

A cluster density functional theory study of the interaction of the hydrogen storage system NaAIH4 with transition metal catalysts Marashdeh, A.A.

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### Chapter 6

# Why Some Transition Metals are Good Catalysts for Reversible Hydrogen Storage in Sodium Alanate, and Others are not: A Density Functional Theory Study

Sodium alanate (NaAlH<sub>4</sub>) is a prototype system for storage of hydrogen in chemical form. However, a key experimental finding, that early transition metals (TMs) like Ti, Zr, and Sc are good catalysts for hydrogen release and re-uptake, while traditional hydrogenation catalysts like Pd and Pt are poor catalysts for NaAlH<sub>4</sub>, has so far gone unexplained. We have performed density functional theory calculations at the PW91 generalised gradient approximation level on Ti, Zr, Sc, Pd, and Pt interacting with the (001) surface of nanocrystalline NaAlH<sub>4</sub>, employing a cluster model of the complex metal hydride. 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 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.

#### **6.1. Introduction**

The realisation of a hydrogen economy requires the development of an efficient system for on-board hydrogen storage [1]. At this stage, promising methods store hydrogen as a pressurised gas [2], a cryogenic liquid [3], an adsorbent to carbon nanotubes [4,5], to water in clathrate hydrates [6,7], and to metal organic frameworks (MOFs) [8,9], and in chemical form [10-12]. So far, all of these systems have their specific problems. Pressurising or liquefying hydrogen requires a significant fraction of the energy present in H<sub>2</sub> [1]. Carbon nanotubes seemed very promising at first [4], but their room temperature storage capacity would appear to be too low at close to 1 wt% [5]. At (close to) ambient conditions, the storage capacity presently achieved for

clathrates [7] and MOFs [8] is likewise too low. A recent overview of storage methods has been presented by Felderhoff *et al.* [13].

So far, the chemical storage system that comes closest to meeting practical requirements is the NaAlH<sub>4</sub> system [11]. Its theoretical reversible storage capacity is about 5.5 wt%. Hydrogen is released in two steps. According to thermodynamics, the first step, in which Na<sub>3</sub>AlH<sub>6</sub>, Al, and H<sub>2</sub> are produced, proceeds spontaneously at close to 30 °C. The second step, in which Na<sub>3</sub>AlH<sub>6</sub> reacts to NaH, Al, and H<sub>2</sub> proceeds at close to 110 °C. A key point is that the release and re-uptake of H<sub>2</sub> can be made reversible by adding a catalyst like Ti, as demonstrated in 1997 by Bogdanovic and Schwickardi [10]. In much of the subsequent work aimed at improving the kinetics of the release and re-uptake of H<sub>2</sub>, Ti was used (in the form of TiCl<sub>3</sub> [14] or of colloid nanoparticles [15,16]). 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  $NaAlH_4$  [17], while early transition metals like Ti, Zr [17,18], and Sc [19], and actinides (Ce [19], Pr [19], and mischmetal (Mm, 42 at.%Ce, 31 at.% La, 18 at.% Nd, and 9 at.% Pr, [20]) are good catalysts (Sc, Ce, Pr [19] and Mm [20] all being even better than Ti). Another interesting observation is that adding different transition metals together may produce synergistic effects, as has been demonstrated for, for instance, Ti/Zr [18] and Ti/Fe [14].

Although much progress has been made at improving catalysed hydrogen release from and uptake in NaAlH<sub>4</sub>, the kinetics of these processes is still too slow [11]. As a result, much recent work aimed at clarifying the role of the much used Ti catalyst has focussed 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 [21-27]. Second, Ti was observed to be present as TiH<sub>2</sub> upon doping a mixture of NaH and Al with pure Ti and ball milling [28,29], following a conjecture that TiH<sub>2</sub> [30] should be the active catalyst. Finally, there are experiments that suggest Ti to be present in NaAlH<sub>4</sub> itself [27,31,32].

Calculations employing periodic density functional theory (DFT) suggest substitution of Ti into the bulk lattice of NaAlH<sub>4</sub> to be energetically unfavourable if standard states of NaAlH<sub>4</sub>, Na, Al, and Ti are used as reference states [33] or if reactant and product states appropriate for describing doping reactions are used as reference states [34]. However, periodic DFT calculations also find substitution of Ti into the NaAlH<sub>4</sub> lattice to be more stable at the surface than in the bulk [34,35]. Calculations employing a cluster model of NaAlH<sub>4</sub> have shown that Ti atoms present on NaAlH<sub>4</sub>(001) in monoatomically dispersed form prefer to exchange with a surface Na ion [36,37], and that the resulting situation (Ti in surface Na sites, the exchanged Na ion adsorbed on top of it) is energetically preferred over the case of two separate bulk phases of NaAlH<sub>4</sub> and Ti [37]. Furthermore, periodic DFT calculations likewise suggest that the initial reaction of TiCl<sub>3</sub> with NaAlH<sub>4</sub> can result in Ti substituting a Na surface ion [38]. Recent plane wave DFT calculations suggested that it is energetically even more favourable for Ti to occupy a surface interstitial site than to exchange with a surface [39,40]. Recent experimental observations also give support to the idea that Ti can be present in the surface of NaAlH<sub>4</sub>, immediately after doping with Ti [27].

The exact role of the much used Ti catalyst still remains elusive [11], although several ideas have been put forward. Isotope scrambling experiments provided evidence that exchange of gaseous  $D_2$  with NaAlH<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub> through the alanate [44-46], but this point is controversial [47].

Addressing the role of Ti, calculations have shown that surface Ti facilitates defect formation in the surface of NaAlH<sub>4</sub>, thanks to the ease with which Ti can change its oxidation state [48]. Another idea that has been suggested is that Ti enables the formation of mobile AlH<sub>3</sub> which would then enable the fast mass transfer required in

the solid state reactions releasing hydrogen [49,50], and volatile molecular aluminium hydride molecules have been identified during hydrogen release from Ti/Sn doped NaAlH<sub>4</sub> using inelastic neutron scattering spectroscopy [51]. Recent work has suggested that an additional role of Ti [52] or the associated anion [53,54] 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<sub>2</sub> are associated with massive mass transfer over long (micrometers) distances [14,23,55,56]. 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<sub>4</sub> particles is possible if they are very small (nano-sized), the decomposition starting at a temperature as low as 40 °C [57]. Also, recent isotope exchange experiments suggest that diffusion of a hydrogen containing species heavier than H (AlH<sub>3</sub>, Al<sub>x</sub>H<sub>y</sub>, or NaH) constitutes the rate limiting step [58].

In Ref.[49], three basic mechanisms were proposed in which Ti could effect the long range mass transport of Al or Na required for de- and re-hydrogenation. 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. [49] already proposed that this could involve the AlH<sub>3</sub> 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" [49].

The goal of this Chapter is to determine the crucial aspect of the role good catalysts like Ti play in hydrogen release from NaAlH<sub>4</sub>. The main idea underlying our work is that the explanation of the role of the catalyst should be based on a key experimental observation, that traditional hydrogenation catalysts like Pd and Pt [17] are poor catalysts for hydrogen release from NaAlH<sub>4</sub>, while early transition metals like Ti [10,17], Zr [17], and Sc [19] are good catalysts for hydrogen release and re-uptake. Our starting point is a model in which the TM is adsorbed on the face of NaAlH<sub>4</sub> which has the lowest surface energy (the (001) face), the TM 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<sub>4</sub> since 1999 [18], or it can arise from the initial reaction of TiCl<sub>3</sub> with NaAlH<sub>4</sub> [38]. Our DFT calculations discussed below show that the bad catalysts, Pd and Pt, prefer to absorb interstitially in the surface of NaAlH<sub>4</sub>, while the good catalysts, Ti, Zr, and Sc, all push Na ions out of the surface and thereby effect a separation between a Na-rich and an Al-rich phase, by exchanging with surface Na-ions. This result suggests that the crucial role of catalysts like Ti is indeed to promote long range mass transport of one of the metal ions, according to the third mechanism outlined above, in which the catalyst moves into the starting phase, eating its way through the material while moving Na ions outward.

The outline of this Chapter is as follows. Section 6.2 explains the DFT methodology we have used to study the interaction of isolated TM atoms with the (001) face of NaAlH<sub>4</sub>. As explained there, we employ a cluster methodology, using a cluster with an exposed (001) face which is energetically, electronically, and structurally close to surface and bulk NaAlH<sub>4</sub>, and which should form a good model system for nano-sized NaAlH<sub>4</sub> particles [36]. The DFT calculations are performed at the generalised gradient approximation (PW91) level [59]. In Section 6.3 we discuss the surface adsorption and absorption of the TM atoms on/in the (001) surface of NaAlH<sub>4</sub>. This section is concluded with a discussion of the mechanism suggested by the DFT calculations. Our conclusions are summarised in Section 6.4.

#### 6.2. Method

**DFT calculations.** The binding energies of all systems incorporating a NaAlH<sub>4</sub> cluster have been calculated using DFT [60,61] as implemented in the ADF code [62]. The exchange-correlation energy is approximated at the generalized gradient approximation (GGA) level, using the PW91 functional [59]. The basis set used is of a triple zeta plus one polarization function (TZP) type. A frozen core was chosen of 1s on Al as well as Na, and of 1s2s2p on Ti as well as Sc. On Pd and Zr, the frozen core was 1s2s2p3s3p3d, and 1s2s2p3s3p3d4s4p4d on Pt. The general accuracy parameter of ADF [62] 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 overcome 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 to achieve results of high enough accuracy.

In our previous studies we found that it was important to consider both spin restricted and spin unrestricted calculations [36,37]. All calculations in the present study have therefore been done at both the spin restricted and the spin unrestricted level. The spin unrestricted calculations were performed allowing one, two, three and four electrons to be unpaired. Below, only the value for the energetically most stable state is reported in the tables. The calculations involving Zr, Pd, and Pt incorporated scalar relativistic corrections, employing the ZORA method [63]. Other computational details of the cluster calculations can be found in Chapters 2–4.

The bulk crystal structure of a semi-spherical NaAlH<sub>4</sub> cluster containing 23 formula units (Z=23) was used as the initial geometry to perform a geometry optimisation of a bare cluster, with a large exposed (001) surface (Chapter 3). The (001) face was selected because it has been shown to be the most stable crystal face of NaAlH<sub>4</sub> [64]. The geometry optimised Z=23 cluster is energetically, electronically, and structurally close to surface and bulk NaAlH<sub>4</sub>, and should form a good model system for nanosized NaAlH<sub>4</sub> particles (Chapter 3). In all geometry optimisations of both the bare cluster and the cluster interacting with a TM atom, I use the standard ADF convergence criteria concerning the force, step length and the energy to locate the minimum.

The optimized bare Z=23 cluster formed the starting point of geometry optimisations of the TM + NaAlH<sub>4</sub> system, where TM is Sc, Ti, Zr, Pd, or Pt. Specifically, the TM atom was put at various sites on the (001) surface (adsorption), and in various interstitial sites in the subsurface region (absorption). We also tried exchanging the TM atom with either a surface Na atom or a surface Al atom, placing the exchanged Na or Al atom at various sites on the surface of the substituted cluster to find the lowest energy TM + (Z=23) cluster with Na or Al exchanged with a surface adsorbed TM atom. The three initial adsorption geometries, the four initial absorption geometries used in exploring exchanges with Na and Al, and the four initial interstitial absorption geometries are all shown in Fig. 6.1. Note that in this Chapter, we explored a larger variety of geometries for Ti than in Chapter 3.



Fig. 6.1: Starting geometries are shown for all geometry optimisations of the TM atom interacting with the (001) surface of the Z=23 NaAlH<sub>4</sub> cluster: (a) The TM atom adsorbed above a first layer Na atom between four  $AlH_4^-$  units [TM@top\_4AlH<sub>4</sub>], (b) between two  $AlH_4^-$  units [TM@top\_2AlH<sub>4</sub>], and (c) above one  $AlH_4^-$  unit [TM@top\_AlH<sub>4</sub>]. Absorption geometries, where (d) the TM atom replaces Na in the surface layer and the exchanged Na atom adsorbs between two  $AlH_4^-$  units [TM@Na\_2AlH<sub>4</sub>], (e) the TM atom replaces Al in the surface layer and the exchanged Al atom adsorbs between two  $AlH_4^-$  units [TM@Na\_2AlH<sub>4</sub>], (e) the TM atom replaces Al in the surface layer and the exchanged Al atom adsorbs between two  $AlH_4^-$  units [TM@Al\_2AlH<sub>4</sub>], (f) the TM atom replaces Na in the surface layer and the exchanged Na atom adsorbs between four  $AlH_4^-$  units [TM@Al\_4AlH<sub>4</sub>]. (g) the TM atom replaces Al in the surface layer and the exchanged Al atom adsorbs between four  $AlH_4^-$  units [TM@Al\_4AlH<sub>4</sub>]. Absorption geometries, where (h) the TM atom replaces Na in interstitial site between the first and second layer, on the C<sub>2</sub> axis [TM@ inter12\_C2], (i) in an interstitial site in the second layer on the C<sub>2</sub> axis [TM@ inter12\_nosym], and (k) in an interstitial site in the surface layer (TM@inter surface).

The ADF code calculates the total binding energy relative to spin restricted spherically symmetric atoms. This is an unphysical reference state, but *all* our calculations have been done relative to this same state of reference. However, since we have some freedom in how to define our energy reference, we have chosen reference systems with a definite physical meaning. When considering one TM atom adsorbed/absorbed on/in the (Z=23) cluster our zero of energy has been set to that of the fully optimized bare Z=23 cluster plus one TM atom in TM bulk. In this way the energy reported for a specific TM + NaAlH<sub>4</sub> system represents the energy gained by taking one TM atom out of TM bulk and putting it on/in the Z=23 cluster. Our adsorption/absorption energies are defined in such a way that a negative number means that it is stable with respect to the bare (Z=23) cluster + one TM atom in TM bulk. The energies of the bulk TM systems have been computed using the periodic ADF-BAND code [65] using the same basis and fit sets as employed in the cluster calculations.

#### 6.3. Results and Discussion

#### 6.3.1 Adsorption of TM atoms on NaAlH<sub>4</sub>(001)

The TM atoms (Sc, Ti, Zr, Pd, Pt) were adsorbed on the (001) surface of the geometry optimized (Z=23) NaAlH<sub>4</sub> cluster in different positions, after which a geometry optimisation of the whole system was performed. Three different starting geometries were attempted. In one geometry, the TM atom sits above a surface Na atom in between 4  $AlH_4^-$  units (a structure denoted TM@top\_4AlH<sub>4</sub>, Fig. 6.1a). In the second geometry, the TM atom sits in between two  $AlH_4^-$  units (denoted TM@top\_2AlH<sub>4</sub>, Fig. 6.1b). In the third adsorption geometry, the TM atom sits on top of a surface  $AlH_4^-$  unit (TM@top\_AlH\_4, Fig. 6.1c). In almost all cases, the TM atom remained in more or less the same position in the relaxed structures. The adsorption energies of the relaxed clusters are listed in Table 6.1. The final optimised geometry is shown in Figs. 6.2a-6.6a for the most favourable adsorption geometry for each TM atom.

As can be seen from Table 6.1, when restricted to surface adsorption the Sc, Ti, and Zr atoms all prefer to be above the surface Na atom, with co-ordination to hydrogen atoms from four surrounding  $AlH_4^-$  units (Figs. 6.2a-6.4a). Of these three atoms, Sc perturbs the arrangement of the surface atoms of the NaAlH<sub>4</sub> cluster most. Also,

ТМ	Pt	Pd	Sc	Ti	Zr
<b>Relative Energies</b>	E <sub>rel</sub>	E <sub>rel</sub>	E <sub>rel</sub>	$E_{rel}$	E <sub>rel</sub>
$E_{Z23} + TM@bulk$	0.00	0.00	0.00	0.00	0.00
TM@top_4AlH <sub>4</sub>	-1.16	-0.84	-0.44	0.61	0.86
TM@top_2AlH <sub>4</sub>	-1.59	-1.47	0.76	1.55	1.59
TM@top_AlH <sub>4</sub>	-1.44	-0.01	0.45	1.77	2.13
TM@Na_2AlH4	-1.67	-2.04	-1.97	-2.15	-2.94
TM@Al_2AlH4	-1.13	-1.43	0.09	1.03	0.47
TM@Na_4AlH <sub>4</sub>	-1.01	-1.58	-1.51	-0.50	-1.35
TM@Al_4AlH <sub>4</sub>	-0.57	-0.13	-1.33	0.76	-0.08
TM@inter12_C2	-1.38	-1.82	0.43	-0.07	0.60
TM@inter2_C2	-1.79	-1.59	0.12	-0.18	0.95
TM@inter_nosym	-2.14	-2.19	-0.61	1.31	-0.97
TM@inter_surface	-2.16	-1.94	-1.03	-0.25	0.03

Table 6.1. The interaction energies (in eV) resulting from geometry optimisations of the transition metal atoms Pt, Pd, Sc, Ti, and Zr adsorbing on or absorbing in the (001) face of NaAlH<sub>4</sub> are given for each system. Both absolute and relative values are presented, where the relative values are relative to the bare cluster and the TM atom in TM bulk. The notations used in the first column are explained in Fig. 6.1.



Fig. 6.2: Final optimised geometry for the Sc atom adsorbed on /absorbed in different positions relative to the (001) surface of the (Z=23) NaAlH<sub>4</sub> cluster, for the most favourable cases concerning adsorption, absorption with exchange, and absorption in an interstitial site: (a) the Sc atom adsorbed above a first layer Na atom between four  $AlH_4^-$  units [Sc@top\_4AlH<sub>4</sub>]; (b) the Sc atom replaces Na in the surface layer and the exchanged Na atom adsorbs between two  $AlH_4^-$  units [Sc@Na\_2AlH\_4]; (c) the Sc atom absorbs in an interstitial site in the surface layer (Sc@inter\_surface).



Fig. 6.3: Final optimised geometry for the Ti atom adsorbed on /absorbed in different positions relative to the (001) surface of the (Z=23) NaAlH<sub>4</sub> cluster, for the most favourable cases concerning adsorption, absorption with exchange, and absorption in an interstitial site: (a) the Ti atom adsorbed above a first layer Na atom between four  $AlH_4^-$  units [Ti@top\_4AlH<sub>4</sub>]; (b) the Ti atom replaces Na in the surface layer and the exchanged Na atom adsorbs between two  $AlH_4^-$  units [Ti@Na\_2AlH<sub>4</sub>]; (c) the Ti atom absorbs in an interstitial site in the surface layer (Ti@inter\_surface).

adsorption of monodispersed Sc to the NaAlH<sub>4</sub>(001) face is energetically preferred above the situation where the NaAlH<sub>4</sub> and Sc are separate and the Sc atom is in atom bulk. In contrast, for the other two atoms, the energetically preferred situation is for the TM atom to be in TM bulk and separate from NaAlH<sub>4</sub>.

The energy difference between NaAlH<sub>4</sub> and TM bulk and the TM atom surface adsorbed to the NaAlH<sub>4</sub>(001) face is smaller for Ti than for Zr. Interestingly, the stability of the TM atom adsorbed to the NaAlH<sub>4</sub>(001) face correlates well with the quality of the catalyst for dehydrogenation, Sc being the best catalyst [19], followed by Ti and then by Zr [17].

The TM atoms Pt and Pd preferentially adsorb at a different site when compared to Sc, Ti, and Zr: the Pt and Pd atoms prefer to adsorb on a "bridge site" between 2 AlH<sub>4</sub>



Fig. 6.4: Final optimised geometry for the Zr atom adsorbed on /absorbed in different positions relative to the (001) surface of the (Z=23) NaAlH<sub>4</sub> cluster, for the most favourable cases concerning adsorption, absorption with exchange, and absorption in an interstitial site: (a) the Zr atom adsorbed above a first layer Na atom between four  $AlH_4^-$  units [Zr@top\_4AlH<sub>4</sub>]; (b) the Zr atom replaces Na in the surface layer and the exchanged Na atom adsorbs between two  $AlH_4^-$  units [Zr@Na\_2AlH<sub>4</sub>]; (c) the Zr atom absorbs in an interstitial site in between the first two layers, but not on the C2 axis [Zr@ inter12\_nosym].

units (Figs. 6.5a and 6.6a and Table 6.1). Just like Sc, Pt and Pd atoms prefer being adsorbed to the NaAlH<sub>4</sub>(001) face over being in their bulk phases. However, in this case this property does not correlate to the quality of the catalyst for dehydrogenation of NaAlH<sub>4</sub>, Sc being a very good catalyst, but Pt and Pd being very poor catalysts [17].

#### 6.3.2 Absorption of TM atoms in the surface of NaAlH<sub>4</sub>(001)

Next, we tried to absorb the TM atoms in the surface of NaAlH<sub>4</sub>(001), either by exchanging the TM atom with a surface Na or Al atom, or by putting the TM atom in an interstitial position (see Table 6.1 for the energy of the relaxed TM + (Z=23) cluster systems, and Figs. 6.2b-6.6b and 6.2c-6.6c). When making an exchange, the exchanged atom (Na or Al) was either put on a bridge site between two  $AlH_4^-$  units (TM@Na\_2AlH<sub>4</sub> or TM@Al\_2AlH<sub>4</sub> Figs. 6.1d and 6.1e), or put in a site between four  $AlH_4^-$  units (TM@ Na\_4AlH<sub>4</sub> and TM@Al\_4AlH<sub>4</sub>, Figs. 6.1f and 6.1g). In



Fig. 6.5: Final optimised geometry for the Pd atom adsorbed on /absorbed in different positions relative to the (001) surface of the (Z=23) NaAlH<sub>4</sub> cluster, for the most favourable cases concerning adsorption, absorption with exchange, and absorption in an interstitial site: (a) the Pd atom adsorbed above a first layer Na atom between two  $AlH_4^-$  units [Pd@top\_2AlH\_4]; (b) the Pd atom replaces Na in the surface layer and the exchanged Na atom adsorbs between two  $AlH_4^-$  units [Pd@Na\_2AlH\_4]; (c) the Pd atom absorbs in an interstitial site in between the first two layers, but not on the C2 axis [Pd@ inter12\_nosym].

putting the TM atom in an interstitial site, four different possibilities were tried. In the first case, the TM atom was placed initially in between the first 2 layers on the C<sub>2</sub>-axis (TM@inter12\_C<sub>2</sub>) (Fig. 6.1h). In the second case, the TM atom was placed within the second layer, again on the C<sub>2</sub>-axis (TM@inter2\_C<sub>2</sub>) (Fig. 6.1i).

In the third case the TM atom was placed initially in between the first 2 layers, but not on the C<sub>2</sub>-axis (TM@inter12\_nosym), in a position above a Na ion (Fig. 6.1j). Finally, in the fourth case the atom was placed initially in a surface interstitial site above an  $AlH_4^-$  unit, as investigated previously by Liu and Ge [(39,40], Fig. 6.1k).

Again, we find a difference between Sc, Ti, and Zr on the one hand, and Pt and Pd on the other hand (see Table 6.1). The Sc, Ti, and Zr atoms all prefer to exchange with a surface Na atom, leaving the Na atom on the surface on a site where it is in between 2  $AlH_4^-$  units (TM@Na\_2AlH4, Figs. 6.2b-6.4b), and high above the surface. In all



Fig. 6.6: Final optimised geometry for the Pt atom adsorbed on /absorbed in different positions relative to the (001) surface of the (Z=23) NaAlH<sub>4</sub> cluster, for the most favourable cases concerning adsorption, absorption with exchange, and absorption in an interstitial site: (a) the Pt atom adsorbed above a first layer Na atom between two  $AlH_4^-$  units [Pt@top\_2AlH<sub>4</sub>]; (b) the Pt atom replaces Na in the surface layer and the exchanged Na atom adsorbs between two  $AlH_4^-$  units [Pt@Na\_2AlH<sub>4</sub>]; (c) the Pt atom absorbs in an interstitial site in the surface layer (Ti@inter surface).

three cases, the TM@Na\_2AlH4 absorbed case is also preferred over the energetically most favourable adsorption case, TM@top\_4AlH<sub>4</sub>.

Furthermore, in all cases the TM@Na\_2AlH4 absorbed case is also preferred over the case where the TM atom is in its bulk phase but separate from NaAlH<sub>4</sub>. On the other hand, the Pt and Pd atoms prefer to be in an interstitial position, in either the TM@inter\_nosym site (Pd, Fig. 6.5c) or the TM@inter\_surface site (Pt, Fig. 6.6c), and in this case no Na ion is pushed out of the surface. Considering only the exchanges, for Pd and Pt the TM@Na\_2AlH4 geometry is preferred over the other two exchange geometries, as was the case for Sc, Ti and Zr, but in the TM@Na\_2AlH4 geometries the exchanged Na ion is hardly pushed out of the surface for Pd and Pt (Figs. 6.5a and 6.6a), in contrast to what is found for Sc, Ti, and Zr

(Figs. 6.2a, 6.3a, and 6.4a). The difference between the preferred absorption sites correlates well with catalyst activity: Sc, Ti, and Zr, which exchange with Na and push Na on to the surface, are good catalysts [17,19], while Pt and Pd, which prefer to go interstitial and leave surface Na ions in their place, are bad catalysts [17].

A few extra comments are in order. The first is that, in our previous work on a single Ti-atom adsorbed to the (001) face of NaAlH<sub>4</sub> (Chapter 3), we did not yet consider the exchange where the exchanged atom (Na or Al) was put on a bridge site, in between 2  $AlH_4^-$  units (for instance, the most favourable TM@Na\_2AlH4 structure of Fig. 6.1d). Instead, in the previous work only the exchanges with the Na atom in between 4 AlH<sub>4</sub><sup>-</sup> units were considered (for instance, TM@Na\_4AlH4). For the latter geometry, in our calculations the exchange with Na is also favoured over the absorption in the surface interstitial site for Ti, in contrast with the results of plane wave periodic DFT calculations by Liu and Ge [39,40]. However, the energy difference between the Ti@Na 4AlH4 and the Ti@inter surface geometries is rather small in our cluster calculations (0.25 eV), the difference apparently being small enough to make the preference concerning these two sites become dependent on the model (cluster vs. plane wave in Refs. [39,40]). The energy difference between the Ti@Na 2AlH4 and the Ti@inter surface geometries is much larger in our calculations (1.9 eV), and we would expect the Ti@Na 2AlH4 geometry to also be the preferred one in plane wave DFT calculations. The idea to explore the TM@Na 2AlH4 geometry arose when we were doing calculations on Pd and Pt adsorbing on the (001) face of NaAlH<sub>4</sub>, and discovered that these atoms preferred to adsorb between 2 rather than between 4  $AlH_4^-$  units, giving rise to the question of whether the same might be true for Na adsorbing to a substituted surface.

A second comment to be made is that for Pd and Pt the favoured exchange geometry is likewise TM@Na\_2AlH4 (Figs. 6.5b and 6.6b) rather than TM@Na\_4AlH4 (see

also Table 6.1). The final point to be made is that for Sc and Ti the most favourable interstitial site is TM@inter\_surface, while for Zr it is the TM@inter\_nosym site.

#### 6.3.3 Interpretation with a zipper model for mass transport

The results are best explained if one assumes that the most important function of the catalyst is to arrange for mass transport to enable a phase separation between a Na rich phase and an Al rich phase. The "zipper mechanism" outlined below is essentially a specific example of the third mechanism for mass transport discussed by Gross *et al.* [49], in which the catalyst moves into the starting phase and "eats" its way into the material, moving one of the two metal atoms (in our case Na) out of it. A difference in mass transport is exactly what distinguishes the absorption behaviour of the good catalysts (Sc, Ti, and Zr) from the absorption behaviour of the bad catalysts (Pt and Pd): the good catalysts prefer to push a Na atom on to the surface by exchanging with it, penetrating the surface and bringing about a mass separation between a Na rich and a Na poor phase. In contrast, the bad catalysts (Pt and Pd) are able to penetrate the surface, but they do not actively enforce mass separation by exchanging with either Na or Al and transporting the exchanged atom away to sit above the surface. Instead, they simply absorb in an interstitial site.

We have previously invoked a "zipper model" [37] to explain the effect one of the good catalysts, Ti, may have, and the same model can be applied to Sc and Zr. In this model, the catalytically active TM-atom acts as a slider, eating itself into a NaAlH<sub>4</sub> nanoparticle as it reacts away, effectively unzipping the structure. The Na ion transported away to sit on the surface should form the nucleus of a Na rich phase (Na<sub>3</sub>AlH<sub>6</sub> or NaH), while the TM atom moving into the NaAlH<sub>4</sub>, being surrounded, could act as a nucleus for an Al rich phase (Al with the TM atom alloyed into it). The precise ordering of the catalytic activity of Sc, Ti, and Zr can be explained assuming that two things are needed for the catalyst to be good: (1) it should prefer to exchange with a surface atom, which would lead to the desired mass transport, (2) it should be possible to initially have the catalyst present on the surface in mono-atomically

dispersed form. Assumption 2 would explain why Sc is the best catalyst (it actually prefers being present on the surface in mono-atomically dispersed form over being separate from NaAlH<sub>4</sub> in its bulk phase, and why Ti is a better catalyst than Zr (less energy is needed to keep Ti separate from its bulk phase and present in monoatomic form on the surface than for Zr). In the latter two cases, the energy required to have the TM be present in monoatomic form on the surface could, for instance, be provided in mechanical form, through ballmilling.

#### 6.4. Conclusions.

We have performed DFT calculations on the interaction of a single TM atom (Sc, Ti, Zr, Pd, and Pt) with the (001) face of NaAlH<sub>4</sub>, using a nano-sized cluster model. In the DFT calculations, the PW91 GGA was used, and both spin restricted and spin unrestricted calculations were performed. The calculations involving Zr, Pd, and Pt incorporated scalar relativistic corrections, employing the ZORA method. The calculations were performed in an attempt to explain a key experimental finding, that Sc, Ti, and Zr are good catalysts for hydrogen uptake and release, while the traditional hydrogenation catalysts Pt and Pd are poor catalysts for hydrogen storage in NaAlH<sub>4</sub>. The key difference found between the good catalysts (Sc, Ti, and Zr) and the bad catalysts (Pt and Pd) is that the good catalysts prefer to exchange with a surface Na atom, while the bad catalysts prefer to absorb in an interstitial site. Thus, the good catalysts are seen to initiate mass transport of the heavy metal atoms, and to bring about an initial separation between a Na-rich and a 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. [49], in which 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 that 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<sub>4</sub> is energetically preferred over the case where the TM atom is in the bulk TM phase, whereas atomic adsorption is not favoured for the Ti and Zr catalyst, and is most unfavourable 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<sub>4</sub> may also be important to the functioning of the catalyst, and that this ability may be used to distinguish the "best catalysts" from the class of "good catalysts". I believe that our calculations have revealed some key points about what are good catalysts for effecting hydrogen release from and uptake in NaAlH<sub>4</sub>, and I hope that experiments can be done to confirm the interpretations given above of what are features of good catalysts.

#### 6.5. References

- [1] L. Schlapbach, A. Züttel, Nature 414, 353 (2001).
- [2] R. S. Irani, MRS Bull. 27, 680 (2002).
- [3] J. Wolf, MRS Bull. 27, 684 (2002).

[4] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, Nature 386, 377 (1997).

[5] A. Züttel, S. Orimo, MRS Bull. 27, 705 (2002).

[6] W. L. Mao, H-k Mao, A. F. Goncharov, V. V. Struzhin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, Y. Zhao, Science 297, 2247 (2002).

[7] L. J. Florusse, C. J. Peters, J. Schoonman, K. C. Hester, C. A. Koh, S. F. Dec, K. N. Marsh, E. D. Sloan, Science 306, 469 (2004).

[8] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, Science 300, 1127 (2003).

[9] Z. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, Science 306, 1012 (2004).

[10] B. Bogdanovic, M. Schwickardi, J. Alloys Comp. 253-254, 1 (1997).

[11] F. Schüth, B. Bogdanovic, M. Felderhoff, Chem.Comm. 2249-58 (2004).

[12] W. Grochala, P. P. Edwards, Chem.Rev. 104, 1283 (2004).

[13] M. Felderhoff, C. Weidenthaler, U. von Helmolt, U. Eberle, Phys. Chem. Chem.Phys. 9, 2643 (2006).

[14] B. Bogdanovic, R. A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, J. Alloys Comp. 302, 36 (2000).

[15] B. Bogdanovic, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte, F. Schüth, Adv.Mater. 15, 1012 (2003).

[16] M. Fichtner, O. Fuhr, O. Kircher, J. Rothe, Nanotechnology 14, 778 (2003).

[17] D. L. Anton, J. Alloys Comp. 356-357, 400 (2003).

[18] R. A. Zidan, S. Takara, A. G. Hee, C. M. Jensen, J. Alloys Comp. 285, 119 (1999).

[19] B. Bogdanovic, M. Felderhoff, A. Pommerin, F. Schüth, N. Spielkamp, Adv. Mater. 18, 1198 (2006).

[20] D. Pukazhselvan, M. S. L. Hudson, B. K. Gupta, M. A. Shaz, O. N. Srivastava, J. Alloys Comp. 439, 243 (2007).

[21] E. H. Majzoub, K. J. Gross, J. Alloys Comp. 356-357, 363 (2003).

[22] C. Weidenthaler, A. Pommerin, M. Felderhoff, B. Bogdanovic, F. Schüth, Phys. Chem. Chem. Phys. 5, 5149 (2003).

[23] M. Felderhoff, K. Klementiev, W. Grunert, B. Spliethoff, B. Tesche, J. M. Bellosta von Colbe, B. Bogdanovic, M. Hartel, A. Pommerin, F. Schuth, C. Weidenthaler, Phys. Chem. Chem. Phys. 6, 4369 (2004).

[24] J. Graetz, J. J. Reilly, J. Johnson, A. Yu, T. A. Tyson, Appl. Phys. Lett. 85, 500 (2004).

[25] A. G. Haiduc, H. A. Stil, M. A. Schwarz, P. Paulus, J. J. C. Geerlings, J. Alloys Comp. 393, 252 (2005).

[26] A. Léon, O. Kircher, M. Fichtner, J. Rothe, D. Schild, J. Phys. Chem.B 110, 1192 (2006).

[27] C. P. Baldé, H. A. Stil, A. M. J. van der Eerden, K. P. de Jong, J. H. Bitter, J. Phys. Chem.C 111, 2797 (2007).

[28] X. D. Kang, P. Wang, H. M. Cheng, J. Appl. Phys. 100, 034914 (2006).

[29] H. W. Brinks, M. Sullic, C. M. Jensen, B. C. Hauback, J. Phys.Chem.B 110, 2740 (2006).

[30] V. P. Balema, L. Balema, Phys. Chem. Chem. Phys. 7, 1310 (2005).

[31] D. Sun, T. Kiyobayashi, H. T. Takeshita, N. Kuriyama, C. M. Jensen, J. Alloys Comp. 337, L8 (2002).

[32] A. Léon, O. Kircher, H. Rösner, B. Décamps, E. Leroy, M. Fichtner, A. Percheron-Guégan, J. Alloys Compd. 414, 190 (2006).

[33] O. M. Løvvik, S. M. Opalka, Phys. Rev. B 71, 054103 (2005).

[34] O. M. Løvvik, S. M. Opalka, Appl. Phys. Lett. 88, 161917 (2006).

[35] J. Íñiguez, T. Yildirim, Appl. Phys. Lett. 86, 103109 (2005).

[36] A. Marashdeh, R. A. Olsen, O. M. Løvvik, G. J. Kroes, Chem. Phys. Lett. 426, 180 (2006).

[37] A. Marashdeh, R. A. Olsen, O. M. Løvvik, G. J. Kroes, J. Phys. Chem. C 111, 8206 (2007).

[38] T. Vegge, Phys. Chem. Chem. Phys. 8, 4853 (2006).

[39] J. Liu, Q. Ge, Chem. Commun. 1822-24 (2006).

[40] J. Liu, Q. Ge, J.Phys.Chem.B 110, 25863-68 (2006).

[41] J. M. Bellosta von Colbe, W. Schmidt, M. Felderhoff, B. Bogdanovic, F. Schüth, Angew. Chem. Int. Ed. 45, 3663 (2006).

[42] S. Chaudhuri, J. T. Muckerman, J. Phys. Chem. B 109, 6952 (2005).

[43] S. Chaudhuri, J. Graetz, A. Ignatov, J. J. Reilly, J. T. Muckerman, J. Am. Chem. Soc. 128 11404 (2006).

[44] O. Palumbo, R. Cantelli, A. Paolone, C. M. Jensen, S. S. Shrinivan, J. Phys. Chem. B 109, 168 (2005).

[45] O. Palumbo, A. Paolone, R. Cantelli, C. M. Jensen, S. S. Shrinivan, J. Phys. Chem. B 110, 9105 (2006).

[46] O. Palumbo, A. Paolone, R. Cantelli, C. M. Jensen, R. Ayabe, Mater. Sci. Eng. A 442, 75 (2006).

[47] J. Voss, Q. Shi, H. S. Jacobsen, M. Zamponi, K. Lefman, T. Vegge, J. Phys. Chem. B 111, 3886 (2007).

[48] J. Íniguez, T. Yildirim, J. Phys. Condens. Matter 19, 176007 (2007).

[49] K. J. Gross, S. Guthrie, S. Takara, G. Thomas, J. Alloys Comp. 297, 270 (2000).

[50] R. T. Walters, J. H. Scogin, J. Alloys Comp. 379, 135 (2004).

[51] Q. J. Fu, A. J. Ramirez-Cuesta, S. C. Tsang, J. Phys. Chem. B 110, 711 (2006).

[52] G. Streukens, B. Bogdanovic, M. Felderhoff, F. Schüth, Phys. Chem. Chem. Phys. 8, 2889 (2006).

[53] P. Wang, X. D. Kan, H. M. Cheng, Chem. Phys. Chem. 6, 2488-91 (2005).

[54] L. C. Yin, P. Wang, X. D. Kang, C. H. Sun, H. M. Cheng, Phys. Chem. Chem. Phys. 9, 1499 (2007).

[55] B. Bogdanovic, M. Felderhoff, M. Germann, M. Härtel, A. Pommerin, F. Schüth,C. Weidenthaler, B. Zibrowius, J. Alloys Comp. 350, 246 (2003).

[56] G. J. Thomas, K. J. Gross, N. Y. C. Yang, C. Jensen, J. Alloys Comp. 330-332, 702 (2002).

[57] C. P. Baldé, B. P. C. Hereijgers, J. H. Bitter, K. P. de Jong, Angew. Chem. Int. Ed. 45, 3501 (2006).

[58] W. Lohstro, M. Fichtner, Phys. Rev. B 75, 184106 (2007).

[59] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J.

- Singh, C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- [60] P. Hohenberg, W. Kohn, Phys. Rev. 136, B864 (1964).

[61] W. Kohn, L. J. Sham, Phys. Rev. 140, A1133 (1965).

[62] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, S.v. Gisbergen, J. G. Snijders, T.

Ziegler, J. Comput. Phys. 22, 931 (2001).

- [63] E. van Lenthe, E. J. Baerends, J. G. Snijders, J. Chem. Phys. 101, 9783 (1994).
- [64] T. J. Frankcombe, O. M. Løvvik, J. Phys. Chem. B 110, 622 (2006).
- [65] G. te Velde, E. J. Baerends, Phys.Rev.B 44, 7888 (1991).