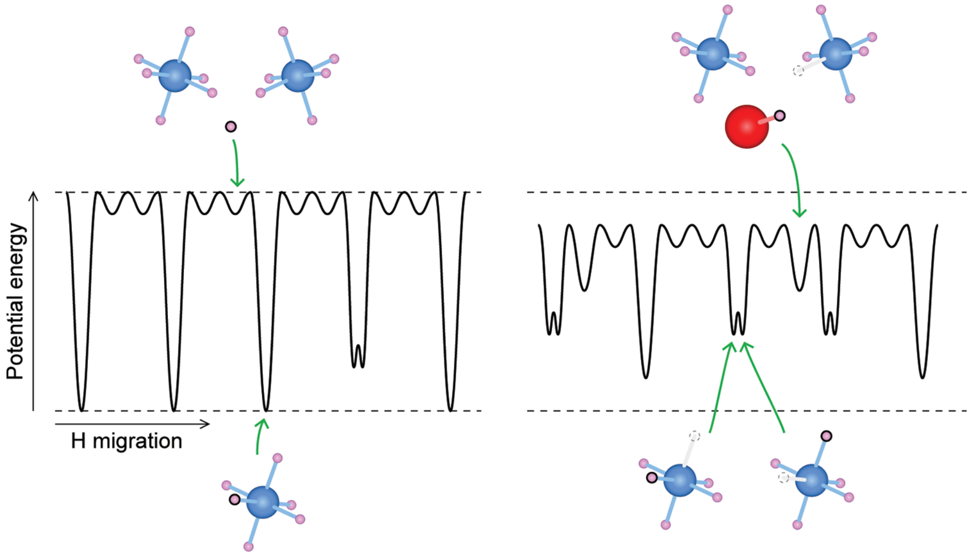

Figure 3. Schematic representation of the model proposed by Palumbo and co-workers, indicating the potential energy felt by a hydrogen atom migrating through the alanate via various sites. Undoped alanate is shown on the left, and Ti doped alanate on the right. In order of increasing depth, the potential wells correspond to H atoms: in interstitial sites, bound to Ti, bound in defective AlH_{6-x} octahedra, and bound in complete AlH_6 octahedra. Adapted from ref 166.

of certain Na-only modes decreased substantially, implying a reduced Na migration rate on deuteration.

Voss et al.[168] do not propose an alternate Ti catalysis mechanism to that of Palumbo et al.[166] It is undetermined whether the mechanism of Palumbo et al. can be adapted to be consistent with the results of Voss et al.

Monteferrante et al.[169] have also studied H vacancy migration processes with DFT-based free energy methods. Monteferrante et al. studied the local vacancy migration within an AlH_5 unit that is favored by Voss et al., as well as the longer range, nonlocal $AlH_6 + AlH_5 \rightarrow AlH_5 + AlH_6$ transfer. Along the calculated minimum free energy paths, it was concluded that reorientation of AlH_5 was actually a substantially higher energy process than previously thought. The calculated energetics of interion H (or vacancy) migration, on the other hand, was found to agree well with that implied by the experimental results of Palumbo et al. However, it is worth noting that only neutral vacancies were considered. This has implications for the charge state of the AlH_5 anions undergoing rearrangement, and thus likely the energetics.

Wang et al.[170] have also investigated H-based and Na-based migration in Na_3AlH_6 using DFT calculations. These authors find vacancy migration energy barriers that suggest rapid rearrangement within AlH_5 units, in agreement with Palumbo et al., but they stress the importance of considering the charge of the vacancy. These authors find that the Na migration proposed by Voss et al. is not excluded but is not energetically favorable. These calculations indicate that positively charged H ion defects should be preferred as the mobile species.

At first glance there appears to be a contradiction between the properties predicted by the three sets of DFT calculations of Voss et al.,[168] Monteferrante et al.,[169] and Wang et al.[170] However, each of these calculations uses a different methodology, each with its own shortcomings. The calculations of Voss et al. are the most "standard" of the three, being plane wave DFT calculations with the PW91 functional, using ultrasoft pseudopotentials and *k*-space integration on a regular grid. Monteferrante et al. use the BLYP functional and Troullier-Martins pseudopotentials but perform only Γ point calculations for the Kohn–Sham wave function. This is a serious limitation on the accuracy of the condensed phase energetics. Wang et al. also use the PW91 functional, in projector augmented wave calculations with Monkhost-Pack *k*-space grids, which are reputed to be more accurate than straight pseudopotential calculations. While Voss et al. and Monteferrante et al. consider only neutral defects, Wang et al. also consider charged defects and find that the charge of the defects is an important, conclusion altering issue. However, it should be noted that treating charged defects in a periodic system with a homogeneous background compensating charge only approximately accounts for induction effects.[171,172] Nonetheless, there is broad agreement between the results of Voss et al. and Wang et al. where they overlap. The overall situation is that the DFT prediction for long-range hydrogen vacancy migration (and hence support for the vacancy-mediated model of Palumbo et al.) is ambiguous.

Gunaydin et al.[173] propose a very different vacancy-mediated mechanism, in which the mobile species are AlH_3 and NaH vacancies. Performing Car–Parrinello molecular dynamics on a DFT potential energy surface, they show that AlH_3 vacancies are stabilized by Coulombic attraction between the vacancy (now representing a Na cation rich region) and the adjacent AlH_5 anion formed with the leftover H atom. Likewise, NaH vacancies exist in conjunction with corner-sharing AlH_4 tetrahedra, together making an Al_2H_7 anion. These complex vacancies can migrate in conjunction with rapid hydrogen hopping around the vacancy, which occurs on picosecond time scales. The proposed mechanism includes initiation of the vacancy formation at phase boundaries, with H_2 being evolved at the Al–$NaAlH_4$ interface, as illustrated in Figure 4. Decomposition of Na_3AlH_6 is not dealt with explicitly in the proposed mechanism. Nor is the direct role of Ti. Rather, the authors argue that because their calculated activation energies for vacancy migration roughly agree with activation energies implied by the kinetics of Ti-doped $NaAlH_4$, then this is the rate-limiting step in doped samples. Undoped samples are assumed to be rate limited by some other unspecified process. It is then this unspecified process that is catalyzed by Ti, removing that

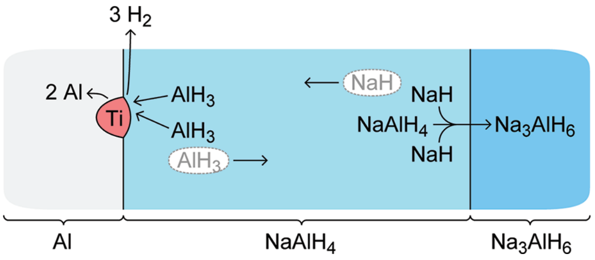

Figure 4. Vacancy-migration-limited interfacial mechanism of Gunaydin et al.[173] and Borgschulte et al[15].

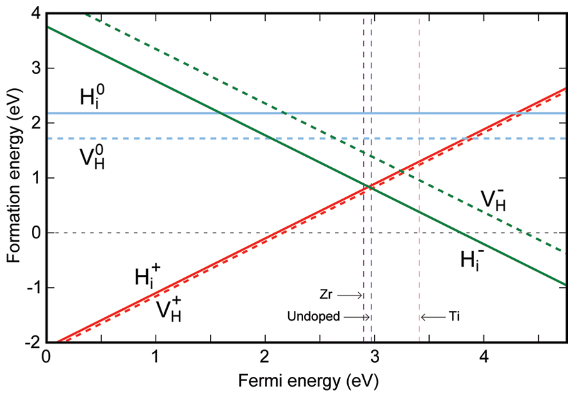

Figure 5. Effect of altering the Fermi energy on the formation energy of hydrogen defects: neutral, positive, and negatively charged interstitial hydrogen (H_i^0, H_i^+, and H_i^-) and similarly charged hydrogen vacancies (V_H^0, V_H^+, and V_H^-). The vertical dashed lines indicate charge-neutral Fermi levels for undoped $NaAlH_4$ (2.97 eV) and for Ti doped (3.41 eV) and Zr doped (2.90 eV) samples. Adapted from ref 174.

bottleneck and allowing the underlying vacancy migration kinetics to become apparent. Borgschulte et al.[15] use observations of H−D exchange in $NaAlH_4$ under D_2 along with the H_2−Ti−Al modeling of Chaudhuri and Muckerman[119] to support this vacancy-diffusion-limited interfacial mechanism, in which Ti is supposed to play a fairly loosely defined role, likely acting at the Al−$NaAlH_4$ interface.

In later work, Jensen and co-workers further probed vacancies in doped $NaAlH_4$ using positron annihilation Doppler broadening.[161] The method used could not probe H defects, but metal atom vacancies. They found that the vacancy concentration in $NaAlH_4$ was not significantly altered by doping or ball-milling. Rather, the vacancy concentration increased as the hydrogen release reaction proceeded, to a value significantly higher than that for the reaction products synthesized by other means. On rehydrogenation, the vacancy concentration returned to the original nanocrystalline $NaAlH_4$ value. Specifically, the vacancies were determined to be primarily located in the Al or Na_3AlH_6 phases. These results do not support the role of Ti as enhancing the formation of vacancies larger than hydrogen atoms or ions. However, the Ti dopant increasing the diffusion rate of native vacancies is not ruled out.

4.3. Altering the Fermi Level

In 2007 Peles and van de Walle presented an analysis that was rather novel in the hydrogen storage literature, using information gleaned from DFT calculations.[174] These authors started from what might be called the "conventional wisdom" that the migration of defects plays a central role in diffusive and mass-transport processes in solid state reactions. In (de)hydrogenation of sodium alanates, it seems reasonable that hydrogen migration and the associated hydrogen vacancies are crucial. Peles and van de Walle observed that the energies associated with such hydrogen defects depend on both the charge on the defect and the Fermi level of the material, as charging and decharging these defects involves electrons being taken from and donated to a bath of electrons, being the valence electrons of the crystal. The general form of the dependence of vacancy formation energies on the Fermi energy is illustrated in Figure 5.

Peles and van de Walle determined that the presence of Ti dopants would alter the Fermi level of the crystal by 0.44 eV, in turn decreasing the energy required to form a charged hydrogen defect by the same amount. Such a decrease in the defect formation energy would increase the thermal defect concentration by 6 orders of magnitude and greatly increase the diffusion rate of these charged defects. This analysis suggests that the activation energy of the dehydrogenation of sodium alanate should be approximately independent of the Ti dopant concentration once sufficient Ti has been added, an observation that is consistent with experimental evidence.[62,63]

Another appealing feature of this charged-defect-based analysis is that it presents a neat explanation of why Ti catalyzes sodium alanate much more effectively that other similar transition metal dopants, such as Zr. Peles and van de Walle demonstrated that their analysis suggests that the change in the hydrogen defect formation energy on doping with Zr is only 0.07 eV, much smaller than the effect of Ti.

In the same paper[174] it was observed that the presence of the various charged hydrogen-related and Ti defects substantially changed the surrounding geometry of the alanate crystal, far beyond the simple presence of the defect. Thus, the authors speculate that—in addition to the main electronic effect on the Fermi level of the crystal—the Ti dopants serve to nucleate the phase transformations that are necessary to complete the (de)hydrogenation reactions.

Subsequently, Peles et al.[175] have studied the energetics of charged defect formation as well as vacancy and ion migration in $NaAlH_4$. This work neatly connects the kinetic and computational work on H-vacancy migration[163−170,176] with the theoretical approach of Peles and van de Walle.[174] In this latter work,[175] these authors conclude that breaking covalent Al−H bonds to form Frenkel pair defects is the rate-limiting step in $NaAlH_4$ dehydrogenation, with an $[AlH_4\cdots H\cdots AlH_3\cdots H\cdots AlH_3]^{3-}$ complex playing a central role. The energetics of the formation and subsequent evolution of these charged defect complexes is explicitly dependent on the Fermi energy of the material in which they reside. They then conclude that the Fermi level alteration mechanism previously proposed by Peles and van de Walle[174] is the correct description of the mode of action of the Ti catalyst.

While the experimental observation that the non-hydrogen vacancy concentration is not altered by doping[161] does not support the interpretation of Peles and van de Walle, it is not directly incompatible.

This importance of interstitial H ions is somewhat supported by the work of Kadono et al.[177] These authors implanted muons into $NaAlH_4$ as analogues of interstitial H ions, detectable through muon spin rotation experiments. Dispersed hydrogen-bonded states were detected, which were said to "lie anywhere on the continuum between AlH_4^-−H^+−AlH_4^- and AlH_3^-−H_3^-−AlH_3", with evidence of significant migration barriers between interstitial sites. Kadono et al. suggested that the migration of these interstitial ions was rate-limiting, but the relative rate of their formation was not addressed.

4.4. Nucleation/Phase Growth

Another common assumption in early work was that the kinetics was limited by the nucleation and growth of compact product phases. Fichtner and co-workers were advocates of this interpretation in a series of papers starting in 2003.[82,83,105,153] In this series, Fichtner et al. fit measured hydrogen evolution and consumption rates to the Johnson−Mehl−Avrami (JMA) equation, which is commonly used to describe solid state nucleation and growth processes. The exponent appearing in this equation, η, is usually interpreted to be indicative of the rate-limiting process of the solid state transformation. In the fits of Fichtner et al., these exponents took values of around 0.7−1.4 for the hydrogen absorption process and around 2−3 for hydrogen release, depending on the form of the catalyst used. These ranges of exponents can be characteristic of either interface or diffusion limited processes, depending on the details of the mechanism.[178]

Two aspects of this analysis are unsatisfying from the point of view of identifying the mode of action of Ti. First, the same JMA kinetic analysis was not performed for the decomposition of undoped $NaAlH_4$, meaning there is no baseline to which to compare it. Second, the JMA exponent, central to the interpretation of the mechanism in this formalism, changed depending on the nature of the doping. It is difficult to see how, for example, doping with Ti_{13} clusters as opposed to doping with $TiCl_3$ can change the dominant decomposition mechanism from, for example, a two-dimensional interface growth mechanism ($\eta \approx 2$) to a three-dimensional phase growth mechanism ($\eta \approx 3$).

Despite these limitations, Fichtner et al.[153] drew on these kinetics fits, as well as other evidence, to propose a model in which the primary kinetic effect of Ti-containing dopants is to create defects in the crystalline phases present. In particular, Fichtner et al. proposed that Ti substitution of Al in the alanate phases induces diffusion-enhancing defects in the lattice. The nature of the proposed defects was not specified in ref 153 beyond "a partial substitution of Al by Ti". The authors asserted that doping with Ti clusters induces more defects than doping with $TiCl_3$.

Sun et al.[179] also proposed a nucleation mechanism, based on qualitative analysis of hydrogen evolution rates. Specifically, they conclude that the decomposition reaction relies on the formation of aluminum phase nuclei. The evolution of hydrogen from the alanate follows, presumably at the aluminum−alanate phase boundaries. In this model the Ti dopant facilitates the nucleation of the aluminum phase nuclei. Sun et al. do not comment on whether the enhancement of nucleation is due to induction of defects, the Ti−Al interaction (as Ti species may themselves nucleate the formation of Al-rich phases, as in Figure 6), or some other effect in their proposed mechanism.

Kang et al.[180] also proposed a mechanism in which the Ti dopant promoted the formation of Al-rich particles (Figure 6). This was based on combined electron microscopy and X-ray imaging of hydrogen-cycled alanate samples doped with Ti powder, believed to react with H_2 to form TiH_2 on milling. The combined electron and X-ray microscopy indicated that, on cycling, the Ti hydride was located in the central regions of Al-rich regions of the product, leading to the conclusion that the Ti hydride promoted nucleation of Al particles, enhancing the kinetics of the dehydrogenation reaction. No comment was made on rehydrogenation mechanisms.

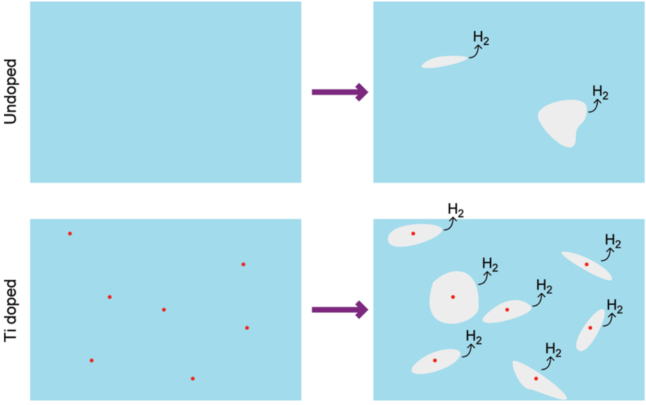

Figure 6. Dopant particles nucleating Al grains.

Singh et al.[68] performed primarily a series of neutron diffraction experiments studying the $NaAlH_4$ system. The $TiCl_3$-doped alanate was decomposed in situ and rehydrogenated under D_2 pressure. These authors did note the importance of vacancies in the diffusion rates within solid state reactions and that they saw convincing evidence of substantially higher fractions of hydrogen vacancies in the hydride phases of the $TiCl_3$-doped system. However, this was not the main mechanism of Ti catalysis proposed by Singh et al.

Rather, Singh et al. have proposed a much simpler primary catalytic effect of Ti. The proposed mode of action has some similarities to the nucleation-type mechanisms discussed above, but a very different interpretation of the effect. Singh et al. noted that the particle sizes of the various phases present grew substantially on dehydrogenation in the undoped alanate, whereas they remained uniformly small in the $TiCl_3$-doped sample when hydrogen cycled (see Figure 7). $TiAl_3$ is known to alter the freezing dynamics of liquid aluminum, producing small grains in the solid material. Singh et al. also hypothesized that NaCl—present in $TiCl_3$-doped sodium alanate samples—could seed NaH crystal growth and hence encourage a greater number of small NaH particles. So the primary mode of catalysis proposed by Singh et al. is the physical effect of nucleating product phases, improving diffusion kinetics, acting in concert with increased vacancy concentrations. This is quite distinct from the kinetic effects of phase nucleation and growth proposed by Fichtner et al.,[153] Sun et al.,[179] and Kang et al.[180]

The grain-size effect proposed by Singh et al. is somewhat at odds with the earlier experimental results of Gross et al.,[76] who remilled doped $NaAlH_4$ after a number of dehydrogenation/rehydrogenation cycles. No effect on the subsequent reaction kinetics was observed, compared to samples that had not been remilled. While being an indirect measure, this suggests that the grain size and phase distribution of the material is not a significant limiting factor in the kinetics of the system. Furthermore, there is good evidence that Ti−Al phases evolve significantly on hydrogen cycling[115,153] whereas the catalysis effect does not require hydrogen cycling to be effective. Similarly, Ti powder (without significant halides or other counterions) works as an active catalyst, arguing strongly against the involvement of NaCl or related species.

Recently, Yang et al.[181] have performed detailed kinetics measurements of (de)hydrogenation reactions. The observed progress of the reactions was compared to predictions from kinetic models with diffusion, moving boundary, and nucleation/growth

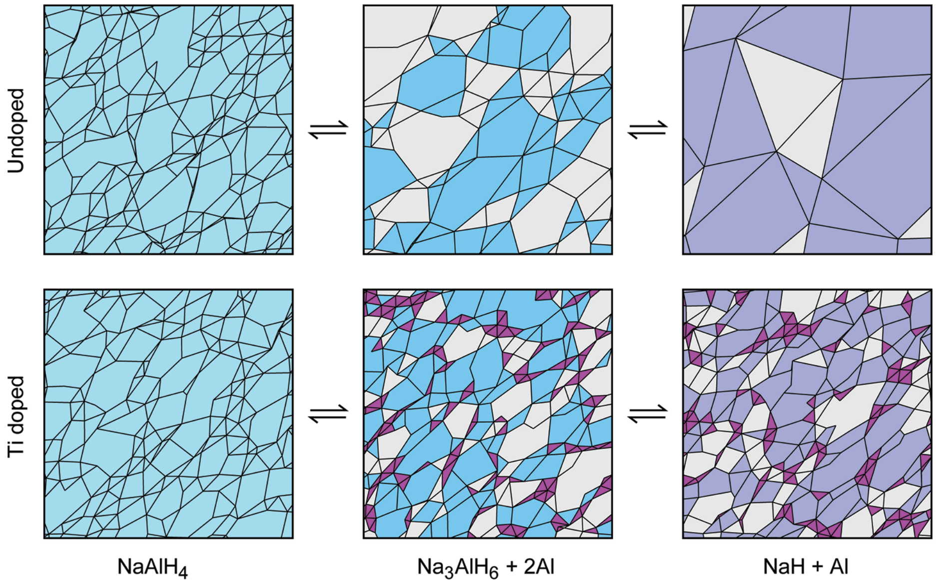

Figure 7. Illustration of the grain size effect mechanism proposed by Singh et al.[68] The presence in the product material of impurity phases derived from the dopant (small dark regions in the lower panels) prevents grain sizes from growing, maintaining rapid intergrain bulk diffusion.

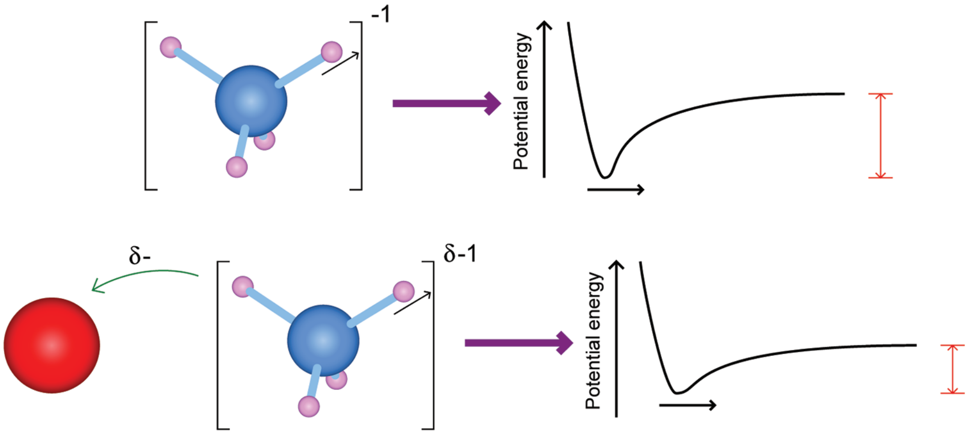

Figure 8. In the mechanism proposed by Du et al.,[185] the electron withdrawing effect of the Ti dopant destabilizes the $[AlH_4]^-$ groups, increasing the lability of hydrogen.

processes as rate-limiting. These authors concluded that while the rehydrogenation reaction followed "moving boundary" kinetics, the dehydrogenation reaction was more complex. It was proposed that while the initial decomposition reaction was limited by nucleation processes, hydrogen diffusion became more important as the reaction proceeded.

4.5. Destabilizes Al—H

Elementary kinetic theory shows that the decomposition temperatures of alanates depend in part on the strength of the Al—H bond. Accordingly, a substantial number of researchers have proposed that the action of Ti catalysts is to somehow destabilize the Al—H bonds in the AlH_n anions of the complex metal hydrides.

Possibly the first to suggest this mechanism were Chen et al.[182,183] in 2001, who speculated that the presence of Ti atoms and ions "influences the affinity to chemisorbed hydrogen of Al sites" in the closely related $LiAlH_4$ system. Sandrock et al.[62] similarly suggested the Ti aided the "breaking and re-forming of covalent Al—H bonds." Subsequently, starting from 2005, a series of researchers have investigated similar ideas.[80,94,102,122,132,143,144,184—186] These mechanisms have mostly been proposed on the basis of computational investigations.

Specifically, several groups have performed periodic DFT calculations on crystals including Ti substituted into the lattice, starting with the ideal $NaAlH_4$ structure,[102,132,144,152,187] the ideal Na_3AlH_6 structure,[143] or $NaAlH_4$ slabs.[122,140] These studies generally (but certainly not universally) see substitution of Ti in Na sites to be coupled with lengthening of Al—H bonds. Where they have been studied, the calculated electronic densities of states, electron densities, and hydrogen vacancy formation energies or dehydrogenation enthalpies for the doped and undoped structures indicate a weakening of the Al—H bond, suggesting increased lability of the hydride.

Du et al.[185] reach a similar conclusion, using a rather different methodology. Apparently motivated by the differing electronegativities of dopants and the presence of charged defects in doped alanate crystals, Du et al. performed gas-phase calculations of AlH_4 tetrahedra. The total charge on these clusters was varied fractionally between $1e^-$ and zero in order to simulate electron-withdrawing effects of Ti dopants. It was established that in these clusters the Al−H bond length and AlH_4 asymmetry increased with decreasing negative charge, implying a weakening of the Al−H bonds. It was concluded that Ti dopants worked to destabilize the Al−H bonds in alanates and, hence, increase hydrogen lability, by withdrawing the charge on the H-containing units rather than through direct Ti−H interaction (Figure 8). These results were supported with further periodic DFT calculations on $NaAlH_4$ crystals and surfaces.

Majzoub et al.[184] also studied the stability of AlH_4 anions, but in undoped $NaAlH_4$. Using a combination of Raman spectroscopy and calculations of phonon modes in the crystal in the vicinity of the melting temperature, these authors concluded that the $[AlH_4]^-$ units retain their integrity through the melting transition. The authors use this to imply Al−H bond-breaking as the rate-limiting step of dehydration, and they further deduce indirectly that Ti dopants must destabilize the Al−H bond.

Wang et al.[80] observed titanium hydrides in $NaAlH_4$ doped with metallic Ti. They subsequently observed similar hydrogen storage performance when doping with TiH_2 directly. From these observations, Wang et al. concluded strongly that the catalytically active species must be a titanium hydride. They went on to note that both Ti−H and Al−H bonds are polar in nature, withdrawing electron density from the metal center, and then they proposed a mechanism in which electrostatic interactions between the $Ti^{\delta+}$ of TiH_x and the $H^{\delta-}$ of AlH_4 destabilize the Al−H bond. After an Al−H bond breaks, these authors suppose the local $NaAlH_4$ structure collapses to release hydrogen.

Furthermore, Wang et al. consider that the specificity of the Ti dopant in allowing rehydrogenation of NaH/Al but not allowing doped Al to form a hydride under hydrogen pressure suggests that the interaction between Na-containing and Ti-containing species is critical. They suggest that interactions with Ti hydride weaken the ionic bonding between Na^+ and H^-. Liberating hydrogen from a strongly bound NaH species would seem to be an important step in allowing covalently bound AlH_n anions to be formed (albeit while possibly remaining associated with Na cations). It is worthwhile to note that TiH_2 has been observed to form when ball-milling a mixture of NaH, Al, and Ti under an inert atmosphere,[66,80,180] and there is evidence for titanium hydrides forming Ti-doped alanate samples.[113,123]

Pukazhselvan et al.[94] studied $NaAlH_4$ doped with mischmetal alloys of lanthanides. Mischmetal was found to also catalyze dehydrogenation. Assuming that the mechanism was the same for mischmetal-doped and Ti-doped $NaAlH_4$, they used characteristics of the mischmetal doped system to draw conclusions about Ti doping. These authors combined the absence of detectable alloys of the dopants with Al with the fact that no metallic sodium is observed to conclude that the active species was metallic clusters of the dopant. The ionization potentials of Na and of small metallic dopant clusters were used to argue that in the doped material there is electron transfer from the dopant to Na ions, neutralizing them. Their proposed mechanism is then that this electron transfer disrupts the interaction between Na^+ and $[AlH_4]^-$, which somehow destabilizes the $[AlH_4]^-$ ion and promotes hydrogen lability. Why the positively charged dopant clusters do not stabilize $[AlH_4]^-$ is not addressed.

Recently, Ljubić and Clary[186] have studied the effect of neutral Ti atoms placed on $NaAlH_4$ surfaces. These authors used wave function-based methods [CCSD(T) and B3LYP] on gas phase cluster models and a DFT approach on periodic $NaAlH_4$ slabs. These calculations were consistent with Ti atoms attracting H atoms from nearby AlH_4 ions. Ljubić and Clary studied H_2 release from these H-rich Ti centers, which was accompanied by significant movement of the Ti−H complex. In this picture, the Ti weakens Al−H bonds directly and provides a site for H_2 to form and migrate to the gas phase.

4.6. Zipper Model

Most calculations on the electronic structure of sodium alanates, and solid state materials in general, are performed using 3D-periodic boundary conditions. While this is usually done for pragmatic reasons, it makes interfacial and phase-separation processes difficult, if not impossible, to study. A few papers have been published which attempt to tease out specific details of the alanate system from small molecular clusters (for example, refs 185 and 186). In contrast, Marashdeh et al. have performed a series of calculations on gas-phase clusters of $NaAlH_4$ interacting with Ti atoms, specifically with the intent of modeling bulk surfaces.[18,51,125] These clusters were constructed with the same local structure as the bulk $NaAlH_4$ crystal and were shown to converge toward bulklike properties for clusters containing a number of $NaAlH_4$ formula units numbering in the tens.

Using these gas phase $NaAlH_4$ clusters, Marashdeh et al. investigated the energetics of monodispersed Ti atoms and TiH_2 molecules interacting with the cluster in various ways. The composition of the clusters was kept constant, sidestepping the issue of appropriate reference energies that haunts substitution studies using periodic boundary conditions. It was determined that it was energetically more favorable for Ti atoms to substitute into the $NaAlH_4$ structure—displacing Na ions or Na−Al pairs—than for them to remain located attached to $NaAlH_4$ surfaces. Similarly, a TiH_2 fragment prefers to displace Na than remain on the surface. Energetically, it is more favorable to take the TiH_2 unit as a whole into the subsurface of the crystal than for Ti to displace Na, leaving the hydrogen behind.

On the basis of these calculations, Marashdeh et al. proposed what they call the "zipper" mechanism of Ti catalysis.[18,125] In this model the catalytically active Ti is a neutral Ti species monodispersed around $NaAlH_4$ grains. At least some of these Ti atoms or Ti-containing fragments will be on the surfaces/grain boundaries of the microcrystalline $NaAlH_4$. Driven by enthalpy differences, in the zipper model these Ti species displace Na ions from the subsurface, ejecting the Na ions and other species to the surface, where they react quickly. In this way, the Ti species effectively eat holes in the $NaAlH_4$ crystals, destabilizing the surface, which decomposes, returning the Ti species to a surface state. The process then repeats. The name for the proposed mechanism comes from viewing the Ti species as the slider of a zip, unhooking the well-ordered crystal, which then reacts, before continuing on. This process is illustrated in Figure 9.

In very recent work, Marashdeh et al. have provided computational evidence for a critical component of their proposed mechanism.[19] These authors have performed "nudged elastic band" calculations and demonstrated that not only is the exchange of Ti atoms adsorbed onto the surface of a $NaAlH_4$ crystallite with subsurface Na atoms energetically favorable, but also the process occurs essentially barrierlessly. In contrast, the authors find that traditional hydrogenation catalysts such as Pd and Pt (that do not effectively catalyze $NaAlH_4$) prefer to absorb into subsurface interstitial sites, not displacing Na atoms.

The zipper model only explicitly deals with decomposition of the alanate. Marashdeh et al. suggest that the simple hydrogen pump mechanism may act to catalyze rehydrogenation.

4.7. Other Surface Processes

A number of other proposals centered around processes at surfaces have been made that do not easily fit into the categories listed above.

In 2004 Walters and Scogin proposed a detailed mechanism for the dehydrogenation and rehydrogenation of sodium alanates.[159] Mobile alanes played a central role in that mechanism, transporting hydrogen to and from the surface of metallic aluminum regions, where it decomposes to release H_2 and grow the Al phase for dehydrogenation, or is formed on the surface of the Al phase for rehydrogenation. The catalytically active Ti in this model is Ti—Al alloys on the surface of the Al phase, which catalyze the $Al + 1.5H_2/3H \rightleftharpoons AlH_3$ reaction on the Al interface. Like many similar proposals, the lack of catalysis when doping with Ti—Al alloys counts against this catalytic mechanism.

Íñiguez and Yildirim performed DFT calculations on 2D slabs of $NaAlH_4$ with exposed (100) and (001) surfaces.[188] The aim of these calculations was to study the energetics of doping Ti atoms into the surface of the $NaAlH_4$ crystallite. They concluded that substituting Ti for either Na or Al in the vicinity of the surface was favorable, with a preference for substituting for Na.

Íñiguez and Yildirim then went on to perform some short-time MD simulations of their doped alanate slabs at 300 K. These MD simulations suggested that while the Ti atoms attract hydrogen atoms, as suggested by many others, these atoms do not form strong Ti—H bonds. Rather, a large number of hydrogen atoms were observed to freely and rapidly migrate backward and forward between Al and Ti metals, with around 7—8 hydrogens associated with Ti dopants at any given time. Furthermore, Ti atoms were observed to associate with multiple Al atoms.

On the basis of these observations, Íñiguez and Yildirim outlined a proposal for the action of the Ti catalyst on dehydrogenation (Figure 10).[188] In their mechanism, finely dispersed Ti atoms stay on or near the surface of the alanate crystallites. The Ti atoms substitute for Na atoms and encourage additional Na vacancies, forcing the Na to migrate elsewhere. The presence of the Ti atoms enhances the lability of the hydrogen in the structure, bringing hydrogen atoms together and facilitating H_2 formation. A $TiAl_y$ phase is formed in the surface, reducing the availability of isolated Al atoms to which hydrogen can migrate back.

Later, Íñiguez and Yildirim presented a rather different argument on the role of Ti.[154] While they argue for a major role for Ti as a site to promote the chemisorption of H_2 and H spillover, they also argue that Ti on the surface of an alanate crystal promotes the formation of surface defects, promoting alanate decomposition. Furthermore, Íñiguez and Yildirim present evidence that pure $NaAlH_4$ surfaces serve as barriers to H atoms, while Ti-containing $NaAlH_4$ surfaces do not. Thus, the very formation of a nascent $NaAlH_4$ phase may stop further hydrogenation reaction in the absence of Ti.

Du et al.[189] performed calculations on 2D slabs of $NaAlH_4$, similar to those of Íñiguez and Yildirim. Du et al. followed the lead of Løvvik and co-workers[18,145] in emphasizing the effect of performing spin polarized DFT calculations, which unpair electron spins. Rather than studying the role of Ti directly, Du et al. studied the implications of any Na surface vacancies that the Ti catalyst may promote. It was shown that surface Na vacancies lead to a number of effects, including the weakening of Al—H bonds; rapid, spontaneous H_2 desorption; and the aggregation of defective AlH_n units into hydrogen-bridged dialane. The observation of spontaneous H_2 desorption, in particular, supports an important role for Ti in forming surface defects.

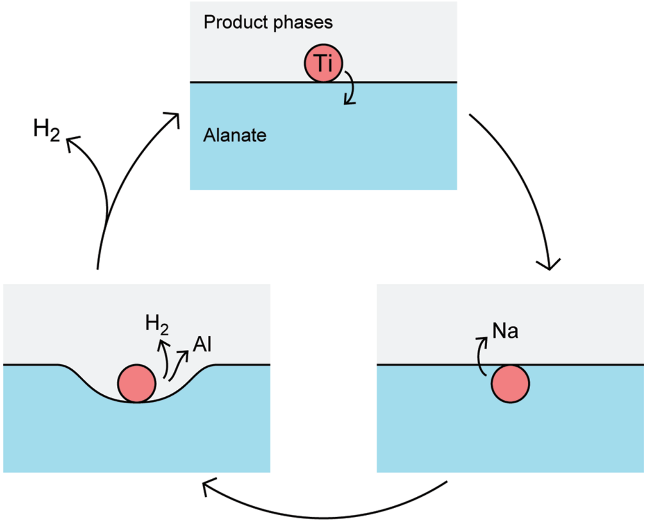

Figure 9. Zipper model of Marashdeh et al.[18,19,125] Enthalpy gradients drive monodispersed Ti into the subsurface of $NaAlH_4$ crystallites, displacing Na and destabilizing the crystal surface, which decomposes.

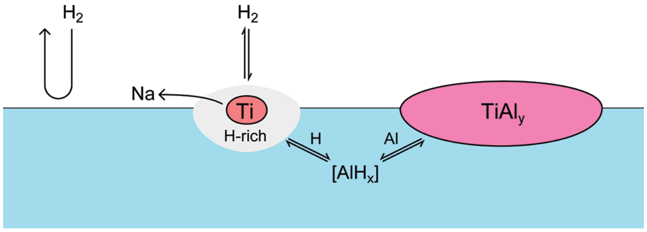

Figure 10. Model of Íñiguez and Yildirim.[154,188]

Dathar and Mainardi have performed a series of MD calculations on pure and Ti-doped $NaAlH_4$ slabs,[155] based on DFT energies. Through the observed behavior of these simulations, they have proposed that the conversion from tetrahydride to hexahydride (the first dehydrogenation step) occurs via four specific fundamental reaction steps:

$$2[AlH_4]^- \rightleftharpoons AlH_3 + [AlH_5]^{2-} \quad (6)$$

$$[AlH_5]^{2-} + [AlH_4]^- \rightleftharpoons [AlH_6]^{3-} + AlH_3 \quad (7)$$

$$2AlH_3 \rightleftharpoons Al_2H_6 \quad (8)$$

$$AlH_3 \rightleftharpoons Al + 3/2\ H_2 \quad (9)$$

With this proposed mechanistic base, with mobile AlH_3 and AlH_4 species, the role of Ti was twofold. First, Ti atoms residing on the alanate surface would provide a low-barrier route to strip hydrogen from AlH_3 and AlH_4 to form H_2 and $TiAlH_x$. These Ti—Al—H species would then nucleate the growth of the Al product phase.

4.8. Mixed Effect Models

Finally, in this section a number of observations and proposals are described which do not fit neatly in the categories above. Generally, these are combinations of the effects proposed above, though mechanisms in which some primary catalytic effect is coupled with a surface hydrogen barrierless dissociation/association have been described elsewhere.

Kiyobayashi et al.[190,191] draw on evidence of equal decomposition rates of doped $NaAlH_6$ and Na_3AlH_6 (as opposed to Na_3AlH_6 as a product of the decomposition of doped $NaAlH_4$), as well as a poor fit to the two-stop dehydrogenation kinetics model at moderate temperatures, to conclude that the rate limiting step in the dehydrogenation process is not the breaking of Al−H bonds. They argue for a mechanism in which phase nucleation and growth or diffusion processes are rate limiting. The implication of this is that the addition of Ti dopants must facilitate these phase nucleation and growth or diffusion processes. However, it should be noted that Kircher and Fichtner performed similar studies, and although they found directly doped Na_3AlH_6 dehydrogenated faster than Na_3AlH_6 produced from doped $NaAlH_4$, this was still slower than the initial rate of dehydrogenation of Ti-doped $NaAlH_4$.[192]

While $TiAl_3$ and related Ti−Al phases have been implicated (by association) in the enhanced dehydrogenation of doped sodium alanate, Brinks et al.[135] have suggested that such phases act as Ti and Al soaks. These phases appear not to form hydrides or to react with hydrogen in other ways. Thus, the aluminum becomes unavailable for forming alanate, the titanium becomes unavailable for independently catalyzing (de)hydrogenation if the Ti−Al phase is not catalytically active, and the hydrogen storage capacity of the system is reduced. This idea is supported by the observation that adding excess aluminum to the doped system increases the hydrogen storage capacity.[66,75]

The work of Bai et al.[140] proposes a model that combines Al−H weakening with the proposition of mobile AlH_3. On the basis of DFT calculations, these authors agree with the general idea that Ti atoms in the alanate material weaken Al−H bonds by attracting H atoms to the Ti. However, rather than using the weakened Al−H bond to explain the enhanced evolution of H_2 directly, they propose that the Ti−H attraction allows an AlH_4 anion to shed a hydrogen atom and become a mobile AlH_3 species. This proposal is consistent with the work of Du et al.[185] showing that electron withdrawal from AlH_4 anions increases their asymmetry. In an analysis reminiscent of that of Peles and van de Walle,[174] Bai et al. invoke the effect of the hydrogen chemical potential on equilibrium defect concentration in an attempt to link low hydrogen concentrations with a reduced Al−H bond weakening effect so as to allow rehydrogenation.

5. CONCLUSION

As should be apparent from the preceding sections, a wide variety of catalytic mechanisms have been proposed for Ti-containing species in $NaAlH_4$. Most, if not all, of these have some sort of experimental or computational evidence supporting them. The proliferation of competing models ably illustrates that none have gained broad-based acceptance as being likely to be representative of reality.

Two particular aspects of Ti catalysis of the sodium alanate system appear to be particularly difficult to address. At least, two aspects are often not addressed. The first challenging aspect is explaining how the presence of Ti facilitates the rapid decomposition of both $NaAlH_4$ and Na_3AlH_6 and, at the same time, how Ti being present in the solid decomposition products allows rehydrogenation to proceed. The second, possibly more important, aspect that is critical to a satisfactory explanation of the catalysis mechanism is explaining what is special about Ti. In many of the proposed mechanisms, there is no immediately obvious reason why other transition metals are not effective catalysts. Only a few authors, Peles[174] and Marashdeh[19] among them, have directly addressed this question.

A number of mechanistic aspects are well-supported and seem likely. Namely: (a) There are mobile vacancies present, likely involving hydrogen at least in part. (b) Ti accumulates in Al-rich phases, but bulk Ti−Al phases do not open critical catalysis paths. (c) Alanes are likely mobile to some degree in the partially hydrogenated material. (d) The presence of Ti affects the grain and particle sizes in the dehydrogenation products (however, this may be unrelated to the catalytic effect). Furthermore, processes occurring at the surface of Al-rich grains are frequently thought to be important to the (de)hydrogenation reactions.

As has been suggested by several authors, there is certainly room in the overall catalytic effect for several different mechanisms to operate simultaneously. More than one mechanism could operate independently of each other, each catalyzing a different step in the overall (de)hydrogenation reaction. Furthermore, there is considerable scope for synergies between the proposed mechanisms presented individually above. For example, there is clearly a relationship between dopants modifying the Fermi level of the doped material and the density of charged defects. The density of defects, charged or otherwise, likely affects the rate of defect migration. Furthermore, the presence of defects affects the stability of AlH_x anions, either enthalpically through charge transfer effects or simply kinetically through equilibrium concentrations of hydrogen in various sites. Extended mechanisms attempting to correlate such interconnected effects beyond one or two steps have not yet appeared in the literature.

After 15 years of investigation, the catalysis mechanism of Ti in $NaAlH_4$ remains unconfirmed, primarily due to its inscrutability. It remains unclear where consensus with regard to the catalysis mechanism—and what makes Ti apparently so special—will come from.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tjf@rsc.anu.edu.au.

BIOGRAPHY

Terry Frankcombe (born 1975, Tasmania) received his B.Sc. (Hons) with a University Medal from the Australian National

University in 1997, which included a period conducting research with Prof. Sture Nordholm at Göteborgs Universitet. He completed his Ph.D. in 2001 under the supervision of Prof. Sean Smith at the University of Queensland. This was followed by postdoctoral work at the University of Queensland (2002−2003) and with Prof. Geert-Jan Kroes at the University of Leiden (2004−2006). He spend a year at Göteborgs Universitet as a Marie Currie Fellow working with Prof. Gunnar Nyman before returning to the Australian National University to work with Prof. Michael Collins. In 2010 he was awarded a Future Fellowship by the Australian Research Council. His theoretical and computational research interests are diverse, from modeling solid state materials to astrochemistry and quantum scattering methodology.

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