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2007 J. Phys.: Condens. Matter 19 176007

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Hydrogen-related catalytic effects of Ti and other light transition metals on NaAlH₄ surfaces

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Received 8 January 2007, in final form 23 March 2007

Published 10 April 2007

Online at stacks.iop.org/JPhysCM/19/176007

Abstract

We report a first-principles study of sodium alanate (NaAlH₄) surfaces, both pure and with Ti atoms on them, focusing on their stability and reactivity with hydrogen. We find Ti causes the dissociation of H₂ molecules and contributes to the stability of the surface exposed to hydrogen. The Ti *catalysts* should thus facilitate the reaction by which NaAlH₄ (7.4 wt% of H) forms from Na₃AlH₆ (5.9 wt% of H), which occurs under hydrogen pressure and requires H₂ dissociation to proceed. The presence of Ti also results in lower defect-formation energies, which should favour the NaAlH₄ decomposition reaction. Indeed, our calculations show that the chemical versatility of Ti brings close in energy a number of *steps* that presumably are relevant in the formation and decomposition of NaAlH₄, which suggests that the catalyst facilitates both processes. We also discuss the possibility of using other light transition metals (Sc, V, and Cr) as catalysts, and conclude that Ti is the best choice overall.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years sodium alanate (NaAlH₄) has become one of the most promising systems to achieve safe and inexpensive storage of hydrogen aboard vehicles. The kinetics of the *reversible* reaction by which pure NaAlH₄ transforms into Na₃AlH₆ and releases hydrogen is relatively slow. However, it was discovered that a few per cent of Ti increases the reaction rates dramatically [1], bringing the system close to what is required for practical applications.

In spite of extensive investigations, the mechanism by which Ti enhances the kinetics of this reaction remains unknown [2–4]. As a matter of fact, only recently have we had convincing experimental [5] and theoretical [6, 7] evidence that the Ti atoms are located on the surface, as opposed to the bulk, of the system. First-principles simulations by several groups also predict that titaniums cause the breaking of multiple Al–H bonds [7, 8], and that Ti atoms in the bulk of the material [9] and Na vacancies [10] facilitate the creation of H vacancies. Such studies suggest mechanisms by which Ti can improve the decomposition and hydrogen-release kinetics

of NaAlH₄, but are far from being complete or conclusive (specially those restricted to the bulk of the system). In addition, little is known about an even more important issue, namely, how Ti accelerates the reaction by which NaAlH₄ is recovered from Na₃AlH₆ under hydrogen pressure.

A direct study of these issues from first-principles is essentially impossible, as the spatial and temporal scales involved are beyond the scope of current computational capabilities. However, it is possible to address partial aspects of the problem and identify mechanisms by which the Ti atoms can enhance the reaction kinetics. That is what we have done in this work, by studying the stability of NaAlH₄ surfaces as well as the energetics of various processes that occur when the surfaces are exposed to hydrogen. We report our results in the form of a comparative study of pure and Ti-containing surfaces, which allows us to easily identify the role that the Ti atoms play as catalysts. Interestingly, our calculations clearly indicate that Ti causes a number of effects (e.g. H₂ dissociation or reduced defect-formation energies) that should result in improved kinetics of *both* the NaAlH₄ decomposition and formation reactions.

2. Methodology

The calculations were performed within the generalized gradient approximation [11] to density functional theory [12] as implemented in the code SIESTA [13]. Thus, we have used a very standard first-principles approach that is known to describe covalent and ionic bonding, which are the relevant ones in this work, in a qualitatively correct way and with acceptable quantitative accuracy. More specifically, binding energies computed with this methods are usually accurate to within 0.1 eV; this is enough for the purposes of this work, which focuses on identifying the effects caused by the transition metal catalysts rather than on their precise quantification. We used a localized basis set including double- ζ and polarization orbitals, and Troullier–Martins pseudopotentials [14]. We tested the convergence of our calculations with respect to the k -point and real space meshes; we typically considered a 4500 Å³ simulation supercell containing about 162 atoms, for which we used a 2 × 2 × 1 k -point grid and a 150 Ryd cutoff for the real space mesh. The accuracy of our SIESTA results had been previously tested against accurate *ab initio* calculations using a plane-wave basis set [7].

Tetragonal NaAlH₄ presents two natural terminations related to the (100) and (001) directions, respectively. The phenomenology associated with the presence of Ti on these two surfaces is known to be essentially the same [7]; thus, for this work we considered the 001-surface, which can be treated using a relatively small supercell. Our slab-type supercell can be regarded as being composed of 3 × 3 × 3 NaAlH₄ groups, i.e. 162 atoms. We imposed that the atoms in the deepest layer be fixed at the bulk atomic positions, and allowed about 13 Å of empty space between slabs. The bulk structural parameters ($a = b = 5.01$ Å and $c = 11.12$ Å) were obtained from first-principles [7]. Structural relaxations were considered to be converged for residual force components smaller than 0.02 eV Å⁻¹. We calculated absorption and vacancy-formation energies as the difference between the energies of products and reactants; thus, a negative value signals an energetically favourable reaction. To study, for example, the deposition of H atoms, we considered several starting configurations chosen in an essentially random way, performed regular structural relaxations, and took the lowest-energy result. In order to determine the reliability of this approach, in a few cases we run short (100 fs) molecular dynamics simulations *prior* to the structural relaxations, and did not find results significantly different from those obtained with the direct relaxations. Note that, ideally, one would like to perform molecular dynamics simulations *of the actual solid state reactions* to identify the relevant catalytic processes; unfortunately, such calculations are enormously costly from the computational point of view and unfeasible in practice. We believe that, while limited,

Table 1. Desorption energies (in eV) of hydrogen and other atom groups for pure and two Ti-containing NaAlH₄ surfaces. We denote by +H^v the surface with one H vacancy, etc. We use as reference the energy of the original pure and Ti-containing surfaces, the energy of the H₂ molecule, and the atomic energies of Na and Al.

Surf. type	+H ^v	+Na ^v	+(NaH) ^v	+(AlH ₄) ^v
Pure	1.98	7.96	5.61	7.51
Ti@Na	0.41	4.89	5.41	5.70
Ti@Al	0.30	5.20	4.50	5.65

our approach leads to relevant and useful insights into the behaviour of these complex systems and processes.

The question of whether the Ti substitutes for Na or Al is somehow controversial, as it critically depends on the choice of energies that are used as a reference to compute the relative stability of the various substitutional models [10, 15]. Usually, the Ti is introduced in the alanates by ball-milling, which is an out-of-equilibrium process that involves individual Ti, Na, and Al atoms, as well as H₂ molecules, rather than the corresponding crystalline phases. Hence, we prefer using atomic energies as reference, which leads to the conclusion that Ti substitutes for Na [7, 8]. However, if the energies of crystalline Ti, Na, and Al are used, the result is that Ti substitutes for Al [6]. Being aware of this issue, in this work we have considered these two situations, i.e. Ti substituting for Na (Ti@Na) and Ti substituting for Al (Ti@Al), and found that both lead to the same qualitative results. Note also that our present discussion is based on how the pure and Ti-containing surfaces differ regarding the energetics of various processes. Our conclusions are thus independent of the chosen energy reference, which is the same for both pure and Ti-containing surfaces.

3. Results and discussion

3.1. Stability of sodium alanate surfaces

Let us begin by discussing the ability of the Ti atoms to destabilize the NaAlH₄ surface and, thus, facilitate the NaAlH₄ decomposition reaction. We can roughly estimate the surface stability by computing the formation energies of surface defects, lower energies corresponding to a less stable surface. We have thus calculated the effect that the Ti catalyst has on the formation energies of the following types of surface vacancies: H, Na, and atom groups like NaH and AlH₄. (We denote the H vacancy by H^v, etc.) Table 1 summarizes our results.

We first note that all the vacancy-formation energies are positive; thus, as expected, we find that the surface, either pure or with Ti, is stable and thermal activation energy is required to decompose it. The second observation is that the pure surface is significantly more stable than the Ti-containing surfaces. For example, the formation energy of H vacancies is about 2.0 eV for the pure surface, while it is below 0.5 eV when the Ti catalyst is present. The same trend is observed in the formation energy of the other studied *defects*, which clearly indicates that the surface with Ti will decompose at temperatures significantly lower than those required in the case of a pure system. Our results generally agree with those obtained by Araújo *et al* for bulk NaAlH₄ [10].

The Ti catalyst is able to reduce the defect formation energies thanks to its chemical versatility. In the case of *charged* defects, the catalyst acquires extra charge (e.g. in the Ti@Na + (AlH₄)^v case) or enables effective passivation of dangling bonds. The latter is best illustrated by the Ti@Al + H^v case depicted in figure 1. The relaxed configuration presents

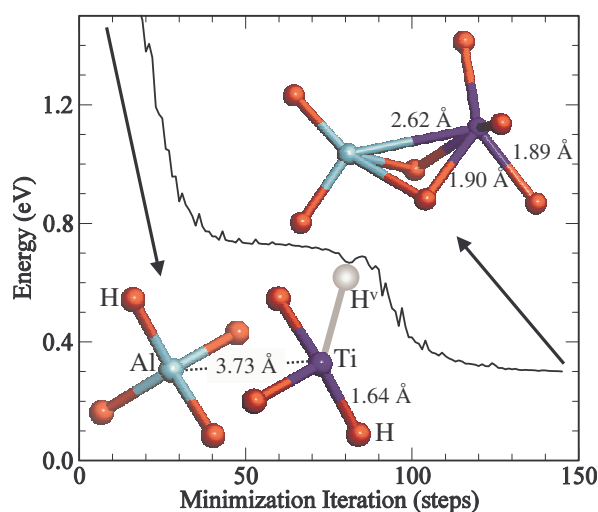


Figure 1. Energy versus structural relaxation step for the relaxation of a Ti@Al surface in which we create a hydrogen vacancy neighbouring the Ti atom (we denote this case by Ti@Al+H^v). The formation of an Al–Ti bond in the final configuration results in a reduced H^v formation energy. The insets show the initial and final configurations of the atoms mainly involved in the structural relaxation.

the Ti and a neighbouring Al atom within bonding distance (2.62 Å) and sharing two hydrogen atoms. This relaxation results in a significant energy reduction and thus facilitates the H^v formation. In the case of *neutral* defects (e.g. (NaH)^v) the Ti catalyst does not seem to play such a relevant role and, thus, the pure and Ti-containing surfaces present relatively similar vacancy-formation energies.

Note that we considered explicitly the case of Na-vacancy mediated H-vacancy formation, which has recently been claimed to be specially important on the basis of first-principles calculations for bulk NaAlH₄ [10]. Indeed, we found that Na-defective pure and Ti@Al surfaces gain energy by releasing a hydrogen atom (about 2.3 and 0.7 eV, respectively), while there is an energy cost of 0.5 eV in the Ti@Na case. On the other hand, the occurrence of the Na vacancy is much more likely when the Ti catalyst is present, for both Ti@Al and Ti@Na, which renders the net (NaH)^v formation energies in table 1. As already mentioned, since (NaH)^v is not a charged defect, there is not a very big difference between the results for pure and Ti-containing surfaces. Our calculations indicate that Ti favours the Na^v-mediated mechanism for H-vacancy formation slightly in the Ti@Na case and more significantly in the Ti@Al case.

3.2. Ti-induced H₂ dissociation and absorption: mechanisms for enhanced kinetics of the NaAlH₄ formation reaction

The reaction by which NaAlH₄ forms from the hexahydride Na₃AlH₆ occurs under hydrogen pressure and requires H₂ dissociation in order to proceed. It thus seems clear that the kinetics of such a reaction would be enhanced by the Ti atoms on the alanate surface if they were able to facilitate the dissociation of H₂ molecules, something that indeed happens in the case of carbon nanostructures coated with Ti [16]. In order to investigate this possibility, we considered the alanate surface (pure and with Ti) exposed to an H₂ molecule as well as to individual H atoms that we deposited one at a time. Table 2 summarizes our results.

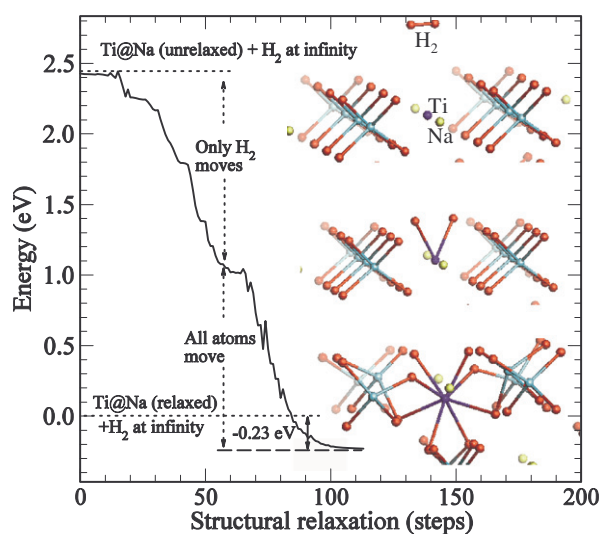


Figure 2. Energy versus structural relaxation step for the H_2 dissociation and absorption by the $Ti@Na$ surface. The starting point is the *unrelaxed* $Ti@Na$ surface with an H_2 molecule close to it, which is taken as the zero of energy. In the first part of the relaxation, only the H_2 molecule is allowed to move; then, all the atomic positions are relaxed. Given for reference is the result for the relaxed $Ti@Na$ plus an H_2 located at infinity. The insets show the various steps of the absorption process.

Table 2. Reaction energies (in eV) of hydrogen(s) deposited on pure and Ti-containing $NaAlH_4$ surfaces. We considered the case of molecular H_2 as well as various nH cases, where the H atoms are deposited on the surface one at a time. Two structural models are considered, in which Ti substitutes for Na ($Ti@Na$) and Al ($Ti@Al$), respectively. We use as reference the energy of the surfaces with no extra hydrogen, and the energy of the H_2 molecule.

Surface type	+ H_2	+H	+2H	+3H	+4H
Pure	-0.07	1.81			
$Ti@Na$	-0.23	-0.49	-0.23	-0.67	-0.38
$Ti@Al$	-0.41	-0.61	-0.41	-0.60	

We found that the surface is able to bind an H_2 molecule in all the cases considered. The molecule dissociates in the $Ti@Al$ case, forming an AlH_6 group, which renders a significant energy gain of 0.41 eV. The molecule also dissociates in the $Ti@Na$ case, and binds with an energy of 0.23 eV. It is interesting to think of the H_2 dissociation and binding in the $Ti@Na$ case as the two-step process depicted in figure 2. In the first step we let the H_2 molecule fall on the *unrelaxed and frozen* $Ti@Na$ surface; the molecule breaks and the H atoms bind to the Ti, with an energy gain of about 1.4 eV, which is very close to what is obtained for H_2 breaking and adsorption on carbon nanostructures coated with Ti [16]. In the second step the whole surface relaxes, rendering the above-mentioned 0.23 eV binding energy, and the Ti catalyst adopts a final configuration with eight neighbouring H atoms (see bottom inset of figure 2). In conclusion, our results for both $Ti@Al$ and $Ti@Na$ clearly show that the Ti facilitates H_2 dissociation and absorption. Interestingly, in the case of the pure surface, the H_2 molecule does not dissociate and the binding energy is significantly smaller (0.07 eV).

Next we studied the deposition of individual H atoms one at a time. We found that the pure surface is unable to absorb an individual H atom (note the positive absorption energy of 1.8 eV

in table 2). In fact, the deposited H destabilizes an AlH_4 group and forms an H_2 molecule. In contrast, the surfaces with Ti are able to absorb the first H atom with significant energy gain (about 0.5 eV); the H atom locates in the vicinity of the Ti, at about 1.9 Å, forming a TiH_5 group in the case of Ti@Al . Moreover, further hydrogens can be absorbed by the surfaces with Ti. For Ti@Na , the +3H situation seems to be particularly stable; for +4H an H_2 molecule forms and stays bound to the surface, but not properly absorbed by it. For Ti@Al , we found that a H_2 molecule forms already in the +3H case. Thus, our results indicate that a Ti atom can take a maximum of three or four extra hydrogens.

We have thus found a marked difference between the behaviours of pure and Ti-containing surfaces in the presence of extra hydrogens. The Ti catalyst is found to favour H_2 dissociation, as needed for the Na_3AlH_6 -to- NaAlH_4 reaction to proceed, and to render a stable surface in the presence of hydrogen. In contrast, we find that the pure NaAlH_4 surface is unstable in the presence of atomic hydrogen, a situation that is likely to occur in the NaAlH_4 formation reaction. This marked difference between the cases with and without Ti clearly suggests a mechanism by which the catalyst may increase the kinetics of the NaAlH_4 formation reaction.

It seems reasonable to assume that the NaAlH_4 -formation kinetics will be further enhanced if the absorbed hydrogens are *mobile* on the system's surface. To check this, we performed computer experiments as follows. We started from the relaxed $\text{Ti@Na} + 2\text{H}$ system, created a H vacancy and thus a defective AlH_3 group, relaxed the system (H migration should occur to recover an AlH_4 group), and compared the obtained structure and energy with the *assumed* lowest-energy solution $\text{Ti@Na} + \text{H}$. We observed two general trends. (1) Large structural distortions and atom migrations occur. Most relaxed structures differ significantly from the lowest-energy solution and are slightly higher in energy (by about 0.1 eV, typically). (2) Hydrogen migration occurs more easily in H-rich surfaces, i.e. in the +3H and +4H cases of table 2. The difficulties to reach the reference, lowest-energy structure reflect the fact that we are dealing with a complicated multi-minima energy landscape. On the other hand, the significant atomic mobility observed suggests that, at room temperature, the H atoms initially bound to the Ti catalyst will indeed migrate and take part in the NaAlH_4 -formation reaction, thus increasing its rate.

3.3. Using other light transition metals as catalysts

Finally, we studied the possibility of using, instead of Ti, other light transition metals as catalysts. More precisely, we tested the performance of Sc, V, and Cr by calculating the energies of absorption and desorption of a single H atom, as well as the possible dissociation of an H_2 molecule, by a Na-substituted surface.

As in the case of Ti [7], the inclusion of Sc, V, or Cr substituting for a superficial Na has an impact on the surrounding AlH_4 groups. In essence, the transition metal drags hydrogens to its vicinity, thus stretching (and weakening) the corresponding Al–H bonds. The smallest effects are associated with Sc and the largest with Cr; Ti and V being intermediate cases. Our results thus clearly indicate that the magnitude of the catalyst-induced structural change strongly correlates with the number of 3d electrons available for sharing with the neighbouring hydrogens. In the Cr case, where the effects are most pronounced, the catalyst attracts four hydrogens with a binding distance of about 1.82 Å, the corresponding Al–H distances being about 1.73 Å (note that the calculated Al–H distance in pure alanate is 1.64 Å). The corresponding Cr–Al distances are also relatively short, of about 2.83 Å; this result too is reminiscent of the case of Ti, where we had previously found Ti–Al bonds of about 2.8 Å [7], a distance that is typical in TiAl_3 alloys [17].

Regarding the formation of hydrogen vacancies, the lowest energy is obtained for Cr with 0.30 eV; V gives 0.75 eV and Sc renders the most stable surface, with a formation energy of 1.13 eV. As in the case of Ti, in all cases the vacancy-formation energy is reduced with respect to the pure-surface case (see table 2) because the transition metal saturates Al dangling bonds. In the case of Cr, which displays the largest relaxation, the Cr–Al distance is calculated to be 2.49 Å (note that the result for Ti, given above, is 2.62 Å).

As for the uptake of an extra hydrogen, only Sc favours it, with a negative absorption energy of -0.27 eV; for V and Cr we get 0.26 and 0.20 eV, respectively. The relaxed structures are qualitatively similar to that obtained for Ti; the extra hydrogen places itself in the proximity of the transition metal atom, at a distance that is about 1.8 Å in all the cases considered. We also found that Sc causes the H₂ molecule to dissociate in the same way as Ti does, while V and Cr do not. Hence, our calculations indicate that Sc and Ti are more reactive with extra hydrogens than V and Cr are; the reason seems to be that V and Cr are highly coordinated, with both hydrogens and aluminiums, thus forming stable complexes to which additional H atoms cannot easily bind.

In conclusion, by comparing the energetics obtained for Sc, V, and Cr with the results of tables 2 and 1, one can expect all the considered transition metals will give an improvement over the pure surface. Further, our results show that Ti performs better overall, Sc being the most appealing alternative. The relaxational effects associated with the different metals considered do not differ significantly, and certainly do not suggest any conclusion in conflict with what the energetics indicate. Thus, our results clearly suggest that Ti is the catalyst of choice among light transition metal atoms, followed by Sc.

4. Summary

We have performed a first-principles study of various processes involving hydrogen and occurring on sodium alanate (NaAlH₄) surfaces. Both pure and Ti-containing surfaces have been studied, so as to make a systematic comparison between them. Our calculations show that, for surfaces exposed to hydrogen, the Ti catalyst will (i) cause the dissociation of H₂ molecules and (ii) bind several H atoms. In contrast, we find the pure surface to be unstable in the presence of atomic hydrogen. Our results thus suggest that the Ti catalysts will facilitate the reaction by which NaAlH₄ forms from the hexahydride phase Na₃AlH₆, since this process occurs under hydrogen pressure and requires H₂ dissociation to proceed. In addition, we found that the surfaces with Ti are less stable than the pure surfaces and, thus, the Ti catalysts should also improve the kinetics of the NaAlH₄ decomposition reaction.

Our calculations show that the catalysts favour both the binding of extra hydrogens, thus rendering a more stable surface under hydrogen pressure, and the formation of vacancies and decomposition of the system. The explanation of this seemingly paradoxical conclusion relies on the chemical versatility of Ti, which brings close in energy the system states involved in these hydrogen uptake and vacancy formation reactions. Such a reduction in energy differences will be accompanied by a concomitant decrease in the energy barriers that must be overcome for the reactions to occur, which should in turn result in faster kinetics.

We have also studied the possibility of using other light transition metals (Sc, V, and Cr) as catalysts, and found that Ti is the best choice overall.

Acknowledgments

We acknowledge financial support from the Spanish Ministry of Science and Education through the ‘Ramón y Cajal’ programme (JI) and project FIS2006-12117-C04-01, the Catalan Regional

Government through project 2005SGR683, FAME-NoE, and the US DoE under BES grant DE-FG02-98ER45701. Use was made of the facilities provided by the CESGA Supercomputing Center.

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