Chapter 5

A density functional theory study of the TiH₂ interaction with a NaAlH₄ cluster

To understand the role of titanium in catalyzing the de/rehydrogenation reactions in NaAlH₄, it is necessary to determine the composition and structure of the catalytically active species that is (are) formed during ball milling and de/rehydrogenation reactions. One of the species that is thought to be catalytic active is TiH₂. We have performed a density functional theory study of TiH₂ interacting with a NaAlH₄ cluster. First, a TiH₂ molecule was adsorbed on the (001) surface of NaAlH₄ in different sites. Next, the TiH₂ molecule or its Ti atom was moved inside the cluster either by exchanging the whole TiH₂ molecule with Na or Al, or by exchanging only the Ti atom with Na or Al and leaving the two hydrogen atoms on the surface together with the exchanged atom. Our calculations suggest that, when restricting the possible outcomes to adsorption, TiH₂ adsorbs on the surface above a Na site, pushing the Na atom subsurface. However, exchanging the whole TiH₂ unit with the subsurface displaced Na atom is favorable compared to leaving the TiH₂ on the surface. All other investigated exchanges were found to be less stable than TiH₂ adsorbed on the surface. The results are consistent with a zipper model that we recently proposed.

5.1 Introduction

“Vehicles can be run either by connecting them to a continuous supply of energy or by storing energy on board. Hydrogen would be ideal as a synthetic fuel because it is lightweight, highly abundant and its oxidation product (water) is environmentally benign, but storage remains a problem” [1]. This direct quote from a 2001 review paper unfortunately still holds true, while a safe and economic high-performance hydrogen storage system is a requirement for providing an onboard hydrogen source for fuel cells in mobile applications [1]. A considerable amount of research has been done on conventional hydrogen storage systems (high pressure or low temperature), but so far they do not meet the requirements for the mobile fuel cell applications. For a long time there seemed to be no alternative. This situation changed in 1997 when Bogdanovic and Schwickardi found that by adding small amounts of Ti to NaAlH₄,
the hydrogenation and dehydrogenations kinetics is greatly improved, which promoted NaAlH₄ to a promising reversible hydrogen storage candidate that is close to meeting the mobile fuel cell requirements [2].

The finding that hydrogen storage in complex metal hydrides can be made reversible with its kinetics improved by adding a catalyst (or dopant) sparked many studies on the light complex metal hydrides, in particular on NaAlH₄ with the goal of understanding the role of the Ti catalyst. Many efforts have been aimed at understanding the composition and structure of the catalytic species. There are suggestions that a fractional amount of the added Ti diffuses and substitutes into the NaAlH₄ lattice [3, 4]. Some studies have found formation of TiAl compounds with different Ti:Al compositions, depending on the ball milling and reaction conditions used [5-13].

Of special interest to this Chapter is the suggestion of Balema et al. [5] that the Al₅Ti alloy produced from Ti-enhanced NaAlH₄ reactions contains a catalytic titanium hydride phase. This catalytic phase may have been hard to detect and analyze in several previous experiments because it might have fallen below the detection limit of the analytical techniques employed [5], in particular since Ti can form a broad range of hydride phases TiHₓ with 0<x<2 [14] which makes it more difficult to detect experimentally. Gross et al. [3] showed that the kinetics can be enhanced either by doping NaAlH₄ with TiH₂ directly or through indirect doping by pre-reacting TiCl₂ with LiH. However, the improved reaction rates were only achieved after about 10 cycles. They suggested that this prolonged activation period allows for Ti diffusion and substitution into the NaAlH₄ lattice. The advantage of using TiH₂ as a dopant is not only to improve kinetics but it should also overcome the problem of hydrogen capacity loss associated with the use of Ti-halides [3].

Experiments have also shown that the milling conditions employed can play a crucial role in the formation of the catalytic species. Experiments on a (1:1) mixture of NaH with Al doped with Ti powder and milled under either an H₂ or an Ar atmosphere showed that the doped material prepared in the presence of hydrogen has significant improvements in hydrogenation rate and hydrogen capacity over the material prepared in the presence of argon. This gave an indication that the presence of
hydrogen affects the nature of the active Ti species [15]. Based on these [15] and other results [2, 3, 5, 6, 7, 9], it was suggested that the doped NaAlH4 materials do not all contain the same active Ti species; rather, they may contain a variety of related active Ti species [15].

Using X-ray diffraction Wang et al. have identified (catalytically active) nanocrystalline Ti hydrides that were formed in situ by ball milling Ti powder with either a NaH/Al mixture or NaAlH4 [16]. They also found that NaAlH4 doped directly with commercial TiH2 has quite similar catalytic activity as the material doped with metallic Ti, and a slight composition variation of the Ti hydrides was found by variation of the preparation conditions during the doping process [16]. They suggested that the formed Ti hydride phase(s) should be highly dispersed in the NaAlH4 matrix. By using electron microscopy with energy dispersive X-ray analysis, the same group found that the TiH2 particles obtained by milling NaH with Al and Ti-powder are randomly distributed in the as-prepared sample, while after cycling the TiH2 particles stay near the centre of the segregated Al rich particles [17].

There are somewhat conflicting results in the literature with respect to the dehydrogenating kinetics of TiH2 doped NaAlH4 materials as compared to Ti(III) doped materials. Gross et al. [3] have shown that the desorption rates of TiH2 doped samples are equivalent to those of doped materials with 1-2 mol.% of TiCl3. Brinks et al. [18] have found that TiCl3 and TiH2 give comparable kinetics. Doping the alanate with Ti powder under a hydrogen atmosphere, resulting in TiH2 formation, has shown slower dehydrogenation kinetics than those arising upon doping the alanate with TiF3 [19]. The reason behind this variation in kinetics might be due to differences in composition of the Ti hydrides [16].

When ball-milling an Al3Ti alloy in a hydrogen atmosphere, nano-sized TiH2 inclusions were found [20]. Al3Ti reacts with hydrogen and produces a TiH2 phase distributed in the material [20]. After an intermetallic powder of Al3Ti was milled under hydrogen and helium atmospheres, very small grains of an Al1.3Ti0.7 phase were found [21]. Continuous heating of this material resulted in hydrogen desorption [21]. It was also found that a nano-crystalline Al3Ti–TiH2 composite forms during ball-milling of Al and Ti powders in a hydrogen atmosphere [22].
Theoretical studies employing density functional theory (DFT) and modeling Ti-doped NaAlH4 using periodic boundary conditions have shown that Na-substitution is favored if the substituted metal (Na or Al) is not allowed to aggregate [23-25], i.e., if the substituted atom is located in the gas phase, while Al-substitution is favored if the substituted metal is allowed to aggregate [26-28]. Recently, Vegge performed DFT slab calculations to determine the deposition energy of Ti/TiH2 and the substitutional energy for Ti@Al and Ti@Na-sites on the exposed surfaces [29]. TiH2 adsorption was modeled by adding two hydrogen atoms to the titanium atom adsorbed on the surface to investigate the effect of changing the Ti-valence [29], since it was found to have a significant effect on hydrogen diffusion [23]. Vegge’s results for the deposition energy of Ti and the substitutional energy for Ti@Al and Ti@Na-sites are consistent with the results of Løvvik et al. [26, 28]. Studying the interaction of Ti with (001) and (100) surfaces of NaAlH4 Ti was found to be in the interstitial sites between three neighboring AlH4 units. The resulting local structure around Ti atom is TiAlH12 [30, 31].

Most of the theoretical work modeling Ti-doped NaAlH4 has used periodic calculations. We use a different approach to study the Ti-doped NaAlH4 system, employing a cluster model. One of the main reasons for choosing the cluster model is that this model might yield a more realistic description than a periodic model of NaAlH4 particles of the size of 150-200 nm [10]. Another important reason for studying (small) cluster models can be found in the fact that particles much smaller than 100 nm can release some of the incorporated H2 even without Ti at lower temperatures than in Ti-catalysed NaAlH4 [32]. Also, a cluster model opens the possibility to model the complicated phase transitions taking place during (de-)hydrogenation.

In our previous work, we used a geometry optimized twenty three formula units NaAlH4 (Z=23) cluster to introduce a new reference system: a Ti atom adsorbed on the surface of the cluster, assuming that some of the Ti can be present in monatomic dispersed form, which could constitute the active catalyst. By exchanging the Ti atom with Na or Al atoms or letting Ti occupy interstitial sites, we measured the stability relative to the newly chosen reference system. We found that the Ti atom preferably exchanges with a Na atom in the subsurface region or occupies an
interstitial site [33]. Then we looked for cooperative effects between two Ti atoms in the cluster. We found that the Ti dimer dissociates on the surface of the cluster and the resulting Ti atoms behave similarly to the mono-atomically dispersed case. After dissociation the two Ti atoms prefer to move to the subsurface region inside the cluster either to exchange with two Na atoms (preferred) or with neighbouring Na and Al atoms, such that the two Ti atoms end up close enough to each other to form a direct bond [34].

In the present work, we continue with our Z=23 model cluster to investigate the stability of TiH$_2$ and its interaction with NaAlH$_4$. One of the important questions we address is whether TiH$_2$ prefers to exchange with Na or Al inside the NaAlH$_4$ cluster, and whether the exchange taking place involves a whole TiH$_2$ unit or only the Ti atom without the hydrogen atoms. We have determined the most stable adsorption and absorption geometries, focusing on the overall energetics. We have also looked into the local structure and bonding around the TiH$_2$, and compared the results with the local structure around a single Ti atom determined in the previous work [33].

5.2 Method

Density functional theory (DFT) [35, 36] as implemented in the ADF code [37] has been used to calculate all the binding energies of the clusters. The bulk crystal structure of the 23 formula units (Z=23) cluster was used as initial geometry to perform a geometry optimization of the bare (Z=23) cluster (see also Ref. [33]), which then served as a starting point for geometry optimizations on the TiH$_2$ + NaAlH$_4$ system (see Section 5.3.1 below). The exchange-correlation energy is approximated at the generalized gradient approximation (GGA) level using the functional of Perdew et al. (PW91) [38]. A triple zeta plus one polarization function (TZP) type basis set is used with a frozen core of 1s on Al as well as Na and 1s2s2p for Ti. In our previous studies we found that it was important to consider both spin restricted and unrestricted calculations [33, 34]. All calculations in the present study have been done both at the spin restricted and unrestricted levels, and they confirm this conclusion. The spin unrestricted calculations were performed allowing one, two, three and four electrons to be unpaired. However, note that below only the values for the energetically most stable states are reported (together with the corresponding number of unpaired electrons). Other computational details can be found in Ref. [33].
The ADF code calculates the total binding energy relative to spin restricted spherically symmetric atoms. The only purpose of this reference state, is to provide a reference energy common to all calculated energies. When considering TiH$_2$ adsorbed/absorbed on/in the Z=23 model cluster our zero of energy has been set to that of the fully optimized bare Z=23 cluster plus TiH$_2$ in TiH$_2$ bulk. Note that we have defined the adsorption/absorption energies in such a way that a negative number means that it is stable with respect to TiH$_2$ in TiH$_2$ bulk. Our periodic bulk TiH$_2$ calculations have been performed using ADF-BAND [39] with the same basis and fit sets as used in the cluster calculations.

### 5.3 Results and Discussion

#### 5.3.1 The adsorption of TiH$_2$ on the (001) surface of the cluster

The geometry optimized structure of the bare twenty three formula units (Z=23) NaAlH$_4$ cluster (see also Ref. [33]) was used as initial geometry to perform geometry optimizations for the TiH$_2$ + (NaAlH$_4$)$_{23}$ system. TiH$_2$ was adsorbed on the (001) surface of the optimized bare cluster (Fig. 5.1a) in different positions. The adsorption energies of TiH$_2$ on the relaxed clusters are listed in Table 5.1 and the surface geometries are displayed in Fig. 5.1. The TiH$_2$ was adsorbed between 4 AlH$_4$ units above the Na atom [TiH$_2$@top$_{4}$AlH$_4$], in the bridge site between 2 AlH$_4$ units [TiH$_2$@top$_{2}$AlH$_4$], and between 3 AlH$_4$ units [TiH$_2$@top$_{3}$AlH$_4$] as shown in Figs. 5.1b, 5.1c and 5.1d, respectively. We also tried to adsorb the TiH$_2$ above a single AlH$_4$ unit, but we could find no stable minimum for this geometry (the TiH$_2$ moved to the bridge site [TiH$_2$@top$_{2}$AlH$_4$]). Comparing the energy of the bare Z=23 cluster and TiH$_2$ in the gas phase [TiH$_2$+Z=23] with the adsorption energies for the three different adsorption sites described above (Table 5.1), TiH$_2$ is clearly found to be more stable on the surface of the cluster than in the gas phase. The adsorption energies for the three different sites on the surface show that the most stable adsorption site is TiH$_2$@top$_{4}$AlH$_4$. As seen from the side views of the TiH$_2$@top$_{4}$AlH$_4$ cluster in Fig. 5.1e and of the bare cluster in Fig. 5.1g, the surface Na atom is pushed down considerably when TiH$_2$ is adsorbed above it.

A similar displacement of the surface Na atom(s) to the subsurface region was also observed when one (two) Ti atom(s) was (were) adsorbed above the surface Na
Fig. 5.1: The figure shows TiH$_2$ adsorbed in different positions on the (001) surface of the Z=23 model cluster viewed from above. The Na atoms are displayed as green balls, Ti as a red ball, the two hydrogen atoms of the TiH$_2$ as light blue balls, and Al as dark blue balls inside the tetrahedrons with the four hydrogen atoms at their corners. (a) The surface of the bare cluster. (b) A TiH$_2$ above Na atom between four AlH$_4$ units [TiH$_2$@top$_4$AlH$_4$]. (c) A TiH$_2$ between two AlH$_4$ units [TiH$_2$@top$_2$AlH$_4$]. (d) A TiH$_2$ between three AlH$_4$ units [TiH$_2$@top$_3$AlH$_4$]. (e) Side view of TiH$_2$@top$_4$AlH$_4$ cluster surface. (f) Side view of Ti@top$_4$AlH$_4$ cluster surface. (g) Side view of bare cluster surface. In the side views (e) and (f), the subsurface displaced Na atoms are indicated by arrows.

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<th>$E_a$</th>
<th>$E_{\text{rel, top}}$</th>
<th>$n$</th>
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Table 5.1: The adsorption/absorption energies ($E_a$) are given for the TiH$_2$ system. The energy reference used is discussed in the method section. The notations used to refer to a given structure are defined in Figs. 5.1 and 5.2. All the energies are given in eV, and all results have been obtained from fully relaxed geometries. The number of unpaired electrons giving the lowest energy is denoted $n$. 

atom(s) [33, 34]. The Na displacement resulting from a mono-dispersed Ti atom adsorbed on the surface, Ti@top_4AlH4 [29] is compared to that of TiH2@top_4AlH4 in Figs. 5.1e and 5.1f, with the reference Na position in the bare cluster displayed in Fig. 5.1g. It is clear that in the case of TiH2@top_4AlH4 the Ti atom sits deeper into the surface and the Na atom is displaced even further into the subsurface region.

### 5.3.2 The stability of TiH2 inside the cluster

We have also investigated the stability of the TiH2 inside the cluster (a side view of the bare cluster is shown in Fig. 5.2a). The TiH2@top_4AlH4 cluster (Fig. 5.1b) was taken as a starting geometry for making TiH2 exchanges with Na and Al. Two kinds of exchanges have been considered. First, the whole TiH2 unit was exchanged with either a Na or Al atom [TiH2@Na, TiH2@Al], as shown in Figs. 5.2b and 5.2d, respectively. Next, only the Ti atom was exchanged with either a Na or an Al atom, leaving the two hydrogen atoms on the surface together with the exchanged Na or Al atom [Ti@NaH2, Ti@AlH2], as shown in Figs. 5.2c and 5.2e, respectively. The reason for making the two different kinds of exchanges is, of course, to check whether the TiH2 molecule prefers to move as a whole, or whether only its Ti atom is involved in the exchange. As may be seen in Table 5.1, the TiH2 molecule prefers to exchange with the subsurface displaced Na atom [TiH2@Na] (Fig. 5.2b). This exchange is found to be more stable than the adsorption of TiH2 on the surface [TiH2@top_4AlH4] by 0.56 eV, indicating that TiH2 prefers to move into the subsurface region of the cluster rather than to stay on the surface of NaAlH4. Note that the exchange takes place through moving the whole TiH2 unit subsurface. Leaving the two hydrogen atoms with the exchanged Na atom on the surface to form a Ti@NaH2 cluster is less stable by 1.32 eV compared to the TiH2@Na cluster, and also less stable than the starting geometry [TiH2@top_4AlH4] by 0.76 eV. Leaving one hydrogen atom with the exchanged Na atom on the surface and taking one H-atom with Ti to form a TiH@NaH cluster (Fig. 5.2f) is also unfavorable, being less stable by 0.92 eV compared to the TiH2@Na cluster. The exchanges with an Al atom are also unstable compared to TiH2@Na: The Ti@AlH2 and TiH2@Al exchanges are unstable by 0.75 and 2.15 eV, respectively, both also being unstable compared to the starting geometry. Note, however, that in the case of Ti exchange with an Al atom it is preferable to leave the two hydrogen atoms on the surface together with the exchanged Al atom.
Fig. 5.2: TiH₂ absorbed in different positions in the Z=23 cluster. The atoms are displayed in the same way as in Fig. 5.1. (a) The bare cluster. (b) TiH₂ unit exchanged with a Na atom [TiH₂@Na]. (c) A Ti atom (of the TiH₂) exchanged with a Na atom while leaving the 2 H atoms on the Na atom [Ti@NaH₂]. (d) TiH₂ unit exchanged with an Al atom [TiH₂@Al]. (e) A Ti atom (of the TiH₂) exchanged with an Al atom while leaving the 2H atoms on the Al atom [Ti@AlH₂]. (f) TiH exchanged with a Na atom while leaving one H atom on the exchanged Na atom [TiH@NaH].

These results are very similar to what we have found when one or two Ti atoms were adsorbed on the surface of NaAlH₄, or exchanged with Na or Al atoms [33, 34]: When restricting the possible outcomes to adsorption on the surface, the adsorbed species (Ti, 2Ti, or TiH₂) prefers to be on top of a Na atom between 4 AlH₄ units, and the surface Na atom is pushed subsurface as a result of the adsorption. However, the energetically most stable situation is in all cases found when the Ti-containing species is exchanged with the subsurface displaced Na atom.

5.3.3 The interaction of H₂ with a Ti, Na or Al atom on the surface of the cluster

By combining the present results with some of our previously published results [33] we have tried to address the question what would happen if a mono-dispersed atom (Ti, Na or Al) on the surface of the NaAlH₄ cluster interacts with H₂. This is important for understanding the stability of the possible different structures formed during the de/hydrogenation processes. The relevant available data are presented in Fig. 5.3, showing an energy difference diagram for different structures.
Fig. 5.3: Diagram showing the energy differences between a number of different structures. A simplified representation is shown for the Z=23 formula units NaAlH₄ cluster with a TiH₂ unit added: The horizontal lines in the figure (both blue and black) represent the surface of each cluster. The two hydrogen atoms are shown as two light blue balls, and the Ti, Na, and Al atoms as red, green, and dark blue balls, respectively. When the Ti atom is below a horizontal line it means that it has been exchanged with a Na or Al atom in the cluster, and the atom with which it has been exchanged is placed above the horizontal line. The arrows with their attached numbers indicate energy changes when moving between the different structures. All black lines and arrows represent results calculated in the present study. The full blue lines and arrows represent results presented in Ref. [33]. The dashed blue arrows represent results that have been obtained by combining the results from these two studies ([33] and the present work).

It is clear from the diagram that any excess of H₂ (e.g. stemming from the dehydrogenation of a nearby NaAlH₄ particle) would gain a significant amount of energy (in the order of 2 eV) if reacting with a NaAlH₄ surface containing Ti. Whether this will happen or not will probably depend on the state of the surface. If Ti has already changed place with Na, there is considerable energy (0.59 eV) to be gained by dissociating H₂ to form NaH on the surface and TiH subsurface, but there is probably a significant kinetic barrier for this process. If Ti is still at the surface, there is a large energy benefit for H₂ to react with Ti, and TiH₂ would probably be formed easily. Similarly, if H₂ is present at the time Ti is introduced to the surface, the
Table 5.2: A comparison between Al-H, Ti-Al and Ti-H bond lengths (in Å), in the bare cluster, the cluster with Ti exchanged with the subsurface displaced Na atom (Ti@Na) and the cluster with TiH2 exchanged with the subsurface displaced Na atom (TiH2@Na).

formation of TiH2 seems to be highly beneficial: formation of TiH2@top_4AlH4 from H2 + Ti@top_4AlH4 is accompanied by a release of more than 2 eV of energy. Only some experimental studies have identified TiH2, and the reason may be that H2 was only present in a high enough concentration during the reaction of Ti with NaAlH4 in some of the experiments.

5.3.4 The local structure around Ti

In our previous studies, we found that the situation in which Ti is exchanged with the subsurface displaced Na atoms is preferred energetically [33, 34]. This is also true for TiH2. It is therefore interesting to compare the local bonding structures for these systems. On the one hand, as seen from the bond lengths in Table 5.2, the presence of a TiH2 in TiH2@Na leads to shorter Ti-H bonds and longer Ti-Al bonds than the presence of a Ti atom in Ti@Na. On the other hand, the presence of a Ti atom in Ti@Na leads to longer Al-H bonds than the presence of a TiH2 in TiH2@Na. Apparently, a Ti atom softens the Al-H bond more than a TiH2 molecule, which might influence the dehydrogenation kinetics.

The Ti atom (TiH2) in Ti(TiH2)@top_4AlH4 clusters is found to be surrounded by 4 close lying Al atoms, of which two are significantly closer, and may be said to be present in the first coordination sphere (CS), while 2 are in the second CS. The Ti-Al distances and coordination numbers for the adsorption states are close to those found in NaAlH4+Ti after ball-milling (the material denoted SAH-start in Ref. [13] (see Table 5.3)). However, in the case of Ti(TiH2)@Na, although the distances of Ti to the Al-atoms in the first three CSs are close to those found for the first two CSs of the NaAlH4+Ti material after H2 desorption, the total numbers of Al atoms in the first and second CS (6 vs 8.5) are not equal. This indicates that Ti(TiH2)@Na can not be the
Table 5.3: A comparison of Ti-Al distances from our theoretical calculations and the experimentally measured values of Baldé et al. [13] in the first, second and third coordination sphere (CS). The number of Al atoms, n, at the indicated distance from Ti is also displayed.

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5.3.5 Further support of the zipper model

Recently we introduced the so-called zipper model to explain how Ti could improve the kinetics in the NaAlH₄ system [34]. In this model, Ti works as a novel kind of catalyst by acting as a slider, eating itself into the nano-particle as it reacts away – effectively unzipping the structure (see Fig. 5.4). In this way, the fully hydrogenated alanate could be decomposed, and at the same time fresh surfaces could be exposed along the route of the zipper. Note that the most reactive of all structures is the one with Ti on the surface. The first reaction according to our zipper model is that Ti moves into the subsurface region of the structure replacing Na. In our model we assume that the Na atom left on the surface can easily react with other species present, because it is an exposed and under-coordinated atom.

In the present study evidence is found that it is rather likely that TiH₂ will be formed sometimes during this process, especially if H₂ is available in the gas phase when Ti is added to NaAlH₄. What would then happen? Are our present results in accordance with the proposed zipper model? Yes, they are. In the case that TiH₂ is formed, the TiH₂ will play the same role as Ti. The essence of the zipper model is that the exchange with a subsurface displaced atom is favored compared to other atomic rearrangements. In that sense the results for one Ti atom [33], two Ti atoms [34], and the present results for TiH₂ present the same, consistent picture: The energetically
Fig. 5.4: A cartoon shows the zipper model. In step 1, the TiH₂ adsorbs on the surface of the cluster forming the most reactive surface. In step 2, the TiH₂ exchanges with a Na atom in the subsurface region, ending with a reactive Na atom on the surface of the cluster. In step 3, the Na atom reacts with any species in the medium, resulting in 1'—a situation that is similar to 1. In step 4, the TiH₂ again exchanges with a Na atom in the subsurface region, resulting in 2', a situation similar to 2. The process repeats itself until the whole NaAlH₄ species has reacted.

Preferred situation is for Ti (TiH₂) to exchange with the subsurface displaced Na atom.

5.4 Conclusion

We have performed density functional theory calculations at the generalized gradient approximation (PW91) level for a NaAlH₄ cluster with TiH₂ adsorbed on (absorbed in) the (001) surface of the cluster. After studying the adsorption of the TiH₂ molecule on the surface, the TiH₂ molecule or its Ti atom was moved inside the cluster either by exchanging the whole TiH₂ molecule with Na or Al, or by exchanging only the Ti atom with Na or Al and leaving the two hydrogen atoms on the surface together with the exchanged atom. In the case that the possible outcomes were restricted to adsorption, we found that TiH₂ adsorbs on the surface above a Na atom, bonding with 4 AlH₄ units and pushing the surface Na atom into the subsurface region. However, it was energetically preferred to exchange the whole TiH₂ unit with the subsurface displaced Na atom. All other exchanges were unstable compared to the situation were TiH₂ was adsorbed on the surface. These results are consistent with our previous results for one and two Ti atoms interacting with the NaAlH₄ cluster. The results are also consistent with our recently proposed zipper model, in which the mechanism by
which the added TiH₂ promotes H₂ release is explained by the TiH₂ molecule working itself down into the alanate particle by replacing Na, effectively unzipping the structure.

5.5 References