Chapter 3

A density functional theory study of Ti-doped NaAlH$_4$ clusters

This chapter is based on:
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Density functional theory calculations have been performed on Ti-doped NaAlH$_4$ clusters. First the electronic structure and stability of undoped clusters of different size and shape were studied, and then one of these clusters was chosen as a model system for a nano-sized NaAlH$_4$ particle. A Ti atom added to the surface of this model preferably substituted a lattice Na near the surface, when using the NaAlH$_4$ cluster with Ti adsorbed as the reference system and keeping the substituted atoms within the model. This may be a first step towards a model explaining the role of Ti during dehydrogenation and hydrogenation.

3.1 Introduction
Non-catalyzed release of hydrogen from NaAlH$_4$ only occurs at high temperatures with slow kinetics [1], and the reverse reaction starting from the decomposed material hardly takes place at all [2]. However, in 1997 Bogdanovic and Schwickardi showed that the reaction can be made reversible at relatively low temperatures and pressures, and with greatly improved kinetics, by adding Ti to NaAlH$_4$ [3]. As a result, sodium alanate has become a possible candidate for a low cost and high density hydrogen storage material.

Among the large number of additives employed in improving the performance of the NaAlH$_4$ hydrogen storage system, Ti is currently believed to be one of the best catalysts for enhancing the reaction kinetics [4]. However, in spite of the intense research efforts to determine the location of Ti in the sodium alanate and the role it plays in improving the kinetics (see e.g. Refs. [5-17]), our understanding of the system is still rudimentary. From experimental studies we know that the final oxidation state of (most of) the titanium is zero [10, 12-13], independent of the initial oxidation state and of how Ti is added to the alanate. It is also known that a large part of the Ti is forming an intermetallic phase with Al. This is either identified as a
crystalline Al$_3$Ti alloy in the surface region [7, 8, 17] or as an amorphous Ti-Al phase of the form Al$_{1-y}$Ti$_y$, with y between 0.1 and 0.18 [11, 13, 14, 17]. The temperature during cycling determines which of these phases is obtained [8, 17]. The remaining Ti has been suggested to occupy bulk Na sites [5, 6, 9], or to be present as a TiH$_x$ species [15, 16].

Several theoretical studies have sought to determine the location of Ti in the sodium alanate. Løvvik and Opalka studied Ti-doped NaAlH$_4$ using as reference bulk systems NaAlH$_4$, Ti, Na, Al and gaseous H$_2$, finding that Ti is unstable on the surface or when substituted into the lattice, with substitution of Al by Ti being the least unfavorable [18]. Íñiguez et al. found that Ti preferably substitutes lattice Na in the first layer [9, 19], and that such substitution is stable when using gas phase atomic elements as reference. Also in the study of Araújo et al. it was found that titanium prefers to occupy a Na site when using the gas phase atomic elements as reference [20]. However, when they used the cohesive energies of Al, Na, and Ti as the reference, their results were in agreement with those of Løvvik and Opalka. Løvvik and Opalka recently repeated their study using comparisons of the product side of various reaction equations involving all known and a number of hypothetical phases in the doped system [21]. This eliminated the necessity of an external reference system for studying the thermodynamic equilibrium of the system, and gave conclusions similar to their previous study.

The questions we seek to answer in this theoretical study are related to the ones addressed by many other studies: Where can Ti be located in NaAlH$_4$? Does it always stay on the surface or may it move subsurface or into the bulk? Would it occupy an interstitial position, or rather exchange positions with a Na or Al atom? However, our approach to the issue is different than that employed by others. We take as starting point a Ti atom absorbed on the surface of NaAlH$_4$, define this as our reference system, and subsequently move the Ti atom to different places or exchange it with Na or Al atoms, asking the question whether any of the resulting structures are more stable than our starting structure. Although our starting point can easily be justified, using this as a reference system is not unproblematic. We will address this in detail and discuss the relevance of our chosen reference system with respect to those employed in other studies.
In this study we have chosen to model the sodium alanate using clusters, in contrast to most other studies where periodically repeated supercells are employed. The main advantage of the cluster approach is that we will (in future studies) be able to describe the dehydrogenation/hydrogenation cycling, including phase separation, without being hindered by the periodic boundary conditions. We also think that it will be fruitful to approach the NaAlH$_4$ hydrogen storage system from the nano-sized particle perspective, since it will provide us with a different (or complementary) view to the one offered from an infinite bulk/surface approach—after all, the real Ti-doped NaAlH$_4$ storage system consists of nano-sized particles [14]. Also, this gives us the possibility to keep the number of atoms constant during substitution, making it possible to directly compare total energies of various models. To the best of our knowledge, only one previous study has been based on a cluster approach, and there it was used to assist in the interpretation and assignment of the characteristic Raman bands of NaAlH$_4$ [22].

This Chapter is organized as follows. In Section 3.2 the computational method is described. This is followed by a presentation of our results and a discussion of them in Section 3.3, with the undoped clusters being addressed in Section 3.3.1, and the Ti-doped cluster in Section 3.3.2. Our conclusions are given in Section 3.4.

3.2 Method

Our ultimate goal is to describe the full dehydrogenation/hydrogenation cycling of NaAlH$_4$, and in particular to determine the role of the Ti catalyst in improving the kinetics. This can best be accomplished through a cluster approach. Our calculations have been performed within a density functional theory (DFT) [23, 24] framework at the PW91 [25] generalized gradient approximation level, as implemented in the ADF code [26]. We have employed a triple zeta plus one polarization function (TZP) type basis set. A frozen core of 1s on Al as well as Na was chosen, together with 1s2s2p for Ti. A large set of tests was performed to ensure that the chosen basis set and frozen core approximation give results reasonably close to the basis set limit and all electron calculations. The general accuracy parameter of ADF [26] was set to 4.0 based on a series of convergence tests. In many of the calculations we applied a non-zero electronic temperature to avoid problems with the SCF convergence. However, we ensured that we eventually ended up in the electronic ground state by gradually
cooling the electrons. The standard ADF fit sets (for the TZP basis sets) used to represent the deformation density were replaced by the fit sets corresponding to the quadruple zeta plus four polarization functions type basis sets. This was necessary since the standard fit sets were found to give inaccurate results. Periodic bulk and slab reference calculations were performed using ADF-BAND [27] with the same basis and fit sets as used in the cluster calculations.

The clusters were built with large exposed (001) surfaces, because the (001) surface has been shown to be the most stable of the different crystal faces [28]. Next, the electronic structure and stability was examined both for bulk-terminated structures and after full geometric relaxations (Section 3.3.1). Based on these results we could choose an appropriate model cluster for studying Ti-doped NaAlH₄. Subsequently, the preferred adsorption/absorption site of Ti in the cluster was determined, after allowing for full structural relaxations, and using mono-atomically dispersed Ti adsorbed on the surface of NaAlH₄ as a reference (Section 3.3.2). In all geometry optimizations of both the bare clusters and the Ti-doped clusters, I use the standard ADF convergence criteria concerning the force, step length and the energy to locate the minimum.

### 3.3 Results and Discussion

#### 3.3.1 Undoped NaAlH₄ clusters: Electronic structure and stability

A number of differently sized and shaped clusters were selected based on suitably chosen cuts from the bulk crystal. They are divided in two classes: (i) Tetragonal clusters with \( Z = 1, 2, 4, 8, 12, 16, 20, \) and 42, respectively (\( Z \) denotes the number of NaAlH₄ formula units), and (ii) semispherical clusters with \( Z = 23 \) and 45, respectively. Some structurally optimized clusters are shown in Fig. 3.1, the starting bulk-cut structures can be inferred from them.

As already indicated in Section 3.2, we encountered difficulties with converging the single point calculations to the electronic ground state for clusters with bulk geometries. This problem was overcome by first applying a non-zero electronic
temperature, followed by subsequent cooling until the electronic ground state configuration was reached. The densities of states (DOSs) of two of the clusters are displayed in Figs. 3.2(a) and 3.2(b), and we see that there is no gap between the valence and conduction bands, i.e., the bulk-cut clusters are metallic. However, after allowing for full structural relaxation, a band gap [i.e., a HOMO-LUMO (highest occupied molecular orbital - lowest unoccupied molecular orbital) gap] opens up and we find quite good agreement between the electronic structure of the geometry optimized cluster and that from periodic surface and bulk calculations [Figs. 3.2(c) through 3.2(f)], although the band gaps are somewhat smaller for the clusters. A more detailed look at the electronic structure of the geometry optimized large clusters and that of the periodic surface and bulk NaAlH$_4$ reveals equally strong similarities between the partial densities of states associated with Na, Al, and H (results not shown). They all show mainly H 1s and Al 3s3p contributions to the valence band and
Fig. 3.2: The density of states (DOS) for bulk terminated (BT) (a, b) and geometry optimized (GO) (c, d) $Z = 20$ and $23$ clusters, respectively, compared to that of the periodic (001) surface (e) and bulk (f) NaAlH$_4$.

Fig. 3.3: Comparison of $Z = 12$ and $23$ cluster structure before (a, c) and after geometry optimization (b, d), respectively. Al atoms are represented by blue spheres, Na atoms by green spheres, and H atoms by small white spheres.
Fig. 3.4: The binding energy per formula unit (a) and band gap (b) of geometry optimized clusters is shown as a function of cluster size, also comparing to results for a slab of NaAlH$_4$ with exposed (001) surfaces (S) and for bulk NaAlH$_4$ (B).

mainly Na 3s3p and Al 3p character of the conduction band.

The structures of small clusters change considerably upon geometry optimization [Figs. 3.3(a) and 3.3(b)], while the structures of large clusters remain similar to that of the bulk cuts [Figs. 3.3(c) and (d)].

We have also considered how the binding energy per formula unit changes as a function of the cluster size. As Fig. 3.4(a) shows, with increasing size of the cluster there is a smooth convergence of binding energy per formula unit towards the slab and bulk values. While the band gap [Fig. 3.4(b)] shows some oscillatory behavior as a function of Z for low Z, its dependence on Z becomes smoother at large Z. That the values do not converge to the (001) surface slab and bulk band gap is to be expected since the clusters also have other exposed surfaces than the (001) surface (Figs. 3.1 and 3.3). The smaller values [compared to that of the (001) surface and bulk] found for the large clusters are consistent with the lower band gap found for slabs with exposed surfaces other than the (001) surface [28].
Table 3.1: The binding energy ($E_B$) and the energetic stability of the clusters relative to Ti @ top ($E_{Rel}$) are given both for spin restricted (SR) and spin unrestricted (SU) calculations. The labels used to refer to a given structure are defined in Fig. 3.5. All the energies are given in eV, and all results have been obtained from fully relaxed geometries.

<table>
<thead>
<tr>
<th></th>
<th>Ti @ top</th>
<th>Ti @ Na</th>
<th>Ti @ Al</th>
<th>Ti @ inter12</th>
<th>Ti @ inter2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_B$ (SR)</td>
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<td>-447.03</td>
<td>-445.92</td>
<td>-446.38</td>
<td>-446.50</td>
</tr>
<tr>
<td>$E_{Rel}$ (SR)</td>
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<td>-1.00</td>
<td>0.11</td>
<td>-0.35</td>
<td>-0.48</td>
</tr>
<tr>
<td>$E_B$ (SU)</td>
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<td>-447.18</td>
<td>-445.92</td>
<td>-446.75</td>
<td>-446.86</td>
</tr>
<tr>
<td>$E_{Rel}$ (SU)</td>
<td>0.00</td>
<td>-1.11</td>
<td>0.15</td>
<td>-0.68</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

In choosing an appropriate cluster model for a small NaAlH$_4$ particle, we are forced to make certain compromises. It is known from experiments that the typical particle size is 150-200 nm after ball milling [14]. A cluster of this size is out of reach for current Kohn-Sham DFT based codes, and unfortunately orbital-free DFT, which can be computationally much more efficient, so far fails to describe NaAlH$_4$ even qualitatively [29]. Furthermore, extensive geometry optimizations have to be performed in order to address the question of where the Ti resides in the sodium alanate during dehydrogenation/hydrogenation cycling. Thus a smaller cluster must be chosen. However, the chosen cluster should of course resemble the real particles both electronically and structurally. Based on these considerations and the results discussed above, we believe that the $Z = 23$ semispherical cluster represents an appropriate model system for a small NaAlH$_4$ particle, for modeling processes on the (001) face of the cluster.

### 3.3.2 Ti-doped NaAlH$_4$ clusters

We started with adsorbing a Ti atom on the surface on the $C_2$ symmetry axis of the $Z = 23$ cluster chosen in the previous section by allowing the structure to relax completely [Fig. 3.5(b)]. Next, different other positions on the surfaces of and inside the cluster were chosen together with a number of adsorption/absorption sites reached by permutation of the Ti atom and a lattice Na or Al. In all cases full structural relaxation was performed. Some of the most stable structures are shown in Fig. 3.5.
Fig. 3.5: The figure shows some of the Z = 23 model systems used to determine the relative stability of Ti-doped NaAlH₄. (a) The undoped cluster, (b) Ti on the surface on the C₂ symmetry axis [Ti @ top], (c) Ti replaces a Na atom on the C₂ axis with Na in the original position of Ti [Ti @ Na], (d) Ti in interstitial site between first and second layer on the C₂ axis [Ti @ inter12], (e) Ti in interstitial site in second layer on the C₂ axis [Ti @ inter2], (f) Ti replaces an Al atom away from the C₂ axis with Al in the original position of Ti [Ti @ Al]. In all cases full structure relaxations have been performed. The labels in the brackets are used in Table 3.1 and in the text to refer to a specific structure. The Ti atom is represented as a red ball, while the other atoms are represented as in Fig. 3.1.

The binding energy of these clusters and their stability relative to our chosen reference are given in Table 3.1, both for spin restricted and unrestricted calculations. (In the spin restricted calculations the α- and β-spin orbitals are assumed to be
degenerate with equal occupations, whereas spin polarization can take place in the spin unrestricted calculations by allowing $\alpha$- and $\beta$-spin orbitals and occupations to be different.)

The results in Table 3.1 clearly show the importance of doing the calculations spin unrestricted. By comparing the results for spin restricted and unrestricted calculations we see that the relative stability of the different configurations change by more than 0.3 eV. Similar effects are present in periodic surface and bulk calculations [21], and should be taken into account in future studies. In the following we will focus on the results obtained from spin unrestricted calculations.

According to the results in Table 3.1 Ti prefers to substitute a Na atom close to the surface [Fig. 3.5(c)]. It is less favorable to place Ti in an interstitial position in the second layer [Fig. 3.5(e)] or between the first and second layer [Fig. 3.5(d)]. Substitution of Al [Fig. 3.5(f)] is not stable compared to leaving the Ti on the surface [Fig. 3.5(b)]. This would probably be somewhat stabilized if substitution could take place subsurface [18], but such a site is unfortunately not available in this cluster. On the one hand, these results are in agreement with what was found in Refs. [9, 19, 20] when gas phase atomic elements were used as reference. Conversely, our conclusions disagree with those obtained when using bulk systems as reference, where Ti substitution of Al is favored above Na substitution [18, 20, 21] (this is mainly due to the about 2 eV larger cohesive energy of Al compared to Na). This, of course, immediately raises the question of which reference system is the most appropriate. In the following we will offer our view on this issue, but we would like to stress that there is still a lot of work to be done before it can be properly settled.

As mentioned above, experimental studies have shown that most of the Ti has a final oxidation state of zero [10, 12-13] and may be alloyed with Al [7, 8, 11, 13, 14, 17]. However, it is not yet known whether this constitutes the active phase of the catalyst. It is possible that a minor part of Ti is the active form of the catalyst, and that it might be present as mono-atomically dispersed Ti. If this is the case, the present reference system is indeed an appropriate starting point, and we can quite safely conclude that the catalytically active Ti prefers to go into the lattice rather than staying at the surface. However, the validity of our conclusions regarding the substitution with Al or
Na, or near-surface interstitial sites, must be treated with more care. As seen from Figs. 3.5(c), 3.5(d) and 3.5(f) the resulting structures leave rather exposed Na or Al atoms on the surface. These structures might represent possible physical transients during the hydrogenation/dehydrogenation cycling, and therefore will be relevant for understanding the role Ti plays as a catalyst in this system. But we are also aware that we are only modeling a small part of the total system and that the presence of other particles close to the exposed atoms might alter the conclusions reached here. To address this properly, one most likely will have to resort to multi-scale modeling.

The use of bulk systems as reference is appropriate when developing notions about the main thermodynamic driving forces in the Ti-doped sodium alanate. As noted, using this reference leads to different conclusions about the most preferred position of Ti than when using mono-atomically dispersed Ti on the surface of NaAlH₄ as reference. However, we think it is conceivable that both references should be considered together in order to develop a full understanding of the catalytic activity of Ti; bulk systems when long-term thermodynamic stability is in focus, and doped clusters when studying the dehydrogenation/hydrogenation kinetics. Much depends on whether Ti is present in mono-atomically dispersed form, and on the local availability of phases stabilizing one or the other adsorbed metal species.

We find it more difficult to provide support for using gas phase atomic elements as reference, since we have not been able to come up with physical scenarios with a large presence of gas phase atoms of Al, Na, H and Ti.

Finally, we note that in Chapter 6 a large set of initial geometries has been considered for Ti in the surface of NaAlH₄. In this Chapter, an even more stable geometry was found for exchange of Ti with Na, but the study presented there leaves the main conclusion of this Chapter, that surface adsorbed Ti atoms prefer to exchange with surface Na ions, unchanged.

3.4 Conclusions
In order to determine the preferred position of Ti in NaAlH₄ we have performed density functional theory calculations at the generalized gradient approximation level on Ti-doped NaAlH₄ clusters. For this, we have first determined what constitutes a
good model cluster. We have found that large geometry optimized clusters (tetragonal cluster of 20 and 42 NaAlH₄ formula units, and semispherical clusters of 23 and 45 NaAlH₄ formula units) are energetically, electronically and structurally close to surface and bulk NaAlH₄, and therefore form good model systems for nano-sized NaAlH₄ particles. Choosing the semispherical cluster of 23 NaAlH₄ formula units as an appropriate model system, we then doped it with a Ti atom. Using this mono-atomically dispersed Ti adsorbed on the surface of NaAlH₄ as a reference system, we found that Ti preferably substitutes a lattice Na near the surface. This particular reference system may be the most relevant when studying the role of Ti in dehydrogenation/hydrogenation reactions. However, there is clearly more effort needed to resolve open questions related to both this and approaches using other reference systems, which may ultimately require multi-scale modeling. Finally, we have found that it is important to perform the calculations spin unrestricted, and that this is something that needs to be checked carefully for periodic calculations as well.

3.5 References
