Summary

In the hydrogen economy, hydrogen is used as a clean energy carrier in the transport sector. Extracting energy from hydrogen using a fuel cell or an internal combustion engine avoids the emission of the harmful greenhouse gas CO₂, provided that the hydrogen was made in a “clean way”, for instance, using solar or wind energy to electrolyze water, or using steam reforming with CO₂ sequestration. However, to bring about the hydrogen economy a number of challenges have to be met. Scientific and technological advances are needed to (i) produce fuel cells at acceptable costs, (ii) to produce “clean” (CO₂ free) hydrogen at acceptable costs, and (iii) to store hydrogen in cars in tanks of not too high weight and volume, again at acceptable costs. This thesis focuses on the third challenge, hydrogen storage.

Sodium alanate (NaAlH₄) contains 5.5 weight percent hydrogen which, in principle, can be released from the storage material and put back into it at close to ambient pressures and temperatures. For about ten years now, it is known that adding transition metal atoms in some form (for example, Ti, in TiCl₃) makes the hydrogen release from and uptake in the material reversible, and improves the kinetics of these processes enormously, although the kinetics of hydrogen uptake is still too slow. Unfortunately, it is still not clear what the role of the transition metal catalyst is. If this would be understood, it might be possible to suggest better catalysts or combinations of catalysts. The main goal of this thesis has therefore been to determine, by computation, how the catalyst acts. In addition, calculations were performed on the decomposition of two calcium alanates, to determine zero-point energy corrected enthalpies of dehydrogenation for these compounds, and to determine whether destabilization of LiBH₄ by CaH₂ might improve the performance of this material.

In order to determine the role of transition metal catalysts like Ti, calculations were performed using density functional theory (DFT) employing the PW91 generalized gradient approximation (GGA). The adsorption of transition metal atoms on and their absorption in the energetically most stable (001) surface of NaAlH₄ was studied employing a cluster model of NaAlH₄ with an exposed (001) face. Geometry optimizations were performed to arrive at a good model for the bare NaAlH₄ cluster,
which contained 23 formula units and was of semi-spherical shape. To model the interaction with one or two transition metal atoms, these atoms were put on various places on or in the surface of the NaAlH₄ cluster, also considering initial geometries in which the transition metal atom replaces a surface Na or Al atom, which is then put on the surface of the cluster. Geometry optimizations were then performed on the transition metal atom(s) interacting with the NaAlH₄ cluster using both spin-restricted and unrestricted DFT calculations, to determine the position of the transition metal atom(s) relative to the cluster atoms, and thereby make inferences about the possible role of the transition metal catalyst. In the modeling of heavier transition metal catalysts, such as Zr, Pd, and Pt, relativistic corrections were incorporated using the ZORA method. All electronic structure calculations involving NaAlH₄ were performed using the Amsterdam Density Functional (ADF) code. Because experiments showed that hydrogenated Ti (TiH₂) is also a good catalyst for hydrogen release, calculations on a TiH₂ “molecule” interacting with the NaAlH₄ cluster were also performed.

In chapter 3, a “good” NaAlH₄ model cluster was determined that could be used to study the interaction of transition metal atoms with the (001) face of NaAlH₄. It was found that large geometry optimized clusters (tetragonal clusters 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. A semispherical cluster of 23 NaAlH₄ formula units was chosen as an appropriate model system, and then doped with a Ti atom. Using this mono-atomically dispersed Ti adsorbed on the surface of NaAlH₄ as a reference system, Ti was found to preferably substitute a lattice Na atom at the surface. It was found that it is important to allow for spin polarisation when performing calculations on Ti interacting with the NaAlH₄ cluster.

In chapter 4, the interaction of a NaAlH₄ cluster with two Ti atoms, either as a dimer or two separated Ti atoms, and adsorbed on the (001) surface of the cluster, was studied. The calculations on surface adsorption were supplemented with a large number of calculations where one or two Ti atoms had been either inserted into interstitial sites or exchanged with a surface Na or Al atom. The calculations showed that: (i) Beginning with the case that a Ti dimer is adsorbed on the surface, it is
energetically preferred for the Ti dimer to dissociate on the surface of the cluster. The most stable adsorption position results when the resulting separate Ti atoms are both above first layer Na surface atoms. These surface Na atoms are found to be displaced into the subsurface region of the cluster, allowing each Ti atom to interact with 4 AlH₄ units. (ii) After dissociation the two Ti atoms prefer to move inside the cluster to the subsurface region, as was also found in chapter 3 for a single Ti atom interacting with the (001) surface. If the two Ti atoms move inside the cluster, exchange with two subsurface displaced Na atoms is preferred, and overall this represents the energetically most favorable case. Absorbing two Ti atoms in interstitial sites close to each other (5.8 – 7.4 Å) is clearly unfavorable; instead, the thermodynamically most stable situation is for Ti atoms to move into Na positions far away from each other. A zipper model was proposed, in which the mechanism by which the added Ti promotes H₂ release is explained by the Ti atom working itself down into the alanate particle, effectively unzipping the structure.

In chapter 5, the interaction of TiH₂ with the (001) face of NaAlH₄ was studied, again using the cluster model. The adsorption of the TiH₂ molecule on the surface was investigated. Also, 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. Restricting the possible outcomes to adsorption, TiH₂ was found to adsorb on the surface above a Na atom, bonding with 4 AlH₄ units and pushing the surface Na atom into the subsurface region, as was found before for a single Ti atom in chapter 3. However, it was energetically preferred to exchange the whole TiH₂ unit with the subsurface displaced Na atom, as also found for one Ti atom in chapter 3. All other exchanges were unstable compared to the situation were TiH₂ was adsorbed on the surface. These results are also consistent with our results for two Ti atoms interacting with the NaAlH₄ cluster, as presented in chapter 4. The results are also consistent with the zipper model presented in chapter 4. In this model, the mechanism by which the added TiH₂ promotes H₂ release involves the TiH₂ molecule working its way into the alanate particle by replacing Na and pushing the Na atom on the surface, effectively unzipping the NaAlH₄ structure.
In chapter 6, the role of transition metal catalysts in promoting de- or rehydrogenation was investigated coming from another angle. Rather than only addressing the popular Ti catalyst, the following question was asked: why are Sc, Ti, and Zr good catalysts for promoting hydrogen release from and uptake in NaAlH$_4$, while traditional hydrogenation catalysts, like Pd and Pt, are poor for NaAlH$_4$?

The key difference found between the good catalysts (Sc, Ti, and Zr) and the bad catalysts (Pt and Pd) was that the good catalysts prefer to exchange with a surface Na atom and push the Na atom on to the surface, while the bad catalysts prefer to absorb in an interstitial site. Thus, the good catalysts initiate mass transport of the heavy metal atoms, and bring about an initial separation between a Na-rich and an Al-rich phase. The calculations therefore suggest the catalyst to effect mass transport according to one of three mechanisms postulated earlier by Gross et al. In this mechanism, the catalyst moves into the starting phase and “eats” its way into the material, moving one of the two metal atoms (in this case Na) out of it.

A difference found among the good catalysts, which correlates with their activity, is that, for the best of the three good catalysts (Sc), atomic adsorption of the catalyst on the (001) face of NaAlH$_4$ is energetically preferred over the case where the transition metal (TM) atom is in the bulk TM phase. Instead, atomic adsorption is not favored for the Ti and Zr catalyst, and it is most unfavorable for the worst of the three catalysts (Zr). This suggests that the ability to disperse the catalyst in atomic form over the surface of NaAlH$_4$ should be important to the functioning of the catalyst, and that this ability can be used to separate the “best catalysts” from the class of “good catalysts”. It is my belief that the calculations have revealed some key points about what are good catalysts for effecting hydrogen release from and uptake in NaAlH$_4$, and I hope that experiments can be done to confirm the interpretations given above of what are features of good catalysts.

In chapter 7, DFT calculations were performed on the dehydrogenation reactions of Ca(AlH$_4$)$_2$, CaAlH$_5$ and CaH$_2$+6LiBH$_4$. The DFT model used was somewhat different from that employed in the calculations on NaAlH$_4$. A periodic model was used of the hydrogen storage materials, using the plane wave DFT code VASP, with the PW91 GGA. Harmonic phonon densities of states (DOSs) were calculated by the direct
method using the PHONON code. From these DOSs, zero-point energy (ZPE) corrections to the dehydrogenation enthalpies were computed. Ca(AlH$_4$)$_2$ was confirmed to be a meta-stable hydride, and thus unsuitable as a medium for a cyclable hydrogen storage system. CaAlH$_5$ was confirmed to be stable, but calculations including ZPE effects indicate that it is not stable enough for a hydrogen storage system operating near ambient conditions. ZPE-corrected enthalpy calculations confirm that the destabilized combination of LiBH$_4$ with CaH$_2$ is a promising system, as previously reported. The computed ZPE corrected dehydrogenation enthalpies were in good agreement with recent DFT results of other research groups. The computed phonon DOS of CaAlH$_5$ differs qualitatively from that found for other alanates, because in CaAlH$_5$ the aluminium and hydrogen atoms do not exist in distinct molecular ions.