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Ti-induced destabilization of NaBH₄ from first-principles theory

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Online at stacks.iop.org/JPhysCM/20/122202**Abstract**

In this work, we have employed first-principles total energy calculations and *ab initio* molecular dynamics simulations to investigate the Ti doping of NaBH₄. We show that Ti destabilizes the BH₄ cages, which in turn increases the mobility of hydrogen atoms. Such an effect is shown to be due to the formation of B–Ti bonds, rather than the lowering of the BH₄ charge state as expected. These results indicate that Ti may catalyse the dehydrogenation process in NaBH₄ as it does for NaAlH₄.

The implementation of hydrogen fuel cell technologies in vehicles and mobile devices is driving on the investigations on new means of producing and storing hydrogen fuel [1–3]. With this purpose, a great deal of research has been conducted to study the alkali complex hydrides (MXH₄ with M = Na, Li and X = Al, B) primarily due to their high gravimetric hydrogen density (even 18.5% in LiBH₄) and low cost [1, 3]. In particular, NaBH₄ slurry has been indicated as the most promising system for applications in fuel cell technology [4–7]. This solution not only constitutes a superefficient storage system in which the hydrogen gravimetric density is 10.9 wt%, but also provides one of the simplest ways of generating hydrogen through the following heat-releasing reaction:



This reaction is activated by adding a proper catalyst and can be operated at ambient conditions. Furthermore, the by-product NaBO₂ can be recycled into NaBH₄ through a fuel recovery reaction which makes the hydrolysis above a renewable process [5]. Additionally, the single-phase compound NaBH₄ is itself also a promising hydrogen storage material since it has one of the highest gravimetric hydrogen densities (10.7 wt%) among the alkali metal hydrides [1]. However, its irreversibility with respect to the hydrogen absorption/desorption cycle, which is thermally activated, and the high dissociation temperature limit its practical application

for hydrogen storage. Therefore, it is worthwhile to conduct studies aimed at finding ways to overcome such limitations, making NaBH₄ a suitable material for on-board applications. An approach that shows promise toward the achievement of this goal is the addition of impurities that are able to weaken the B–H bond and raise the hydrogen mobility.

One decade ago, it was discovered that an addition of Ti-based catalyst in NaAlH₄ can not only significantly improve the kinetics of the hydrogen release but also make the process reversible [8]. Following this work, a great deal of effort has been made by many researchers to understand how Ti accomplishes such a task [9–26]. In this respect, we have recently performed a systematic investigation of 3d transition metal doped crystalline NaAlH₄ by means of first-principles calculations [24]. Our main conclusion from this study is that the transition metals tend to form chemical bonds with Al, which appears to be an important contribution in the weakening of the Al–H bond, and in the raising of hydrogen mobility. In fact, the formation of Ti–Al intermetallic phases on the surface of NaAlH₄ is shown to play an important role in the catalytic effect of Ti [10–13]. In the wake of these results two questions arise. Would Ti be energetically stable in NaBH₄? If so, would it work as a catalyst for the hydrogen release process?

In this work, we investigate the effect of Ti doping on the strength of chemical bonds holding hydrogen atoms in NaBH₄. Using *ab initio* theory, we show that Ti diminishes the H removal energy. Furthermore, *ab initio* molecular dynamics

at 400 K revealed that Ti–B bond formation might play an important role in the catalytic process. In the following, we provide the details of our theoretical methods and a discussion of our results.

The calculations are carried out within the framework of generalized gradient approximation [27] to density functional theory [28] using the PAW method [29], as implemented in the VASP code [30]. We have used 48-atom supercells, which are built up from the fcc phase [31], to model the substitution of Ti in NaBH₄. Three supercells are considered for the calculation of the total energy and *ab initio* molecular dynamics [30] at 400 K. The compositions of the supercells are: Na₈B₈H₃₂, (TiNa₇)B₈H₃₂ and Na₈(TiB₇)H₃₂. The first supercell models the pristine sodium borohydride while the second and third supercells model Ti substituted at the Na and B sites, respectively, as it is not known *a priori* which site Ti would occupy. The PAW potentials with the valence states 3p, 3d and 4s for Ti, 2p and 3s for Na, 2s and 2p for B and 1s for H were used. The convergence with respect to cut-off energy and number of *k*-points was carefully checked for all results reported here. The optimization of the geometry has been done without imposing any symmetry constraints. The *ab initio* molecular dynamics simulations were performed by employing a time step of 1 fs throughout. We have run this simulation for 10 000 steps (10 ps) where the control over the temperature was achieved by rescaling velocities every second time step. We have observed that after about 2 ps both systems (Ti at Na and at B sites) reach a dynamical equilibrium. This is obtained by averaging the radial distribution function over different time intervals throughout the simulation.

At low temperature the NaBH₄ crystallizes in the tetragonal structure corresponding to the space group *P*4̄₂*c* [32, 33]. However, the compound undergoes a temperature-induced phase transformation to fcc structure at around 190 K [33]. Since practical applications of NaBH₄ in fuel cell technology have been performed above the room temperature, we have chosen to build up the supercells from the fcc structure. In figure 1, we show the supercell geometry where Na and B atoms that were substituted by Ti and the hydrogen atom that was removed are identified. In the pristine sodium borohydride the nearest Na–B and B–H bond lengths are 3.06 Å and 1.22 Å respectively. These compare very well with the experimental values of 3.07 and 1.169 Å for the cubic phase [31]. The bond length between B and H atoms is also close to the theoretical value of 1.21 Å for LiBH₄ [34]. This system displays an electronic and crystalline structure similar to that of NaBH₄.

In order to determine whether Ti is energetically stable in NaBH₄ as well as its preferential site, we compare the cohesive energies of Na₈B₈H₃₂, (TiNa₇)B₈H₃₂ and Na₈(TiB₇)H₃₂. Such energy is defined as the total energy of the system minus the sum of individual energies of atoms. By setting the cohesive energy of pure sodium borohydride to zero, we have found the values of –1.83 and 4.39 eV when Ti occupies the Na and B sites, respectively. The negative signs mean that Ti doped NaBH₄ is more stable than the pure one. Therefore, one can see that only the Na substituted configuration is energetically favourable. The higher energy

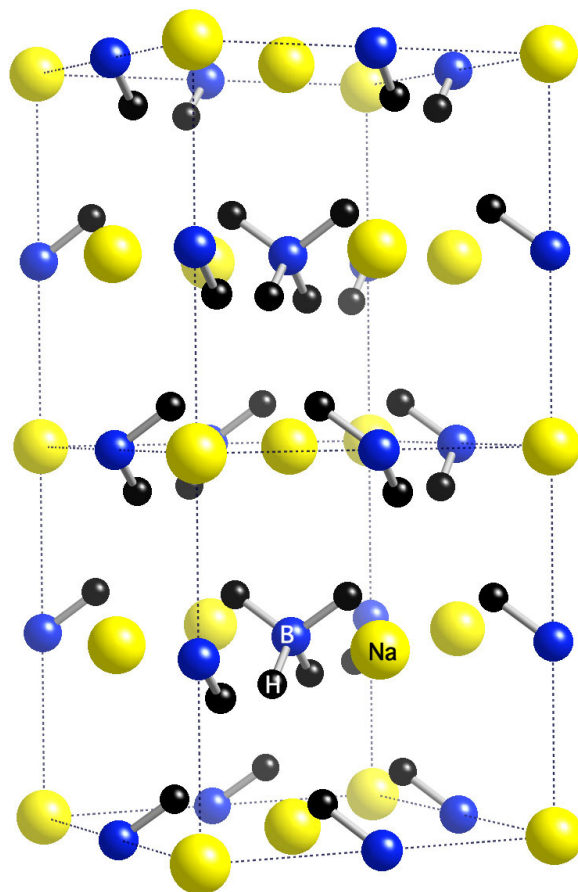


Figure 1. The supercell geometry used to model the Ti substitutional doping in NaBH₄. The yellow (big), blue (medium) and black (small) balls represent the sodium, boron and hydrogen atoms, respectively. The sodium and boron sites that Ti occupies and the hydrogen that was removed are marked by Na, B and H, respectively. (This figure is in colour only in the electronic version)

of the B substitution configuration may be due to the cost of energy in the crystal expansion required to adjust the Ti at the B site. It should be pointed out that such stability analysis is made by using as the atomic chemical potential the total energies of isolated atoms in the gas phase. Different conclusions may be reached if other atomic chemical potentials are considered.

To estimate the change in the strength of the B–H bond induced by the presence of Ti, we have evaluated the energy needed to remove a hydrogen atom from Na₈B₈H₃₂ and (TiNa₇)B₈H₃₂ supercells. Therefore, we have computed the total energies of Na₈B₈H₃₁ and (TiNa₇)B₈H₃₁ supercells in which one of the hydrogen atoms bound to Ti and its equivalent atom bound to Na were respectively removed. The supercells again were fully optimized as discussed previously. Since hydrogen atoms are released associatively forming H₂ molecules, half of total energy of the latter is also removed so that the hydrogen removal energy is defined as

$$\Delta E_0 = E_T(\text{Na}_8\text{B}_8\text{H}_{31}) + (1/2)E_T(\text{H}_2) - E_T(\text{Na}_8\text{B}_8\text{H}_{32}) \quad (2)$$

and

$$\Delta E_{\text{Ti}} = E_T(\text{TiNa}_7\text{B}_8\text{H}_{31}) + (1/2)E_T(\text{H}_2) - E_T(\text{TiNa}_7\text{B}_8\text{H}_{32}). \quad (3)$$

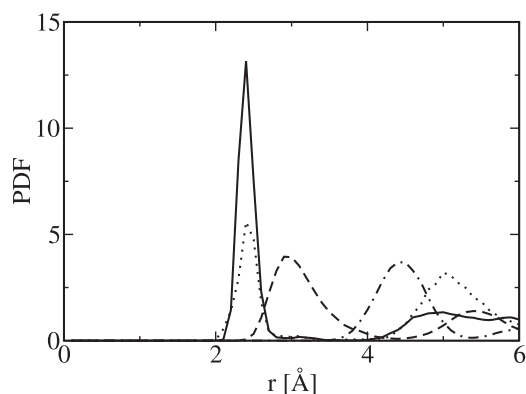


Figure 2. Pair distribution function of 400 K *ab initio* MD simulations. Solid and dotted lines represent Ti–B pairs when Ti substitutes for Na (in $\text{TiNa}_7\text{B}_8\text{H}_{32}$ supercell) and B (in $\text{Na}_8\text{TiB}_7\text{H}_4$ supercell), respectively. Dashed and dotted–dashed lines represent the Na–B and B–B pairs in the pure NaBH_4 , respectively.

The energies needed to remove a H atom from $\text{Na}_8\text{B}_8\text{H}_{32}$ and $(\text{TiNa}_7)\text{B}_8\text{H}_{32}$ supercells are found to be $\Delta E_0 = 2.24$ eV and $\Delta E_{\text{Ti}} = 1.37$ eV, respectively. This confirms that Ti doping does weaken the B–H bond. Now, we need to understand how Ti accomplishes such a task. Since the ionization potential of Ti (6.83 eV) is higher than that of Na (5.13 eV), we first thought that the charge state of the BH_4 unit was lower in the doped system resulting in the weakening of the B–H bond. In fact, it was recently shown that BH_4 cages with lower charge states display weaker B–H bonds [35], as was also shown to be the case for AlH_4 [21, 22, 35]. However, from the Bader analysis, we have found that the BH_4 unit nearest neighbours of Ti still display a charge state of $-1e$, contradicting our first hypothesis.

As a second step, we decided to evaluate the distance between Ti and the nearest B atom before and after the hydrogen removal. For the former case, there was found the value of 2.8 Å, which is quite close to the Na–B distance in the intrinsic system ($\text{Na}_8\text{B}_8\text{H}_{32}$) showing that there is not much relaxation following the Ti substitution. However, as hydrogen is removed the Ti–B distance reduces to 2.3 Å. The formation of chemical bonds between transition metals and Al was shown by us in the previous work [24] to play an important role in determining the hydrogen removal energy in NaAlH_4 . Such a conclusion was possible due to the systematic investigation that we have performed where the hydrogen removal energy was calculated for all 3d elements. Therefore, we believe that such a trend holds for NaBH_4 since the B–Ti distance decrease from 2.9 to 2.3 Å is rather significant. However, to further confirm the formation of B–Ti bond as being the main contribution in the destabilization of NaBH_4 we need to go beyond 0 K calculations. We have done that by employing *ab initio* molecular dynamics simulations at 400 K for $\text{Na}_8\text{B}_8\text{H}_{32}$, $\text{TiNa}_7\text{B}_8\text{H}_{31}$ and $\text{Na}_8\text{TiB}_8\text{H}_{32}$ supercells.

To analyse the bond formations we have evaluated the pair distribution functions (PDF). In figure 2, we display the PDF curves for Ti–B (in $\text{TiNa}_7\text{B}_8\text{H}_{31}$ and $\text{Na}_8\text{TiB}_8\text{H}_{32}$), Na–B and B–B (in $\text{Na}_8\text{B}_8\text{H}_{32}$) pairs averaged over about 8 ps. The first Ti–B PDF peak is located at around 2.3 Å regardless of

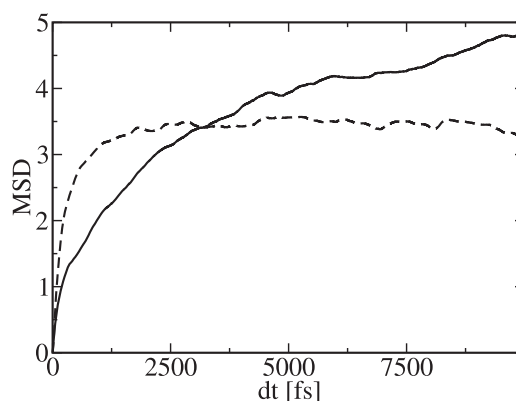


Figure 3. Mean square displacements of hydrogen atoms in $\text{Na}_8\text{TiB}_7\text{H}_{32}$ (solid line) and $\text{Na}_8\text{B}_8\text{H}_{32}$ (dashed line) supercells.

which site Ti occupies. It should be highlighted that when Ti occupies the B site (in $\text{Na}_8\text{TiB}_8\text{H}_{32}$ supercell) the Ti–B distance changed from the initial value of 4.4 Å (the position around which the B–B peak is situated) to the value of 2.3 Å. These results strongly confirm the tendency of Ti and B to form bonds. Therefore, the introduction of Ti in NaBH_4 may lead to formation of Ti–B intermetallic phases, which may work as a catalyst. Actually, the latter is corroborated by the fact that in the doped system the hydrogen atoms travel more freely between Ti and B which could facilitate their migration. Such higher mobility of hydrogen atoms was evaluated from their mean square displacement curves, which are shown in figure 3. The curve for the hydrogen atoms in $\text{Na}_8\text{TiB}_7\text{H}_{32}$ is significantly more tilted than that for hydrogen atoms in $\text{Na}_8\text{B}_8\text{H}_{32}$ meaning that the hydrogen atoms are more mobile in the doped systems.

In summary, we have employed first-principles calculations to investigate the effect of Ti on the lattice of NaBH_4 . It was found that the substitution of Ti at the Na site is the most stable configuration when the total energies of isolated atoms are taken as the reference energy. The calculation of the hydrogen removal energies revealed that as Ti replaces at the Na site, the B–H bond becomes weaker. Such an effect is not due to the lower charge state on BH_4 cages induced by the presence of Ti but, instead, is mainly driven by the formation of Ti–B bonds following the hydrogen removal. To further understand this effect, we have employed *ab initio* molecular dynamics simulations at 400 K. It was found that regardless of whether Ti occupies the Na or B sites it always forms chemical bonds with the nearest B atoms for which we have calculated a length of 2.3 Å. Furthermore, we have observed that the mobility of hydrogen near to Ti is higher than the corresponding one for the intrinsic systems. Such new dynamics may help with hydrogen migration. Thus, we have found that Ti may also act as a catalyst in the dehydrogenation of NaBH_4 as it does for NaAlH_4 . It should be pointed out that NaBH_4 displays much higher hydrogen storage capacity which make the investigations of its hydrogen sorption properties worthwhile. We hope that our present findings will motivate further experimental works.

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