Chapter 1

Introduction

1.1 Renewable energy technology

1.1.1 The source of energy

Energy can be obtained from different sources [1] such as chemical (fossil fuels), solar (photovoltaic cell), nuclear (uranium) and thermo-mechanical (wind, water and hot water). Each kind of energy has its own problems. The use of fossil fuels leads to the production of the green house gas CO$_2$ that warms the earth; the use of nuclear energy leads to nuclear wastes from radioactive fission products; solar and wind energy require the use of large surface areas [1].

Currently, fossil fuel and nuclear sources are the main energy suppliers for the world [1]. The increase of the energy need with time is expected to lead to increased atmospheric concentrations of the green house gas CO$_2$ and to the depletion of fossil fuel supplies (especially oil) in the coming decades.

The continuous emission of CO$_2$ is a serious threat to the global environment. Increasing the CO$_2$ concentration in the atmosphere will lead to global warming [1] and as a result the climate will change. In the coming hundred years, the expected increase of the world population together with a rapid growth of the economies of e.g. China and India, will lead to a large increase in the world’s use of energy [2].

In order to meet the growing global demand for energy, while producing less CO$_2$, the current energy sources have to be replaced by new ones. The use of fossil fuels such as oil, coal and natural gas has to be reduced. In their place we have to increase our use of renewable energy sources like solar, geothermal and wind [3].

1.1.2 Energy storage

The energy needs to be stored in a form that can be used for our purposes. In creation of the universe, (some of the) energy has been stored in the stars. Our sun is one of these
stars, and its energy is being used by humans either directly by solar cells or indirectly through fossil fuels, hydro power or wind power.

The widespread use of electricity and refined chemical fuels has made energy storage a major factor in economic development. All of the chemical energy carriers are readily converted to mechanical energy (and to electrical energy, e.g. with combustion engines that are used to power electrical generators). A great deal of the world’s consumption of the liquid hydrocarbon fuel is accounted for by the transportation sector, especially automobiles.

Electric road vehicles powered by fuel cells (running on hydrogen) are a suitable alternative for vehicles running on combustion engines. Hydrogen is oxidized in the fuel cell to generate electricity (and heat) with only water as an exhaust gas [2].

1.2 Hydrogen
Hydrogen is a chemical energy carrier that is a possible alternative to hydrocarbon fuels. Hydrogen is the only carbon-free chemical energy carrier and this characteristic makes hydrogen a unique fuel. Hydrogen can be produced using different energy sources in our world and it can be stored for future use. It can be used to fuel combustion engines. Pure hydrogen can (together with oxygen) also be used to produce electricity through the proton exchange membrane (PEM) fuel cell [4].

1.3 Hydrogen storage
The energy density by weight of hydrogen is 142 MJ kg⁻¹, which is three times larger than that in other chemical fuels, such as e.g. liquid hydrocarbon (47 MJ kg⁻¹) [5].

Hydrogen is a gas at ambient temperatures, it has a critical temperature of 33 K and it has low energy density per volume. These are the main reasons why hydrogen is not the major fuel of today’s energy consumption.
Automobiles run on hydrogen either by burning hydrogen with oxygen from air in an internal combustion engine [5] or by “burning” hydrogen electrochemically with oxygen from air in a fuel cell, which produces electricity that drives an electric engine [6].

To run a standard sized car for 400 km, 24 kg of petrol or 8 kg of hydrogen is needed in a combustion engine, while 4 kg of hydrogen is needed for an electric car with a fuel cell. 4 kg of hydrogen occupies a volume of 45 m$^3$ at ambient conditions. This volume is not practical for automobiles and requires the development of an efficient system for on-board hydrogen storage [5].

The most important methods to store hydrogen are: as a pressurized gas [7], a cryogenic liquid [8], an adsorbent to carbon nanotubes [9, 10], to water in clathrate hydrates [11, 12], to metal organic frameworks (MOFs) [13, 14], and in chemical form [15-17]. So far, all of these systems have their specific problems. Pressurising or liquefying hydrogen requires a significant fraction of the energy present in H$_2$ [5]. The tanks holding liquid H$_2$ cannot be totally isolated, because hydrogen needs to be able to escape to avoid pressure build-up [18]. Hydrogen losses due to boil-off can reach about 3% per day, which makes liquid hydrogen a less attractive choice for hydrogen storage [18]. Carbon nanotubes seemed very promising at first [9], but their room temperature storage capacity would appear to be too low at about 1 wt% [10]. At (close to) ambient conditions, the storage capacity presently achieved for clathrates [12] and MOFs [13] is also too low.

So far, the system that comes closest to meeting practical requirements is the NaAlH$_4$ system [16], in which hydrogen is stored in chemical form.

1.4 NaAlH$_4$

The theoretical reversible storage capacity of NaAlH$_4$ is about 5.5 wt%. Hydrogen is released in two steps. According to thermodynamics, the first step, in which Na$_3$AlH$_6$, Al, and H$_2$ are produced, proceeds at close to ambient conditions. The second step, in which Na$_3$AlH$_6$ reacts to NaH, Al, and H$_2$ proceeds at close to 110 °C. A key point is that the release and re-uptake of H$_2$ can be made reversible by adding a catalyst like Ti, as demonstrated in 1997 by Bogdanovic and Schwickardi [15]. In much of the subsequent
work aimed at improving the kinetics of the release and re-uptake of H₂, Ti was in the form of TiCl₃ [19] or of colloid nanoparticles [20, 21]. However, other transition metals have also been tried. An intriguing observation is that traditional hydrogenation catalysts like Pd and Pt are poor catalysts for hydrogen release from NaAlH₄ [22], while early transition metals like Ti, Zr [22, 23], and Sc, and the actinides Ce, and Pr are good catalysts (the latter three being even better than Ti [24]). Another interesting observation is that adding different transition metals together may produce synergistic effects, as has been demonstrated for, for instance, Ti/Zr [23] and Ti/Fe [19].

Although much progress has been made at improving catalysed hydrogen release from and uptake in NaAlH₄, the kinetics of these processes is still too slow [16]. As a result, much recent work aimed at clarifying the role of the much used Ti catalyst has focused on determining the form in which it is present. So far, Ti has been found to be present in at least three different forms. First, Ti has been observed to be present in Al as a Ti-Al alloy of varying compositions [25-31]. Second, Ti was observed to be present as TiH₂ upon doping a mixture of NaH and Al with pure Ti and ball milling [32, 33], following a conjecture that TiH₂ [34] should be the active catalyst. Finally, there are experiments that suggest Ti to be present in NaAlH₄ itself [31, 35, 36]. Calculations employing periodic density functional theory (DFT) suggest substitution of Ti into the bulk lattice of NaAlH₄ to be energetically unfavorable if standard states of NaAlH₄, Na, Al, and Ti are used as reference states [37] or if reactant and product states appropriate for describing doping reactions are used as reference states [38]. However, periodic DFT calculations also find substitution of Ti into the NaAlH₄ lattice to be stabler at the surface than in the bulk [38, 39]. Cluster DFT calculations have shown that Ti prefers to exchange with a surface Na ion (this thesis), and that the resulting situation is energetically preferred over the case of two separate bulk phases of NaAlH₄ and Ti (this thesis). Furthermore, periodic DFT calculations likewise suggest that the initial reaction of TiCl₃ with NaAlH₄ can result in Ti substituting a Na surface ion [40]. Recent experimental observations give further support to the idea that Ti can be present in the surface of NaAlH₄ after doping with Ti [31].
The exact role of the much used Ti catalyst still remains elusive [16], although several ideas have been put forward. Isotope scrambling experiments provided evidence that exchange of gaseous D\textsubscript{2} with NaAlH\textsubscript{4} only occurred in the presence of Ti used as dopant [41]. This effect was attributed to the presence of a Ti-Al alloy [41], with support coming from DFT calculations that show that dissociation of H\textsubscript{2} on a surface of Al(001) with Ti alloyed into it can occur without barriers [42, 43], whereas high barriers are encountered on low index surfaces of pure Al. However, the experimentalists pointed out that the hydrogen exchange observed to take place under steady state conditions occurs much faster than the full decomposition reaction, suggesting that the key role of Ti should be to enhance mass transfer of the solid as rate limiting step [41]. Experiments employing anelastic spectroscopy have suggested that Ti enhances bulk diffusion of H\textsubscript{2} through the alanate [44-46], but this point is controversial [47]. Another idea that has been suggested is that Ti enables the formation of mobile AlH\textsubscript{3} which would then enable the fast mass transfer required in the solid state reactions releasing hydrogen [48, 49], and volatile molecular aluminium hydride molecules have been identified during hydrogen release from Ti/Sn doped NaAlH\textsubscript{4} using inelastic neutron scattering spectroscopy [50]. Recent work has suggested that an additional role of Ti [51] or the associated anion [52, 53] used in doping may be to improve the thermodynamics of the system. Perhaps most crucially, several experiments have shown that the release and uptake of H\textsubscript{2} are associated with massive mass transfer over long (micrometers) distances [19, 27, 54, 55]. The idea that the crucial role of Ti is to enable mass transfer over large distances is further supported by experiments showing that partial decomposition of undoped NaAlH\textsubscript{4} particles is possible if they are very small (nano-sized), the decomposition starting at a temperature as low as 40 °C [56].

Three basic mechanisms were proposed in which Ti would affect the long range mass transport of Al or Na required for de- and re-hydrogenation [48]. In the first mechanism, long-range diffusion of metal species through the alanates to the catalyst would occur as a first step. Gross et al. already proposed that this could involve the AlH\textsubscript{3} species. In the second mechanism, the driving force would be hydrogen desorption at the catalyst site, followed by long range transport of the metal species, the catalyst acting as a hydrogen
dissociation and recombination site and possibly also as a nucleation site. In the third mechanism proposed, the catalyst itself would migrate through the bulk. In this mechanism, “the starting phase is consumed and product phases are formed at the catalyst while it ‘eats’ its way through the material” [48].

1.5 My research goal
The goal of my research has been to determine, by computation, the different aspects of the role good catalysts play in hydrogen release from and uptake in NaAlH$_4$. One of the main ideas underlying my work is that the explanation of the role of the catalyst should be able to account for the key experimental observation that traditional hydrogenation catalysts like Pd and Pt [22] are poor catalysts for NaAlH$_4$, while early transition metals like Ti, Zr [22, 23], and Sc [24] are good catalysts for NaAlH$_4$.

My starting point is a model in which the Ti, Sc, Zr, Pd, Pt is adsorbed on the face of NaAlH$_4$ which has the lowest surface energy [the (001) face], the Ti, Sc, Zr, Pd, Pt being present in monoatomically dispersed form. Such a situation can arise from ballmilling, a technique that employs mechanical energy to achieve a fine dispersion of the catalyst, which has been in use in Ti-doping of NaAlH$_4$ since 1999 [23], or it can arise from the initial reaction of TiCl$_3$ with NaAlH$_4$ [40].

1.6 The outline of my thesis
After the introduction in this chapter, chapter 2 outlines the different methods and approximations used during my thesis work. Then, in chapters 3 and 4 the focus is on the interaction of Ti with NaAlH$_4$. Next, chapter 5 concerns the interaction of TiH$_2$ with NaAlH$_4$, and chapter 6 describes how Ti, Sc, Zr, Pd and Pt interact with NaAlH$_4$. Finally, chapter 7 presents zero-point energy corrected enthalpies of dehydrogenation for Ca(AlH$_4$)$_2$, CaAlH$_5$ and CaH$_2$+6LiBH$_4$.

In chapter 3, the electronic structure and stability of NaAlH$_4$ clusters of different size and shape were studied, and based on these results a (NaAlH$_4$)$_{23}$ cluster was chosen as a model system for a nano-sized NaAlH$_4$ particle. Results are also presented on the interaction of monoatomically dispersed Ti atom with the (NaAlH$_4$)$_{23}$ cluster.
In chapter 4, the interaction of the 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.

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.

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 NaAlH₄, while traditional hydrogenation catalysts, like Pd and Pt, are poor for NaAlH₄?

In chapter 7, DFT calculations were performed on the dehydrogenation reactions of Ca(AlH₄)₂, CaAlH₅ and CaH₂+6LiBH₄. The DFT model used was somewhat different from that employed in the calculations on NaAlH₄. A periodic model was used of the hydrogen storage materials, using the plane wave DFT code VASP. Harmonic phonon densities of states (DOSs) were calculated by the direct method using the PHONON code.

1.7 Outlook
As known in science, while one answers questions more interesting ideas and questions appear that make the scientific research exciting and motivating. This thesis is not an exception to that rule. This section provides an outlook summarizing some of the new questions that have arisen during my research.
1.7.1 Ti + NaAlH₄
Using mono-atomically dispersed Ti adsorbed on the surface of NaAlH₄ as a reference system to study Ti + NaAlH₄, the research done on Ti + NaAlH₄ has shown that Ti preferably exchanges with a lattice Na atom near the surface. This particular reference system may be the most relevant when studying the role of Ti in dehydrogenation/hydrogenation reactions. However, this research opens other questions: what is the barrier for the Na exchange process compared to the barrier for exchange with Al and for adsorption in a surface interstitial site?

1.7.2 Ti₂ + NaAlH₄
The results of Ti₂ + NaAlH₄ research imply that Ti is more stable in the subsurface region of the cluster than on the surface, and that exchange with Na is preferred. Almost equally stable is the exchange with one Na and one Al, as long as the resulting structure contains a direct Ti-Ti bond. The calculations also show that when considering adsorption on the surface only, Ti prefers to adsorb as atomic Ti rather than as a Ti₂. In this case the Ti atoms adsorb above Na sites, with the Na atoms being displaced towards the subsurface region. An interesting question not yet addressed in this thesis is whether the dissociation of Ti₂ on the surface has a barrier associated with it, and if so, how high that barrier is?

1.7.3 TiH₂ + NaAlH₄
After studying the adsorption of the TiH₂ molecule on the (001) surface of NaAlH₄ in different sites, 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.
After determining the thermodynamic fate of the TiH₂ in NaAlH₄, it is important to study the diffusion path of the TiH₂ + NaAlH₄ species. This will provide information about barriers for TiH₂ diffusion and exchange with Na. A question that could be addressed is whether TiH₂ has to dissociate at some point along the reaction path to reform at a later stage.

Relevant barrier heights can be computed by taking appropriate adsorption and absorption states as reactants and products, and locating the barrier between them using a suitable transition state searcher, such as the nudged elastic band (NEB) [57] method. Such calculations should be expensive but feasible.

### 1.7.4 (Ti, Zr, Sc, Pd, Pt) + NaAlH₄

I have also studied the interaction of Zr, Sc, Pd, and Pt with the (001) surface of NaAlH₄ after doing research on Ti + NaAlH₄. The importance of this study is to understand why Ti, Zr, and Sc are good catalysts for hydrogenation and dehydrogenation of NaAlH₄ while Pd and Pt are not. The results have shown that a key difference between Ti, Zr, and Sc on the one hand, and Pd and Pt on the other hand is that exchange of the early transition metal (TM) atoms with a surface Na ion, whereby Na is pushed on to the surface, is energetically preferred over surface absorption in an interstitial site, as found for Pd and Pt. The theoretical findings are consistent with a crucial feature of the TM catalyst being that it can be transported with the reaction boundary as it moves into the bulk, enabling the starting material to react away while the catalyst eats its way into the bulk, and effecting a phase separation between a Na-rich and a Al-rich phase. However, so far I have only looked at energy minima in my studies, and I have not computed barrier heights to see if the exchanges between the TM atoms and surface Na atoms are kinetically allowed. This is clearly the next step to be taken. In addition, it should be interesting to study H₂ desorption from the TM + NaAlH₄ clusters, to see whether H₂ desorption might become easier (occur with a lower barrier) upon exchange of the TM atom with a surface Na atom.

Based on my results I think there is one urgent experiment that has been done using Ti [41] that should be performed: The hydrogen–deuterium exchange experiment should be
repeated with both Pd and Pt as catalysts. The question is whether exchange still will take place. If this is indeed the case one would have firmly established that the dissociation of hydrogen is not an important part of the overall process with respect to the role the TMs play in improving the kinetics.

1.7.5 The hydrogenation process and dehydrogenation of Na$_3$AlH$_6$

Starting from totally dehydrogenated material (NaH + Al$_x$Ti$_{1-x}$) is important to understand the H$_2$ interaction with an Al surface with Ti atoms in it. By comparing the dissociation of H$_2$ on Al surface with H$_2$ on an Al$_x$Ti$_{1-x}$ surface, as has already been done computationally for specific surface coverage of Ti in Al [42, 43], we will get a complete picture about the role of Ti in the hydrogenation process. Besides that, the dissociation of H$_2$ on Al(Zr, Sc, Pd, Pt) surfaces becomes an important playing ground for comparing the role of the TM catalysts in the hydrogenation process.

My study has completely focused on dehydrogenation of doped NaAlH$_4$. So far, few researches have tackled the dehydrogenation of Na$_3$AlH$_6$. It would be interesting to investigate how Ti and other good TM catalysts interact with stable Na$_3$AlH$_6$ faces, in a manner similar to that used here. Also it should be interesting to investigate the role of the TM catalyst in rehydrogenation of NaH + Al. Earlier studies have already established that Ti in the surface of Al may help the dissociation of H$_2$ into atoms [42, 43]. An interesting question is whether the same would be true for Sc and Zr, but not for Pd and Pt. Another interesting question is whether TMs might also play additional roles in rehydrogenation (like e.g. improving mass transport to the reaction center).

1.8 References
