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NaAlH₄ Clusters with Two Titanium Atoms Added

Ali Marashdeh,*,† Roar A. Olsen,† Ole Martin Løvvik,‡ and Geert-Jan Kroes†

Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands, Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1126 Blindern, N-0318 Oslo, Norway, and Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway

We present density functional theory calculations on a NaAlH₄ cluster with two titanium atoms added. The two titanium atoms were adsorbed on the (001) surface of NaAlH₄ as a Ti dimer or as two separate atoms. Various absorption sites inside the cluster were investigated, either by placing the Ti atoms in interstitial sites or by exchanging them with Na and Al atoms. The results 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 toward the subsurface region. A zipper model is proposed for explaining the enhanced kinetics due to Ti.

1. Introduction

After Bogdanovic and Schwickardi found that hydrogenation and dehydrogenation kinetics of NaAlH₄ are improved by adding small amounts of Ti, NaAlH₄ became a promising candidate for a reversible hydrogen storage material.[1] Different transition metals have been added to compare their effect on the hydrogenation kinetics, and Ti was found to be one of the best.[2] After this finding, much effort has been directed at understanding the role of Ti in improving the reaction kinetics, mainly focusing on understanding the structure of Ti in NaAlH₄. Some studies have shown that Ti is present in a dispersed amorphous phase with metallic aluminum in the form of Al₃Ti.[3–6] Brinks et al. showed that an amorphous phase is formed after ball milling, while a solid solution (Al₁₋ₓTiₓ) is formed after cycling.[7,8] Haiduc et al. found that the form of the TiAl compound depends on the cycling temperature.[9] Below 175 °C, an amorphous phase is produced. This phase was correlated with the best kinetics, while slightly poorer kinetics was observed for an ordered intermetallic Al₁₋ₓTiₓ phase, which is formed above 200 °C.[9] Baldé et al. suggested that about 70% of the Ti occupied interstitial spaces in the NaAlH₄ lattice after ball milling with TiCl₃, with the remaining Ti present on the surface of Al.[10] After desorption at different temperatures, they found results very similar to those of Haiduc et al.[10] Léon et al. showed after ball milling and during cycling that Ti is present primarily in the zero oxidation state.[11] Streukens et al. suggested that, as a result of the generation of Al in the dehydrogenation process, the Ti state changes from a Ti-rich TiAl₃ state to a Ti-poor Al₁₋ₓTiₓ solid solution.[12] Ti hydride (TiH₂) has also been observed during NaAlH₄ reversible hydrogenation and shown to be catalytically active.[3,13,14]

Palumbo et al. have found evidence from inelastic spectroscopy that Ti increases the mobility of hydrogen vacancies, but it is not clear from this study where the active form of Ti is located.[15] A computational study by Li and Jena concluded that

hydrogen vacancies may be promoted by Ti substituted in the lattice of NaAlH₄.[16] Inelastic neutron scattering experiments have demonstrated the existence of volatile molecular aluminum hydrides, which are proposed to be shuttles of hydrogen during (re-)hydrogenation.[17] A recent combined density functional theory (DFT) modeling and EXAFS study concluded that the role of Ti could be explained by the catalytic effect of Ti in solid solution Al₁₋ₓTiₓ on the dissociation of H₂.[18] From hydrogen isotope scrambling experiments, it was suggested that part of the role of Ti is to catalyze the dissociation of hydrogen at the surface of the material *and* to facilitate the diffusion of hydrogen into the bulk of the material.[19] However, it was also suggested that the rate-limiting step in the (de-)hydrogenation process seemed to be mass transfer of the solid,[19] which emphasizes the need to understand the role Ti plays in this process.

Since three different majority phases (TiAl₃, Al₁₋ₓTiₓ solid solution, and TiH₂) have been observed and the kinetics is comparable when either of these phases is present, it is reasonable to believe that a minority phase may be responsible for the kinetics enhancement. Some studies have suggested that a fractional amount of the Ti diffuses and substitutes into the alanate lattice,[14,20] where it occupies bulk Na sites.[21] Theoretical studies of Ti-doped NaAlH₄ using a standard state reference system,[22–24] or the product side of the reaction equations as the reference state,[25] show that, in these conceptual frameworks, Ti on the surface or substituted into the lattice is unstable compared to Ti in Ti bulk, with substitution of Al by Ti being the least unfavorable. On the other hand, substitution of lattice Na by Ti is found to be stable if gas-phase atoms are used as the reference state.[26–28] In summary, Na substitution is favored if the substituted metal is not allowed to aggregate, while Al substitution is favored if the substituted metal is allowed to aggregate, because of the larger cohesive energy of Al and AlTi compounds.

Most of the theoretical work on modeling Ti-doped NaAlH₄ has been done using periodic calculations. These periodic calculations assume the system to be infinite, but from experi-

* Corresponding author. E-mail: a.marashdeh@chem.leidenuniv.nl.
† Leiden University.
‡ University of Oslo and Institute for Energy Technology.

NaAlH$_4$ Clusters with Two Titanium Atoms Added

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ments it is known that the real NaAlH$_4$ particles are nanometer-sized.[8] This was one of the reasons why we recently chose to work with a 23 NaAlH$_4$ formula units ($Z = 23$) semispherically shaped cluster as a model for a nanosized NaAlH$_4$ particle.[29] The chosen cluster is about 2-nm large, which is small compared to a real NaAlH$_4$ particle (typical particle sizes after ball milling are 150−200 nm).[8] Nevertheless, our model cluster was structurally, electronically (density of states and band gap), and energetically (bonding energy per formula unit) close to bulk NaAlH$_4$.[29] The cluster was chosen to have a large exposed (001) surface, because this has been shown to be the most stable surface of the different crystal faces.[24,30] We introduced a new reference system: a Ti atom adsorbed on the surface of the cluster, assuming that some of the Ti can be present in monoatomically dispersed form and that this could constitute the active catalyst. Subsequently, the Ti atom was exchanged with Na or Al atoms or absorbed in interstitial sites, and we measured the stability relative to the newly chosen reference system. We found that the Ti atom preferably exchanges with a subsurface Na atom, while the occupation of an interstitial site was also found to be favorable.[29] Note that in these calculations the Na or Al atom being exchanged was adsorbed on the surface and not moved into the gas phase or the bulk.

The cluster approach offers a number of advantages beyond the periodic approach. It is known that during dehydrogenation and hydrogenation large structural changes take place. Modeling this properly might require very large periodic unit cells, making the calculations extremely demanding. By limiting the size of the unit cells to make the calculations feasible, one might introduce artifacts by allowing structural rearrangements to interact with their periodic images, thereby not obtaining the correct energetics. Another point is that the real materials exhibit a range of surface facets, while a slab only has one. The edges and corners inherent in a cluster approach might therefore resemble the actual situation more closely than when employing slabs. An argument already stated is that the real NaAlH$_4$ particles are nanosized, as is our model cluster. It has recently been shown that when the alanate particles are (significantly) smaller than 100 nm, NaAlH$_4$ *without* Ti can release some of the incorporated H$_2$ at even lower temperatures than in Ti-catalyzed NaAlH$_4$.[31] All this supports the view that a cluster model can provide very useful information. Of course, the cluster approach is not unproblematic, since the calculated properties might depend on both size and shape. Also, model clusters are surrounded by vacuum, while other particles surround the large majority of real-world particles. Our view is that cluster and periodic calculations are complementary with strong points contained in both of them.

In the present work, we extend our previous study by adding two titanium atoms to our $Z = 23$ model cluster. This has given us access to a large range of relevant Ti adsorption and absorption geometries that have not yet been studied theoretically and has allowed us to look for cooperative effects of the Ti added. This may be regarded as the first step toward experimental conditions in which nanosized Ti clusters are present. We have determined the most stable adsorption and absorption geometries by focusing on the overall energetics, but also looking into the local structure and bonding around the Ti.

2. Methods

The binding energy of all the clusters has been calculated using DFT[32,33] as implemented in the ADF code.[34] In each case, a geometry optimization is performed, starting from a suitably chosen initial geometry based on the bulk crystal structure. The exchange-correlation energy is approximated at the generalized gradient approximation (GGA) level using the functional of Perdew et al. (PW91).[35] The basis set used is a triple-ζ plus one polarization function (TZP) type. A frozen core of 1s on Al as well as Na was chosen, together with 1s2s2p for Ti. The general accuracy parameter of ADF[34] was set to 4.0 on the basis of a series of convergence tests. In many of the calculations, we applied a nonzero 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-ζ plus four polarization function-type basis sets. This was necessary since the standard fit sets were found to give inaccurate results. In our previous study, we found that it was important to consider both spin-restricted and -unrestricted calculations.[29] All calculations in the present study have been done at both the spin-restricted and -unrestricted levels, and they confirm this conclusion. The spin-unrestricted calculations were performed allowing one, two, three, and four electrons to be unpaired. However, note that only the value for the energetically most stable state is reported in the tables (together with the corresponding number of unpaired electrons). Other computational details can be found in ref 29.

The ADF code calculates the total binding energy relative to spin-restricted spherically symmetric atoms. The only purpose of this reference state is to provide a reference energy common to all calculated energies. However, since we have some freedom in how to define our energy reference, we have chosen additional reference systems that have a physical meaning and allow for a straightforward comparison of the two Ti and one Ti systems. When considering two Ti atoms adsorbed or absorbed on or in the $Z = 23$ model cluster, our zero of energy has been set to that of the fully optimized bare $Z = 23$ cluster and two Ti atoms in Ti bulk. When considering one Ti atom adsorbed or absorbed on or in the $Z = 23$ model cluster, our zero of energy has been set to that of the fully optimized bare $Z = 23$ cluster and one Ti atom in Ti bulk. In this way, the energies reported for the two and one Ti systems can be directly compared and represent the energy gained by taking one (two) Ti atom(s) out of Ti bulk and putting it (them) on or in the $Z = 23$ cluster. Note that we have defined the adsorption and absorption energies in such a way that a negative number means that it is stable with respect to Ti in Ti bulk. Our periodic bulk Ti calculations have been performed using ADF-BAND[36] with the same basis and fit sets as used in the cluster calculations.

3. Results and Discussion

3.1. Adsorption of Two Titanium Atoms on the Surface of the $Z = 23$ Cluster. Two titanium atoms were adsorbed on the (001) surface of the $Z = 23$ formula units NaAlH$_4$ cluster in different positions and orientations relative to each other. The adsorption energies of Ti on the relaxed clusters are listed in Table 1, and the surface geometries are displayed in Figure 1. As a first step, a Ti dimer was adsorbed above a Na atom in the Al−Al direction [Ti$_2$@top_AlAl] and in the Na−Na direction [Ti$_2$@top_NaNa] as shown in parts a and b of Figure 1, respectively. Ti$_2$@top_NaNa has a Ti$_2$ bond length (1.91 Å) shorter than Ti$_2$@top_AlAl (2.20 Å) and is more stable by 1.33 eV. The stability exhibited by the Ti$_2$@top_NaNa cluster might be partly attributed to its shorter Ti$_2$ bond length, which is close to the Ti dimer bond length in the gas phase (1.93 Å). As a

TABLE 1: Adsorption Energies (E_{ads}) for the Two Titanium Atoms Adsorbed on the (001) Surface of the $Z = 23$ Cluster[a]

	2Ti@top_4AlH₄	2Ti@top_2AlH₄	Ti₂@top_AlAl	Ti₂@top_NaNa
E_{ads}	0.70	3.38	3.88	2.55
d_{Ti-Ti}	10.16	5.11	2.20	1.91
n	4	3	0	2

[a] The energy reference used is discussed in section 2. The notations used to refer to a given structure are defined in Figure 1. All the energies are given in electronvolts, and all results have been obtained from fully relaxed geometries. The distance between the two Ti atoms is denoted d_{Ti-Ti} and is given in angstroms. The number of unpaired electrons giving the lowest energy is denoted *n*.

comparison, the energy penalty for stretching the Ti dimer bond from 1.93 to 2.20 Å in the gas phase is 0.45 eV. In the next step, the Ti dimer bond was broken and each Ti atom adsorbed separately between two AlH₄ units [2Ti@top_2AlH₄] or above sodium atoms between four AlH₄ units [2Ti@top_4AlH₄], as shown in parts c and d of Figure 1, respectively. As seen from the adsorption energies in Table 1, the 2Ti@top_2AlH₄ cluster is less stable than the Ti₂@top_NaNa cluster. This can be attributed to the loss of the Ti₂ bond: apparently, the separated titanium atoms do not compensate for this through their bonding to two AlH₄ units each. In the case of the 2Ti@top_4AlH₄ cluster, the Ti atoms have the chance to bond with four AlH₄ units each by pushing the Na atoms into the subsurface region, thereby forming the most stable cluster (Figure 1d).

The above results are in accordance with those obtained for a single Ti atom adsorbed on the surface of the $Z = 23$ cluster, as can be seen from the following results (see also ref 29). One Ti atom was adsorbed on the surface of the cluster above a Na atom between four AlH₄ units [Ti@top_4AlH₄], between two AlH₄ units [Ti@top_2AlH₄], and above one AlH₄ unit [Ti@top_AlH₄] as shown in parts e, f, and g of Figure 1, respectively. The adsorption energies of Ti in the relaxed geometries are given in Table 2, indicating that Ti@top_4AlH₄ is the most stable one. In Ti@top_4AlH₄, the Ti atom pushes a Na atom into the subsurface region, thereby forming high coordination bonding with the AlH₄ units. All these results point to the same tendency: the surface Na atoms are displaced into the subsurface region, facilitating Ti adsorption above a Na surface atom.

Before continuing, we need to address the issue of possible cluster-edge effects for the two Ti systems, especially for 2Ti@top_4AlH₄. As can be seen in Figure 1d, the two Ti atoms are rather close to the cluster edge as compared to the case where only one Ti atom is adsorbed in the middle of the cluster (Figure 1e). One should note that atoms and complexes at the edge are missing some Na−H bonds and may thus interact differently with Ti near the edge. From Table 2, we can calculate twice the adsorption energy of one Ti atom [Ti@top_4AlH₄] (2 × 0.61 eV = 1.22 eV), and the adsorption energy of two Ti atoms [2Ti@top_4AlH₄] (0.70 eV) can be taken from Table 1. The energy difference between them is 0.52 eV, which can be mainly attributed to an edge effect. However, the edge effect is significantly smaller than the energy difference between the dissociated Ti dimer [2Ti@top_4AlH₄] and the intact Ti dimer [Ti₂@top_NaNa], which is 1.85 eV (Table 1). Thus, we can safely conclude that it is energetically preferred for the Ti dimer to dissociate on the surface of NaAlH₄. Note, however, that this conclusion relates to the overall thermodynamics and not to the kinetics. It might be that there is a kinetic barrier for dissociation of Ti₂ on the surface of NaAlH₄, but we have not yet investigated this.

3.2. Stability of the Two Titanium-Doped NaAlH₄ Clusters. The 2Ti@top_2AlH₄ cluster (Figure 1c) described in the

(a) Ti₂@top_AlAl (b) Ti₂@top_NaNa

(c) 2Ti@top_2AlH₄ (d) 2Ti@top_4AlH₄

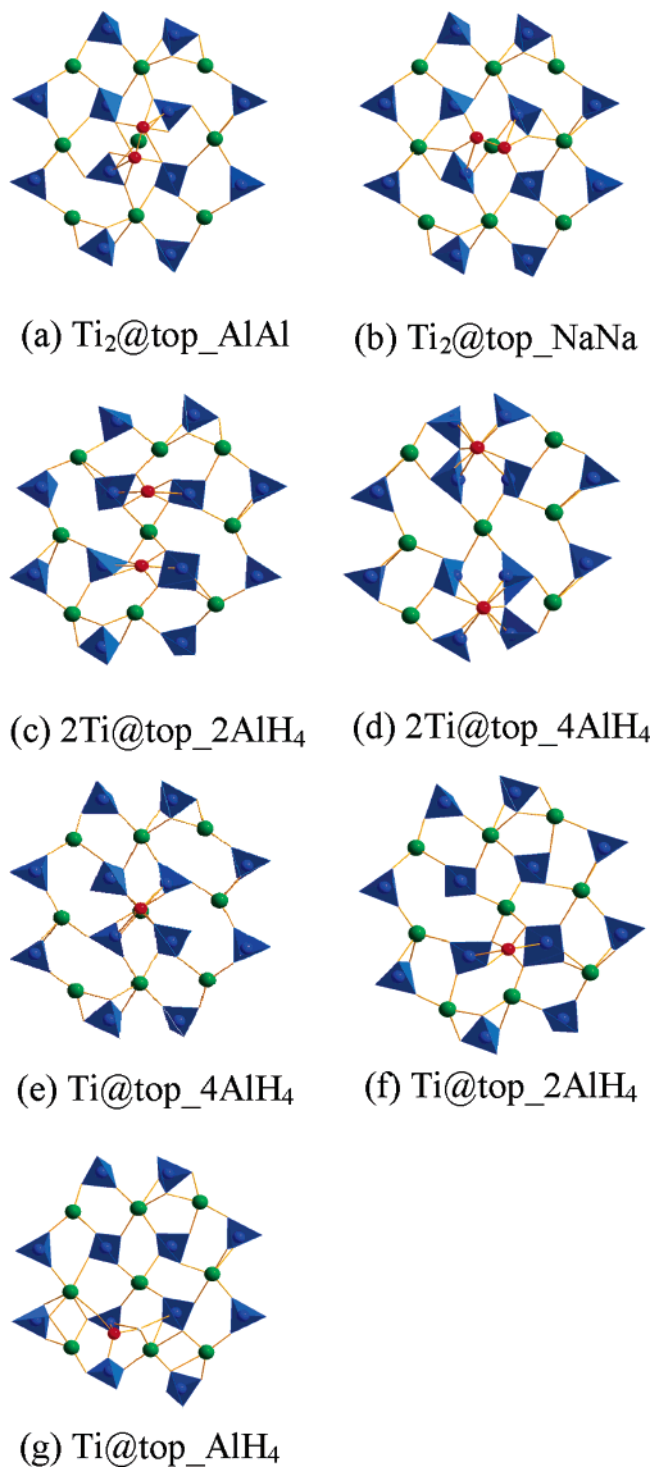(e) Ti@top_4AlH₄ (f) Ti@top_2AlH₄

(g) Ti@top_AlH₄

Figure 1. One and two titanium atoms adsorbed in different positions on the (001) surface of the $Z = 23$ model cluster viewed from above. (a) A Ti dimer above (first layer) Na along the Al−Al direction [Ti₂@top_AlAl]. (b) A Ti dimer above (first layer) Na along the Na−Na direction [Ti₂@top_NaNa]. (c) Two Ti atoms separated, adsorbed between two AlH₄ units [2Ti@top_2AlH₄]. (d) Two Ti atoms separated, adsorbed above sodium atoms between four AlH₄ units [2Ti@top_4AlH₄]. (e) A single Ti atom adsorbed above (first layer) Na between four AlH₄ units [Ti@top_4AlH₄]. (f) A single Ti atom adsorbed between two AlH₄ units [Ti@top_2AlH₄]. (g) A single Ti atom adsorbed above an AlH₄ unit [Ti@top_AlH₄].

previous section was used as a starting point for putting the Ti atoms into interstitial sites and for exchanging one or two Ti atoms with one or two Na, or Al, or with one Na and one Al. Full structural relaxation was performed for all clusters, and

TABLE 2: Adsorption Energies (E_{ads}) for One Titanium Atom Adsorbed on the (001) Surface of the $Z = 23$ Cluster^a

	Ti@top_4AlH₄	Ti@top_2AlH₄	Ti@top_AlH₄
E_{ads}	0.61	1.02	1.11
n	2	2	2

^{a} The energy reference used is discussed in section 2. The notations used to refer to a given structure are defined in Figure 1. All the energies are given in electronvolts, and all results have been obtained from fully relaxed geometries. The number of unpaired electrons giving the lowest energy is denoted n.

the most stable structures are displayed in Figure 2. We also investigated whether the absorption energy computed for the exchange of Ti with Na and Al could be further decreased by displacing the adsorbed atom (Na, Al) along the surface. The most favorable absorption energies are given in Table 3.

3.2.1. Ti Exchanging with Na. According to the results in Table 3, the two Ti atoms prefer to exchange with the two Na atoms that have been displaced into the subsurface region, 2Ti@2Na (Figure 2a). The number of Na, Al, and H atoms within the range of 3 Å around the Ti atoms is 22, as indicated in Table 3 as the coordination number (CN). The local structure around the Ti atoms can be described as that of a Ti₂Al₆H₁₂ complex, possibly indicating the very first step in the formation of a (TiAl₃)₂ alloy. We also see that this structure is considerably more stable than 2Ti@(Na, top), which is formed by replacing one Ti atom with a subsurface-displaced Na atom while the second Ti atom remains on the surface of the cluster (Figure 2b).

An important question is whether the contribution of the second Ti atom to the stability of the cluster is the same as the first one. This can be answered by comparing the absorption energy of one and two Ti atoms in the cluster relative to that of bulk, as done in Table 4. It is seen that the absorption energy of one Ti atom exchanging with a Na atom [Ti@Na] is −0.50 eV, and the absorption energy of two Ti atoms exchanging with two Na atoms [2Ti@2Na] is −0.71 eV. The energy difference between them (−0.21 eV) is the second Ti atom's contribution to the stability of the cluster, which is considerably less than that of the first Ti atom (−0.50 eV). If we assume the subsurface Ti to be the active catalyst, this might explain why the effect of adding Ti is limited to a certain concentration range with respect to its catalytic activity: As the concentration of Ti increases, the stability of NaAlH₄ containing subsurface Ti decreases, until it reaches a point where the Ti does not mix well with sodium alanate, and the subsequently added Ti goes to another (majority) phase, which does not lead to additional increase of the kinetics.[37,38]

3.2.2. Ti Exchanging with Na and Al. By exchanging two Ti atoms with a subsurface-displaced Na and a surface Al atom (Figure 2c), we find that a cluster [2Ti@(Al, Na)] is formed that is similar in its stability to the most stable 2Ti@2Na cluster. The energy difference is small (0.2 eV). As shown in Table 3, this exchange results in the two Ti atoms being in their closest position inside the cluster, forming a 2.81 Å bond. The CN is 21, and a Ti₂Al₅H₁₀ complex is formed that is similar to the one formed in the 2Ti@2Na cluster. This explains the similar stability of these two clusters.

3.2.3. Ti Exchanging with Al. Exchange of the two Ti atoms with two surface Al atoms [2Ti@2Al] (Figure 2d) is more stable than exchanging one Al atom and leaving the second Ti atom on the surface [2Ti@(Al, top)] (Figure 2e) or leaving the two Ti atoms on the surface [2Ti@top_4AlH₄] (Figure 1d). Still, these exchanges are less favorable than the exchanges of two subsurface-displaced Na atoms or the exchanges with a sub-
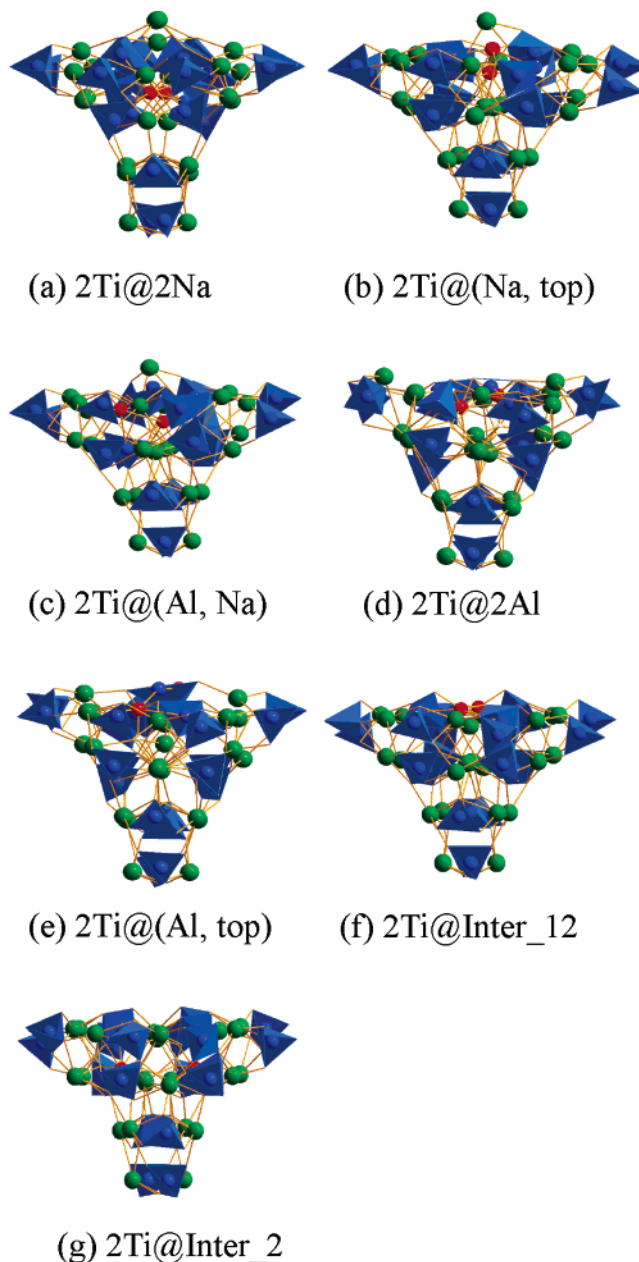

(a) 2Ti@2Na

(b) 2Ti@(Na, top)

(c) 2Ti@(Al, Na)

(d) 2Ti@2Al

(e) 2Ti@(Al, top)

(f) 2Ti@Inter_12

(g) 2Ti@Inter_2

Figure 2. Two titanium atoms adsorbed in different positions on or in the $Z = 23$ cluster. (a) Two Ti atoms exchange with two Na atoms [2Ti@2Na]. (b) The first Ti atom exchanges with a Na atom, and the second remains on the surface [2Ti@(Na, top)]. (c) The first Ti atom exchanges with a Na atom, and the second exchanges with an Al atom [2Ti@(Al, Na)]. (d) Two Ti atoms exchange with two Al atoms [2Ti@2Al]. (e) The first Ti atom exchanges with an Al atom, and the second remains on the surface [2Ti@(Al, top)]. (f) Two Ti atoms absorb in interstitial sites between the first and the second layer [2Ti@Inter_12]. (g) Two titanium atoms are placed in interstitial sites in the second layer [2Ti@Inter_2].

surface-displaced Na and a surface Al. A single Ti atom adsorbed on the surface of the cluster was found to be more stable than the Ti@Al-exchanged cluster by about 0.1 eV.[29] A similar finding does not apply to the 2Ti@2Al system. From Tables 1 and 3, we see that the 2Ti@2Al system is about 0.5 eV more stable than leaving the two Ti atoms on the surface. The reason is that the two Al atoms stabilize each other on the surface by forming a 2.88 Å long bond and clustering with the exchanged Ti atoms.

3.2.4. Ti in Interstitial Sites. The two Ti atoms are placed in interstitial positions between the first and the second layers

TABLE 3: Absorption Energies (E_{abs}) for the Two Ti Systems[a]

	E_{abs}	CN	d_{Ti-Ti}	n
2Ti@2Na	−0.71	22	4.47	2
2Ti@(Na, top)	0.35	15	2.46	2
2Ti@(Al, Na)	−0.52	21	2.81	2
2Ti@2Al	0.21	16	4.90	4
2Ti@(Al, top)	2.50	14	4.89	2
2Ti@Inter_2	1.72	22	7.38	2
2Ti@Inter_12	4.10	14	5.77	2

[a] The energy reference used is discussed in section 2. The notations used to refer to a given structure are defined in Figure 2. All the energies are given in electronvolts, and all results have been obtained from fully relaxed geometries. The number of atoms within the distance of 3 Å for the Ti atoms is denoted CN. The distance between the two Ti atoms is denoted d_{Ti-Ti} and is given in angstroms. The number of unpaired electrons giving the lowest energy is denoted n.

TABLE 4: Absorption Energies (E_{abs}) for One and Two Titanium Atoms Exchanging One and Two Na Atoms, Ti@Na and 2Ti@2Na, Respectively[a]

	Ti@Na	2Ti@2Na
E_{abs}	−0.50	−0.71
n	2	2

[a] The energy reference used is discussed in section 2. All the energies are given in electronvolts, and all results have been obtained from fully relaxed geometries. The number of unpaired electrons giving the lowest energy is denoted n.

[2Ti@Inter_12] (Figure 2f) and in the second layer [2Ti@Inter_2] (Figure 2g). From Table 3, we see that the structure with two Ti atoms in the second layer is more stable than when they are inserted between the first and second layers. Actually, when the Ti atoms are placed between the first and the second layers the Ti atoms move to a final position in the surface of the cluster (Figure 2f). This position is less stable than that of 2Ti@top_2AlH$_4$ (Figure 1c) by 0.7 eV (Tables 1 and 3). Even if the second interstitial structure [2Ti@Inter_2] is considerably more stable than the first [2Ti@Inter_12], it is still less stable than the most stable structure with both Ti atoms on the surface [2Ti@top_4AlH$_4$]. The latter is favored by about 1 eV if the numbers are compared directly, but also when the estimated edge effect of 0.5 eV is subtracted there is a clear preference for leaving the Ti atoms on the surface. This is in contrast to the case where one single Ti atom was placed in an interstitial position and found to be comparable in stability to the Ti@Na exchange.[29] Having Ti atoms close together in interstitial positions is clearly unfavorable, even if the distance between them is in the range 5.8−7.4 Å.

3.3. Is Ti Found on the Surface or inside the Cluster? Combining the results described in sections 3.1 and 3.2, we can address the question whether Ti prefers to stay on the surface of the cluster or prefers to move inside. This important question can be answered by comparing the most stable cluster for Ti adsorption on the surface of the cluster, 2Ti@top_4AlH$_4$, with the most stable clusters where Ti can be found inside the cluster, 2Ti@2Na and 2Ti@(Al, Na). From Tables 1 and 3, we see that Ti is more stable inside the cluster by 1.41 and 1.22 eV, respectively. Thus, our cluster model clearly indicates that Ti prefers to move into the subsurface region of NaAlH$_4$. Similar conclusions are reached when performing periodic calculations for the *exchange* reactions, supporting the results from our cluster model.[39] Note that in these calculations the Na or Al atom being exchanged is adsorbed on the surface and not moved into the gas phase or the bulk (see also comments below). Note that there is no evidence from our results that Ti would move further into the lattice and that periodic calculations imply that

bulk substitution is substantially less stable than surface or subsurface substitution.[22,25] We thus expect that the subsurface site is the most stable option for Ti in the NaAlH$_4$ lattice.

3.4. Does Ti Prefer To Be inside the NaAlH$_4$ Cluster or in Ti Bulk? The preference for Ti to be in the subsurface region of the cluster or in Ti bulk can be determined for systems with one and two Ti atoms added from Tables 3 and 4. One Ti atom is more stable inside the cluster than in Ti bulk by 0.5 eV, and two Ti atoms are more stable in the cluster than two Ti atoms in bulk by 0.71 eV. Thus, when present in the form of two atoms, Ti clearly prefers to be inside the cluster than to be in Ti bulk. This is in strong contrast to the results of periodic supercell calculations where a clear preference for Ti bulk has been found.[22−25] The reason is quite obvious: The slab calculations removed the *substituted* atoms and put them in their corresponding bulk state when Ti was added, so that the cohesive energies of bulk Na, Al, and so forth entered the stability calculations.[22,24,25,28] Al has a higher cohesive energy than Na, and this will therefore tend to favor Al substitution. In our case, the *exchanged* atom(s) is(are) placed on the surface of the cluster and the difference in cohesive energies does not play a role in the relative stabilities. Which answer is correct depends on, for example, whether Al bulk particles are present in the vicinity of the exchanged Al atom.

The only energy being comparable to published slab studies is that of Ti being placed interstitially, since then the composition of the cluster and slab is similar. Interstitially absorbed Ti in the second layer was found to be unstable by 2.07 eV relative to Ti bulk for the slab model,[22] while for the cluster model it is stable by 0.18 eV. However, the slab model contains $Z = 16$ formula units, and the cluster model contains $Z = 23$ formula units, which means that the numbers still are not directly comparable. Perhaps most importantly, when using periodic supercell calculations the possibilities for structural rearrangements to accommodate the extra atom are much more limited than when using a cluster model. As a result of the limited size of the supercells, self-interaction between the periodic images of the Ti-containing complexes may also be expected in that case. At the moment, it is hard to say which approach, periodic or cluster, is better. It is known from experiments that the typical particle size is 150−200 nm after ball milling,[8] although experiments have also been done on particles smaller than 100 nm.[31] On the one hand, our $Z = 23$ cluster model is considerably smaller, but on the other hand, the periodic calculations assume infinite particle size and impose geometric constraints on NaAlH$_4$ by modeling this material as a slab. Also, the slabs only exhibit one surface termination, while clusters may have several different terminations simultaneously, in addition to edges and corners.

3.5. Density of Electronic States of Ti-Doped Clusters. The densities of electronic states have been calculated, and they are displayed for the 2Ti@2Na system in Figure 3a, for the Ti@Na system in Figure 3b, and for the bare $Z = 23$ cluster in Figure 3c. The bare cluster has a band gap (i.e., a highest occupied molecular orbital−lowest unoccupied molecular orbital gap, HOMO−LUMO) of 3.0 eV, as seen from the total density of state (TDOS) plot in Figure 3c. Figure 3c also shows the partial densities of states (PDOS) associated with Al, Na, and H of the bare cluster. They show mainly H 1s and Al 3s3p contributions to the valence band and mainly Na 3s3p and Al 3p character of the conduction band. Figure 3a,b shows the TDOS and the PDOS associated with Ti, Al, Na, and H of doubly Ti-doped [2Ti@2Na] and singly Ti-doped [Ti@Na] clusters, respectively. By comparing the TDOS and the PDOS
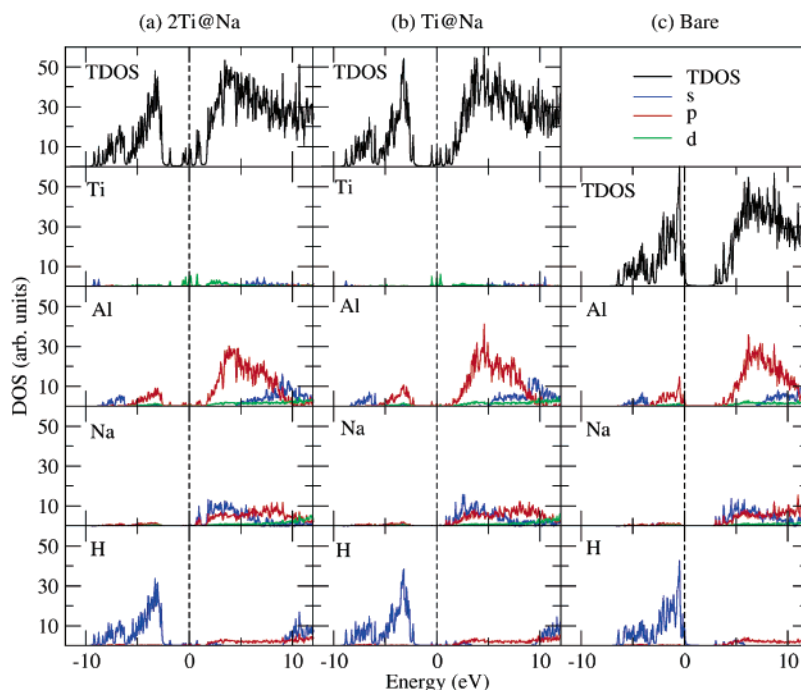
NaAlH₄ Clusters with Two Titanium Atoms Added

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Figure 3. TDOS and partial densities of states associated with Ti, Na, Al, and H of the (a) 2Ti@2Na, (b) Ti@Na, and (c) bare clusters, respectively. The partial and total densities of states have been shifted so that the HOMO is at the zero of the energy scale (indicated with a dashed line).
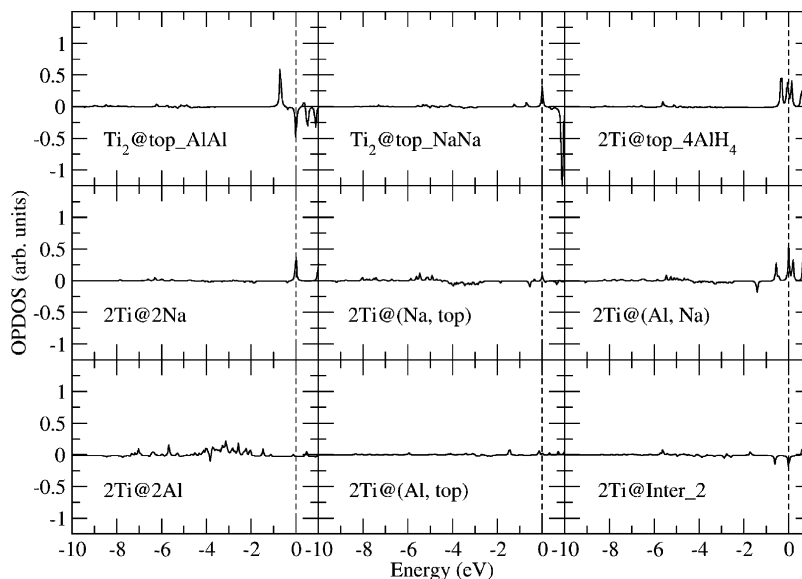

Figure 4. OPDOS of the Ti with the Na. The notations used to label the different panels are defined in Figures 1 and 2. The OPDOSs have been shifted so that the HOMO is at the zero of the energy scale (indicated with a dashed line).

of the bare cluster with that of the doped clusters, we see that Ti introduces states in the band gap, forming a metallic-like cluster. The difference between the singly Ti- and the doubly Ti-doped clusters is that in the doubly Ti-doped system there are more states introduced in the band gap. One should note that the Ti 3d orbitals not only introduce new states in the band gap, but also mix into both valence and conduction bands, as can be seen from the PDOS plots of Ti in Figure 3a,b.

To unravel some more detail in the bonding of Ti to NaAlH₄, we have plotted the overlap population density of states (OPDOS) in Figures 4 and 5 for most of the clusters depicted in Figures 1 and 2. Figure 4 shows the OPDOS between all Ti orbitals and all Na orbitals, and Figure 5 shows the OPDOS between all Ti orbitals and all Al and H orbitals. From Figure 4, it is clear that there is very little direct interaction between Ti and Na, and then only in the HOMO region. From Figure 5, we

see that the Ti orbitals have a positive overlap with the Al and H orbitals throughout the valence band and that the Al and H orbitals also mix favorably into the Ti band gap states. Thus, the Ti interaction with Al and H is bonding at and below the HOMO.

3.6. Proposed Model for the Role of Ti. It is clear from the discussion above that exchange of Ti with subsurface Na atoms is preferred, or with a combination of Na and Al atoms when a direct bond between the Ti atoms can be established. These exchanged structures exhibit surfaces that most likely are very reactive (see also below). It is conceivable that the reactive species (Na, Al, H) left behind will be removed because of interactions with other subspecies, eventually leading to the removal of the whole top layer. The result of such a reaction could be that Ti again resides on the surface of the nanoparticle and will then try to move into the subsurface of the nanoparticle once more.
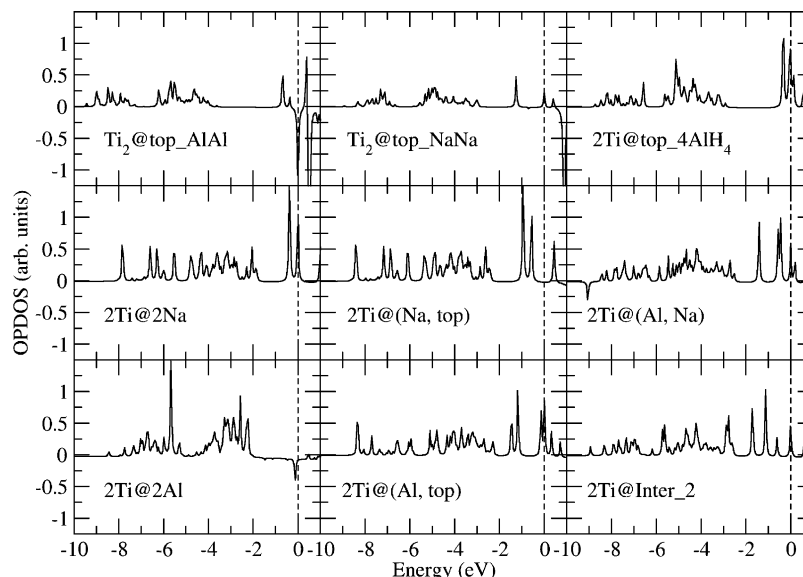
Figure 5. OPDOS of the Ti with the AlH$_4$. The notations used to label the different panels are defined in Figures 1 and 2. The OPDOSs have been shifted so that the HOMO is at the zero of the energy scale (indicated with a dashed line).

This constitutes what we introduce as the zipper model. In this model, Ti works as a novel kind of catalyst in NaAlH$_4$ by acting as a slider, eating itself into the nanoparticle as it reacts away, effectively unzipping the structure. In this way, the fully hydrogenated alanate would be decomposed, and at the same time fresh surfaces would be exposed along the path of the zipper. Note that the most reactive of all structures is the one with Ti on the surface. The first reaction according to our zipper model is that Ti moves into the subsurface region of the structure replacing Na. In our model, we assume that the Na left on the surface can easily react with other species present. The reason for claiming this is that they are exposed undercoordinated atoms.

Is this model consistent with previous studies on the Ti-enhanced sodium alanate? It is easy to envision that Ti could work as the zipper slide and at the same time also as a traditional (de-)hydrogenation catalyst. This could explain why catalysts that usually are better hydrogenation catalysts than Ti (such as Pd) do not work very well in NaAlH$_4$:[2] they may be able to split hydrogen molecules, but they lack the mobility and tendency of Ti to move into the alanate lattice. The zipper model could also be consistent with the studies observing defects in Ti-enhanced sodium alanate;[15,16] since defects have been shown to promote Ti substitution in the alanate lattice by several modeling studies,[16,24,28,40] defects could further facilitate the primary steps of the zipper model. Also, it is easy to imagine that formation of alanes could result from a zipper mechanism; this could happen in parallel to reaction of the adsorbed Na atoms on the surface.

There is one possible problem with the zipper model: the hypothesized monodispersed Ti has thus far not been observed by any experimental study. The majority of Ti that has been observed seems to be in a zerovalent state, surrounded primarily by Al.[41] This could be explained by the experimental techniques not being sufficiently sensitive to find the minority phase proposed in this study. It could also be that these minority phases, being metastable of nature, only exist off equilibrium, that is, during the hydrogenation and dehydrogenation processes. Even so, it should be checked if subsurface exchange of Ti still is feasible when it is present together with Al. Work on this question is in progress. All in all, it seems that the zipper model may be a crucial part of the complicated role of Ti in the sodium

alanate system. To the best of our knowledge, we are the first to propose such a model.

4. Conclusions

We have performed density functional theory calculations at the generalized gradient approximation level for a NaAlH$_4$ cluster with two Ti atoms, either as a dimer or two separated Ti atoms, adsorbed on the (001) surface of the cluster. These calculations have been followed by a large number of calculations where one or two Ti atoms have been inserted into interstitial sites or exchanged with Na or Al. The results support the following conclusions: (i) Starting from 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 for the resulting atomic Ti is above first-layer Na surface atoms. The surface Na atoms are found to be displaced into the subsurface region of the cluster upon Ti adsorption, allowing the Ti to interact with four AlH$_4$ units. (Note that we have not yet investigated whether there is a barrier to dissociation of the Ti dimer; thus far we have only considered the initial and final stable geometries). (ii) After dissociation, the two Ti atoms prefer to move inside the cluster to the subsurface region. When 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. Almost equally stable is the exchange with one subsurface-displaced Na and one surface Al, provided the two Ti atoms end up close enough to each other to form a direct bond. In both cases, small local TiAl clusters are formed. Absorbing two Ti atoms in interstitial sites close to each other (5.8−7.4 Å) is clearly unfavorable. The thermodynamically most stable situation is for Ti atoms to move into Na positions far away from each other. A zipper model is proposed, in which the mechanism by which the added Ti promotes H$_2$ release is explained by the Ti atom working itself down into the alanate particle, effectively unzipping the structure.

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