Adsorption of Ti on LiAlH₄ surfaces studied by band structure calculations

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Abstract

LiAlH₄ is a potential light-weight hydrogen storage material if hydrogenation can be made reversible. In NaAlH₄ this may be done by adding small amounts of Ti, but the same effect has not yet been observed in LiAlH₄. To understand these mechanisms, detailed studies of the materials with and without the additive are necessary. In this study, two-dimensional slabs representing the open (0 1 0) and densely packed (1 0 1) surfaces of LiAlH₄ have been used to model adsorption of titanium atoms on those surfaces. The results show that the Ti atom tends to move below the surface towards interstitial sites rather than binding to a Li ion or AlH₄ complex at the surface.

1. Introduction

The introduction of hydrogen as a major global energy carrier depends on solving a number of fundamental and technical problems. The perhaps largest challenge today is to find hydrogen storage solutions that at the same time are safe, compact, light, reversible, and cheap. One of the most promising solutions has been metal hydrides, but they have long suffered from poor hydrogen weight density. Light complex hydrides like NaAlH₄ and LiAlH₄ have been known for decades, but it has been believed that they can not be hydrogenated with hydrogen gas at moderate pressure and temperature. This picture changed in 1997, when Bogdanovic and Schwickardi demonstrated that it is possible to make hydrogenation reversible in some alanates (NaAlH₄, Na₃AlH₆, and Na₂LiAlH₆) by adding small amounts of Ti [1]. It was later shown by Chen et al. [2] that it is possible to achieve reversibility in Li₃AlH₄ by addition of Ti; they did not, however, find the same effect in LiAlH₄.

So far the information available on the microscopic properties of alanates with and without the addition is limited [3–5], and the mechanism making the reversibility possible is still unknown. It is still unclear where Ti resides in the hydrogenated and dehydrogenated alanates, it is even unknown whether it is located at the surface or in the bulk of the material.

The aim of this study is to describe where Ti moves if added to a crystalline alanate surface. This has been done by calculating the adsorption energy of Ti at two of the most stable surfaces of LiAlH₄ [6], using accurate band structure calculations.

2. Methods

We have used density functional theory as implemented in the ADF-BAND package [7,8] for our calculations. The program makes use of atomic orbitals in the form of Slater-type orbitals and Herman–Skillman numerical atomic orbitals as basis functions; this gives enough flexibility to describe the total electron density. The core is frozen, and relativistic corrections are included via the zeroth order regular approximation [9]. Gradient corrections are due to Perdew et al. [10]. All numerical parameters and basis set effects are thoroughly checked, and the overall convergence is well within 0.1 eV. The only remaining approximations are the gradient approximation and the size of the unit cell, which has been chosen to be the conventional cell, that is four formula units. This gives a thickness of eight metal atoms or 7.3 Å...
for the (0 1 0) surface. Since the (1 0 1) surface has two metal atoms in each layer, its thickness is only four metal atoms or 2.39 Å.

Our calculations are true two-dimensional, representing the surfaces as semi-infinite slabs. We have chosen to study the (0 1 0) and (1 0 1) surfaces of LiAlH₄, which in a previous study were found to be the most stable surfaces of this system [6]. They represent quite different possibilities, since the (1 0 1) surface is the most densely packed surface of the hydride, while the (0 1 0) surface is the most open. They are also quite different in that the (1 0 1) surface is covered by a mixture of Li atoms and AlH⁻ tetrahedra, while the (0 1 0) surface is covered by Li atoms. A sideview of the surfaces is shown in Fig. 1.

When Ti is added to the alanate, it will first interact with the surface. After that, it may react with the alanate to form an interstitial species or to replace one (or more) of the atoms of the structure. We focus here on the first part of this reaction, namely when the Ti atom first encounters the surface. The various adsorption sites that we have chosen for Ti on the two surfaces are shown in Fig. 2. These sites include on-top adsorption above Li and Al ions as well as bridge

Fig. 1. Sideview of the (0 1 0) and (1 0 1) surfaces of LiAlH₄.
sites and hollow sites. At each site, the height of the Ti atom above the surface has been varied, and the preferred height has been found by interpolation using a simple spline fit.

The accurate crystal structure of LiAlH$_4$ has recently been found by powder X-ray and neutron diffraction [11], and the experimental structure has been used in our calculations. We have not tried to perform any relaxation of the surface atoms, since this must be done by hand in the ADF-BAND program. This is clearly a weakness of our method, and makes it difficult to draw any clear quantitative conclusions. We still believe that we are able to obtain good qualitative information about binding preferences and electronic properties of this system, and the results should provide useful information as input to more elaborate studies on the same system.

3. Results

The adsorption energy of Ti as a function of the height $Z$ above the alanate surface is plotted in Fig. 3 for the various adsorption sites of the two surfaces. The adsorption energy...
The adsorption energy $E_{\text{ads}}$ in eV of the sites specified in Fig. 2 as a function of the height of the Ti atom above the surface, $Z$. $E_{\text{ads}}$ is defined in the text. The labels correspond to those in Figs. 1 and 2. The midpoint between two sites is labeled by the two sites’ labels, e.g. Al3 Li2 denotes the midpoint between the Al3 and Li2 sites.

$E_{\text{ads}}$ is defined as

$$E_{\text{ads}} = E_{\text{coh}}(\text{LiAlH}_4 + \text{Ti}) - E_{\text{coh}}(\text{LiAlH}_4) - E_{\text{Ti}}, \tag{1}$$

where $E_{\text{coh}}(\text{LiAlH}_4 + \text{Ti})$ is the cohesive energy of the slab with Ti adsorbed, $E_{\text{coh}}(\text{LiAlH}_4)$ is the cohesive energy of the slab before adsorption, and $E_{\text{Ti}}$ is the energy of a spin-restricted Ti atom. The adsorption energy has been calculated for various heights $Z$ above the surface. The separation between the calculated points in the $Z$ direction is 0.53 or 0.26 Å, with smallest separation around the minima.

We see from Fig. 3 that the most stable site on both surfaces is below the surface defined by the uppermost metal atoms. On the open (0 1 0) surface, it is the site called “Al2” in Fig. 2. The Ti atom is in this site located directly above one of the Al atoms in the fourth metal layer, and the minimum is 2.28 Å below the surface plane. Its nearest metal atoms are Al1 and Al4, both lying about 2.44 Å away. Two of the hydrogen atoms surrounding Al1 are even closer, lying 2.04 Å away, while the nearest hydrogen atom around Al4 is 2.08 Å away. The nearest Li atom is Li4, lying 2.66 Å away.

The situation is slightly different for the most stable adsorption site on the dense (1 0 1) surface. The most stable site is located directly above the midpoint between Al3 and Li2, and is denoted by Al3Li2 on Fig. 2. The minimum energy is obtained when the Ti atom is 2.19 Å below the surface plane. The nearest metal atom of Ti at the minimum is Li2, 2.33 Å away. The nearest Al atom is Al3, 2.45 Å away. But the nearest H atom is surrounding Al4, and is 2.08 Å away.

If we also regard a selection of the most stable sites, we find that there is no clear trend whether Al or Li is the nearest metal atom of the adsorbed Ti atom: of the four most stable sites on the (0 1 0) surface, Li is the nearest at two sites, and of the six most stable sites on the (1 0 1) surface, Li is the nearest at two. We must keep in mind that a full relaxation is not performed, and this may of course affect these results considerably. For instance, the hydrogen atoms may relatively easily move around the Al atoms, possibly making it more attractive for the Ti atom to move closer to an Al atom.

The most notable trend of the most stable sites is that the sites are hollow or bridge sites, that is they are not located directly above surface atoms. For instance, the most stable site on the (1 0 1) surface, Al3 Li2, is located at the quasi-threefold hollow site between the surface atoms Al2, Al4, and Li3. Likewise, the most stable site on the (0 1 0) surface, Al2, is located at the bridge between the surface atoms Al4 and Li1.

We note that both the energy curves of the most stable sites involve a small activation barrier when moving the Ti atom towards the surface. This barrier is, however, most probably not going to remain if we made a full representation of the three-dimensional potential energy surface of the adsorption process: Since the restriction of these curves is quite severe (keeping two of the dimensions fixed), we anticipate that there should be possible to find a diffusion pathway towards the most stable site without a transition barrier.

We have also calculated the total and local density of states (DOS) of LiAlH4 before and after the adsorption of a Ti atom. Fig. 4 shows this for Ti adsorption at the most favorable site on the (0 1 0) surface. We see that the overall electronic structure is severely influenced by the Ti atom. The total DOS valence band is moved about 2.7 eV upwards, most of it now lying above the Fermi level. This means that the slab has become conducting after the inclusion of the Ti atom—not surprising, taking into account the extra valence electrons added. (The reason why it looks like there are some conduction electrons in the pure slab is the Gaussian smearing of the DOS plot. The calculated DOS shows that pure LiAlH4 should be a perfect insulator.) The lower valence band centered around $-5$ eV has not moved, but it has become both significantly broader and higher. From the local DOS we can see that the only contribution to this band was from the Al-H interaction. With Ti in the lattice, the same band gets contributions from Li s and p electrons, Al p and d electrons and H s electrons in addition to Ti s, p,
and d electrons. Interestingly we see that the Al s band has almost disappeared.

4. Conclusions

Adsorption of Ti on the (0 1 0) and (1 0 1) surfaces of LiAlH$_4$ has been studied with density functional band structure slab calculations. The most stable sites were hollow sites below the surface. The calculated density of states shows that the electronic structure is changed significantly when Ti is added: The upper valence band is moved across the Fermi level, making the slab a conductor, while the lower valence band is broader and higher after the inclusion of Ti.

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References