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Dehydrogenation from 3d-transition-metal-doped NaAlH₄: Prediction of catalysts

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A fundamental understanding of the role of catalysts in improving the kinetics and thermodynamics of hydrogen sorption in NaAlH₄ is the key for using this material in hydrogen storage. The authors present a systematic theoretical study of energies needed to desorb hydrogen in 3d transition metal (Sc–Cu)-doped NaAlH₄. They show that Cr and Fe atoms can be far more effective catalysts than Ti in desorbing hydrogen. The role of the 3d metal atoms in improving the thermodynamics of dehydrogenation is attributed to a significant shortening of the bond length with neighboring Al atoms. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719244]

The development of hydrogen storage materials capable of operating at near ambient conditions with fast kinetics is essential for hydrogen economy.^{1–3} Complex light metal hydrides such as NaAlH₄, which have high gravimetric and volumetric densities, show promise following the pioneering work of Bogdanovic and Schwickardi.⁴ These authors have demonstrated that the addition of a small amount of TiCl₃ during ball milling can significantly improve both the thermodynamics and kinetics of hydrogen sorption. Since this initial work, a great deal of effort has been made by many researchers in order to understand the role of metal dopants on the hydrogenation/dehydrogenation process.^{5–18}

In spite of considerable experimental work,^{5–11} a complete understanding of the role of the catalysts is still lacking. A fundamental understanding of how the metal dopants influence the nature of hydrogen bonding and hence its rate of desorption has to come from a detailed study of the electronic structure of NaAlH₄ before and following doping. Recently, a number of theoretical attempts have been made toward this goal.^{12–18} These can be classified into three categories: (1) Some authors have studied the electronic band structure of pure aluminates to understand the nature of Na–H and Al–H bonds,¹² (2) others have replaced the Na and Al sites with Ti to determine its preferred site and the manner in which it affects the bonding between metal atoms and hydrogen,^{13–15,18} and (3) our group has gone a step further in calculating not only the energy needed to desorb hydrogen atoms from the vicinity of Ti and subsequent changes it causes on the electronic structure, but also the role of metal vacancies that could form during ball milling.^{16,17} No calculations where the role of different metal atoms on hydrogen desorption have been studied systematically are available.

In this letter, we provide a systematic study of the role of 3d metal atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) on hydrogen desorption by substituting both the Na and Al sites

in NaAlH₄. The objectives of our study are to determine the energy cost to remove a hydrogen atom from the vicinity of the dopant and the changes in the local atomic environment around the dopant before and after hydrogen is removed. The ability of a transition metal dopant to promote dehydrogenation is found to be correlated to its tendency to form bonds with Al atoms supporting the most widely accepted explanation of the role of Ti on the hydrogen sorption.^{8,10,11,13} In particular, we show that Cr and Fe atoms can be even more effective catalysts than Ti for hydrogen desorption.

The calculations are carried out using the supercell electronic structure approach and the spin density functional theory¹⁹ with generalized gradient approximation.²⁰ The supercell consists of a 2 × 2 × 1 structure and contains 96 atoms (Na₁₆Al₁₆H₆₄). To model 3d transition metal (TM) substitution at the Na and Al sites, we have used the (Na₁₅TM)Al₁₆H₆₄ and Na₁₆(Al₁₅TM)H₆₄ supercells, respectively. The removal of hydrogen is modeled by the Na₁₆Al₁₆H₆₃, Na₁₆(Al₁₅TM)H₆₃, and (Na₁₅TM)Al₁₆H₆₃ supercells. We have used the projector augmented plane wave method,²¹ as implemented in the Vienna *ab initio* simulation package²² (VASP) following the same methodology as presented earlier.¹⁶

The substitution of 3d metal atoms has an important effect on the local atomic structure and leads to lattice relaxation around the substitutional sites. In the perfect sodium aluminide crystal the distances between nearest Na–Al, Na–H, and Al–H atoms are 3.50, 2.37, and 1.64 Å, respectively. As the TM replaces a Na atom, we find a similar effect for all the 3d elements. They all have a hydrogen coordination number of 8 with the TM–H bond lengths being shorter than the corresponding Na–H bond length in the pure system, namely, 2.06, 2.02, 1.99, 1.93, 1.82, 1.68, 1.70, 1.76, and 1.91 Å for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, respectively. More importantly, these distances decrease as we proceed from Sc to Fe. Similarly, the distances between the TM and Al atoms [see Fig. 1(b)] also decrease, followed by a

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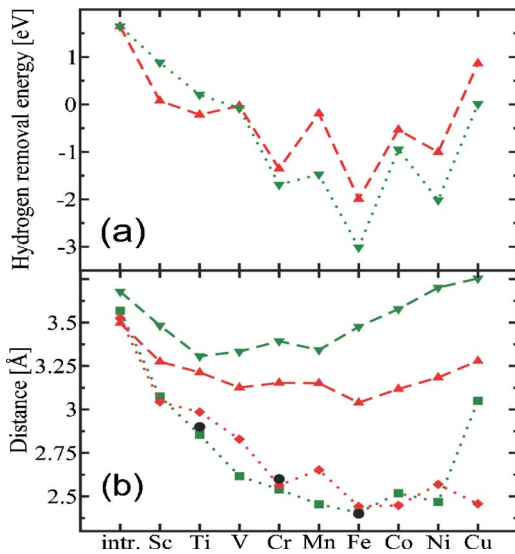


FIG. 1. (Color online) (a) Hydrogen removal energy when TM is at Al site (\blacktriangledown) and TM is at Na site (\blacktriangle); (b) TM–Al distance before removal of hydrogen when TM is at Al site (\blacktriangledown) and when TM is at Na site (\blacktriangle); TM–Al distance after removal of hydrogen when TM is at Al site (\blacktriangle) and when TM is at Na site (\blacktriangledown); First pair distribution function TM–Al peak from molecular dynamics (MD) simulations (\bullet).

stretching of the Al–H bond (1.69, 1.70, 1.76, 1.71, 1.72, 1.71, 1.72, 1.72, and 1.70 Å for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu). When an Al site is replaced by a transition metal atom, all the 3d elements have a hydrogen coordination number of 4. The Na–H bond lengths are 2.17, 2.17, 2.22, 2.24, 2.36, 2.32, 2.26, 2.34, and 2.47 Å for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, respectively. The corresponding TM–H bond lengths decrease in the order from Sc to Cu, namely, 1.90, 1.81, 1.72, 1.67, 1.59, 1.56, 1.54, 1.52, and 1.51 Å. Note that compared to the pure alanate, these bond lengths are longer for Sc, Ti, V, and Cr, whereas they are shorter for Mn, Fe, Co, Ni, and Cu. Nevertheless, as we shall show below, the hydrogen binding energy in all transition-metal-doped systems is lower than that in the pure system. This is due to the electronic structure modification (not shown here) and, most importantly, due to the TM–Al bond formation.

We now calculate the energy needed to remove a hydrogen atom from the intrinsic system and compare it with that containing a transition metal atom (ΔE_H^{TM}). Such energies are defined as

$$\Delta E_H^{\text{TM}} = E(\text{TM}_{x+y}\text{Na}_{16-x}\text{Al}_{16-y}\text{H}_{63}) - E(\text{TM}_{x+y}\text{Na}_{16-x}\text{Al}_{16-y}\text{H}_{64}) + \frac{1}{2}E(\text{H}_2). \quad (1)$$

The hydrogen removal energy in the pure NaAlH_4 ($x=y=0$) is 1.7 eV when one considers molecular hydrogen as reference. This large value is a consequence of the strong bonds that are holding the H atoms. The energies needed to remove a hydrogen atom from the vicinity of a transition metal atom substituted at the Na and Al sites are found to be smaller than those in the intrinsic NaAlH_4 for all the 3d elements [Fig. 1(a)]. This could be due to the change in the electronic structure caused by TM substitution, as was seen from both the electron localization functions and the electronic density of states (not shown here). For further clarification the reader is referred to Ref. 16. The transition metal atom weakens the strength of the covalent bond between Al

and H, thus reducing the energy necessary to remove a hydrogen atom. This is also consistent with the structural changes where the Al–H bond lengths in $\text{TMNa}_{15}\text{Al}_{16}\text{H}_{64}$ supercell have increased. However, a close examination of the values of the Al–H bond lengths discussed above and the hydrogen removal energies in Fig. 1(a) reveals that they do not always follow exactly the same trend; i.e., longer bond length does not necessarily mean lower hydrogen binding energy.

In order to understand this counterintuitive result, one also needs to compare the TM–Al distances before and after a hydrogen atom is removed. These distances are plotted in Fig. 1(b). The top two lines correspond to the TM–Al bond distances when a transition metal atom replaces Na and Al sites in $\text{TMNa}_{16-x}\text{Al}_{16-y}\text{H}_{64}$ supercell, whereas the bottom two lines correspond to the same distances after a hydrogen atom is removed ($\text{TMNa}_{16-x}\text{Al}_{16-y}\text{H}_{63}$ supercell). We note that while both sets of lines in Fig. 1(b) follow the same trend [except for Ni and Cu in the $\text{Na}_{16}(\text{TMA}_{15})\text{H}_{64}$ supercell], namely, a shortening of the TM–Al bonds, there is a considerable quantitative difference between these two sets of values. For example, while the Fe–Al bond distance in the $\text{TMNa}_{16-x}\text{Al}_{16-y}\text{H}_{64}$ supercell is 3.0 Å/3.4 Å ($x=1, y=0/x=0, y=1$), it is considerably less, namely, 2.4 Å/2.4 Å, in the $\text{TMNa}_{16-x}\text{Al}_{16-y}\text{H}_{63}$ supercell. Through molecular dynamics simulations, we will demonstrate later in this letter that this quantitative difference is due to energy barriers in the $\text{TMNa}_{16-x}\text{Al}_{16-y}\text{H}_{64}$ supercell that could not be overcome at 0 K. The shortening of the TM–Al bonds and hence the tendency to form a TM–Al intermetallic phase play an important role in lowering the hydrogen binding energy and, therefore, in improving the kinetics of the dehydrogenation process. Thus, our systematic investigation comes to corroborate with the most accepted proposal in explaining the role of Ti and other transition metal atoms on the hydrogen sorption.^{8,10,11,13}

In order to demonstrate the role of temperature in overcoming energy barriers and hence in structural relaxation, we have performed *ab initio* molecular dynamics simulations on the $\text{TMNa}_{16-x}\text{Al}_{16-y}\text{H}_{64}$ supercells, where the systems were heated up for 3 ps at 400 K. This value was chosen around the experimental desorption temperature. In this simulation the velocities of the atoms were rescaled every time step in order to keep control over the temperature. Such calculations are necessary since the potential energy barrier may prevent structure relaxations around the impurity when the optimization is performed at 0 K. Note that the experiments are *not* performed at 0 K either. We have chosen to work only with Ti, Cr, and Fe mainly due to the following reasons. Ti-doped NaAlH_4 is a widely studied system acting as a good reference for our results. Cr and Fe have given rise to the lowest hydrogen binding energy and therefore might be good candidates as catalysts. In this investigation, we have mainly determined the average bond length between TM and Al atoms by calculating the pair distribution function between TM and Al.

When the Na atom is substituted by Ti, we find that it is surrounded by eight-H atoms, whereas Cr and Fe atoms are surrounded by seven and six hydrogen atoms, respectively. In these systems the hydrogen atoms travel more freely between TM and Al atoms than the corresponding ones in the pure alanate. Such dynamics can facilitate the migration of hydrogen atoms. Iniguez and Yildirim¹³ have already re-

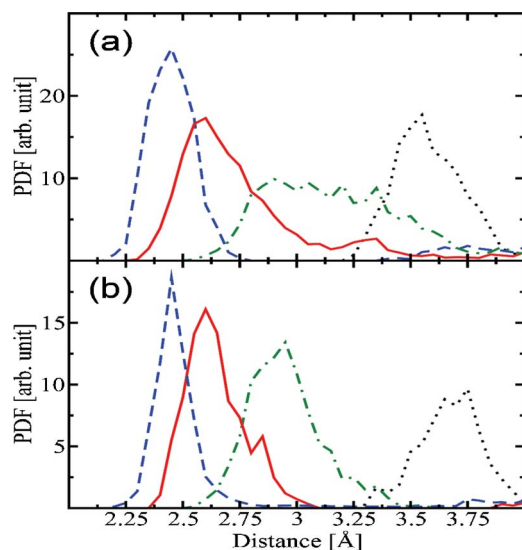


FIG. 2. (Color online) Pair distribution function of 400 K *ab initio* MD simulations. (a) Fe–Al (blue dashed), Cr–Al (red solid), and Ti–Al (green dashed dotted) when TM is at Na site and Na–Al (black dotted) in pure NaAlH₄. (b) Fe–Al (blue dashed), Cr–Al (red solid), and Ti–Al (green dashed dotted) when TM is at Al site and Al–Al (black dotted) in pure NaAlH₄.

ported similar results for the Ti-doped system. Most importantly, we have also observed the formation of TM–Al bonds. When transition metal atoms are substituted at the Na site, the first TM–Al peak in the pair distribution function for Fe, Cr, and Ti are centered at around 2.4, 2.6, and 2.9 Å involving four, six, and eight Al atoms, respectively [see Fig. 2(a)]. Similar results are also obtained when the Al atom is substituted. Here, the Fe–Al, Cr–Al, and Ti–Al peaks are located at around 2.4, 2.6, and 2.9 Å involving now two, three, and four Al atoms, respectively [see Fig. 2(b)]. Note that the distances are the same irrespective of whether TM occupies the Na or the Al site. One can see, therefore, that the tendency of TM–Al bond formation is quite strong with the bond strengths increasing from Ti to Fe. Given that the typical bond length of FeAl, CrAl, and TiAl dimers are 2.2, 2.4, and 2.6 Å, our systematic investigation corroborates the previous indications of a Ti–Al intermetallic phase formation. Furthermore, since the Al–H bond strength diminishes with increasing TM–Al binding, the lattice relaxation leading to the formation of an intermetallic phase would play an important role in the catalytic process. We should emphasize that the relaxed Ti–Al, Fe–Al, and Cr–Al bond lengths calculated from molecular dynamics simulation at 400 K in the TMNa_{16-x}Al_{16-y}H₆₄ supercell [see values marked by solid black circles in Fig. 1(b)] are identical to those obtained from the TMNa_{16-x}Al_{16-y}H₆₃ supercell at 0 K. This demonstrates an important point regarding geometry optimization in VASP

at 0 K—that potential energy barriers may prevent reaching the global minimum. The results in Fig. 1(a) clearly suggest that Cr and Fe should be far more effective in improving hydrogen desorption than Ti.

In summary, we have carried out a systematic study of the effect of the 3*d* metal substitution on the dehydrogenation energetics of NaAlH₄ by using the supercell electronic structure and gradient corrected density functional theory. Our conclusions can be summarized as follows: (1) Cr and Fe are shown to be more effective than Ti in desorbing hydrogen. (2) The relaxation of the lattice following doping has an important role on the desorption mechanism. Considerable shortening of the transition metal–Al bond reflects the tendency for forming an intermetallic phase, which is a key ingredient in promoting hydrogen desorption. (3) Molecular dynamics simulations at 400 K showed that the formation of intermetallic bonds between transition metal atoms and Al is possible as energy barriers can be overcome at finite temperature.

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