

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ije

Energetics of hydrogen desorption from highly reactive clusters based on the sodium and magnesium alanates and boranates

C. Paduani*

DF-UFSC, Florianópolis, CEP 88040-900 SC, Brazil

ARTICLE INFO

Article history:

Received 28 May 2014

Received in revised form

22 July 2014

Accepted 6 August 2014

Available online 19 September 2014

Keywords:

Density functional theory

Superhalogen

Alanate

Boranate

Hydrogen storage

ABSTRACT

The structure and electronic properties of sodium and magnesium aluminohydrides (alanates) and borohydrides (boranates) are systematically investigated in first-principles calculations using density functional theory. A study of the result of successive attachments of AlH_4 and BH_4 complexes to Na and Mg reveals superhalogen behavior for the clusters $\text{Na}(\text{AlH}_4)_2$, $\text{Na}(\text{BH}_4)_2$, $\text{Mg}(\text{AlH}_4)_3$ and $\text{Mg}(\text{BH}_4)_3$, whose electron affinities are 4.93 eV, 5.07 eV, 5.20 eV and 5.13 eV, respectively, which far exceed that of chlorine (3.6 eV). The energetics of the H-removal from these clusters is also investigated and the results show that the hydrogen release is substantially less energy demanding for the superhalogen moieties. The energy cost for H-removal decreases from 3.72 eV in $\text{Na}(\text{AlH}_4)$ to 0.49 eV in $\text{Na}(\text{AlH}_4)_2$, and from 4.63 eV in $\text{Mg}(\text{BH}_4)_2$ to 0.37 eV in $\text{Mg}(\text{BH}_4)_3$. For the closed shell clusters, the alanates have superior performance with respect to the release of hydrogen as compared with the boranates. For the superhalogens, the energy cost for H-removal from $\text{Na}(\text{AlH}_4)_2$ is half of that one for the $\text{Na}(\text{BH}_4)_2$ cluster, whereas for the Mg clusters $\text{Mg}(\text{AlH}_4)_3$ and $\text{Mg}(\text{BH}_4)_3$ it is nearly equivalent (0.41 eV and 0.37 eV, respectively). This arises from the formation of an insurgent dimerized unit where the H atoms exhibit considerable loss of bonding charge.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen storage systems are aimed at the enhancement of the volumetric hydrogen density while maintaining high gravimetric hydrogen densities. Sodium alanate NaAlH_4 is a medium-temperature complex hydride with a high reversible hydrogen content (5.6 wt%) which has been considered as an agent for the reversible storage of hydrogen, with the advantage of having high storage capacity combined with low cost.

Nevertheless, although the pure material offers a suitable compromise with relatively large gravimetric storage capacity at temperatures of around 125 °C, it shows very slow kinetics during both hydrogen absorption and desorption. Improvement of the desorption/absorption kinetics has been also obtained by mechanical grinding and chemical modification of the alloys, and NaAlH_4 so modified is capable of reversible hydrogen storage at the relatively low temperatures of around 80–140 °C, with a capacity of between 2.5 and 3.0 wt.%. The hydrides have an even higher reversible capacity of about

* Tel.: +55 (48) 3721 9234; fax: +55 (48) 3721 9946.

E-mail addresses: clედerson.paduani@ufsc.br, paduanic@gmail.com, <http://dx.doi.org/10.1016/j.ijhydene.2014.08.049>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

4.5–5 wt.% when operated at temperatures around 150–180 °C [1]. However, in 1997 Bogdanović and Schwickardi [2] showed that hydrogen can be reversibly stored in and released from sodium alanate if doped with titanium compounds. The dehydrogenation thermodynamics and kinetics of the Ti-doped NaAlH₄ have been also investigated via the mechanical milling of a NaH–Al mixture under 2 MPa hydrogen pressure [3]. Thermodynamic analysis show that the dehydrogenation rate in the presence of the catalyst clearly increases with a corresponding increase of dehydrogenation temperature. The onset dehydrogenation temperature is thus lowered to about 100 °C.

Magnesium alanate Mg(AlH₄)₂ otherwise retains a higher capacity for hydrogen storage (9.3 wt%) than sodium alanate (7.4 wt% H) and has been also proposed as a candidate material for high-density reversible solid-state hydrogen storage [4–10]. It readily decomposes at temperatures below 200 °C, but so far has not been shown to exhibit reversible hydrogenation. It can be synthesized in a metathesis reaction of magnesium chloride and sodium alanate followed by purification. Thermal analysis shows a decomposition with a release of hydrogen proceeding in two major steps: the first step at 163 °C and the residue consists of MgH₂ and Al which continues to release hydrogen and transforms into an Al₃Mg₂/Al mixture at higher temperatures. In the first decomposition step 6.6 wt.% of hydrogen is released. The kinetics of the decomposition is improved for Ti-doped Mg(AlH₄)₂ [5]. The addition of a small amount of titanium to the solvent-free Mg(AlH₄)₂ greatly reduces the hydrogen evolution temperature of titanium-doped Mg(AlH₄)₂. However, the maximum amount of hydrogen evolution of the titanium-doped Mg(AlH₄)₂ is smaller than that of the solvent-free Mg(AlH₄)₂ [11]. A study of the dehydrogenation kinetics and storage capacity for a magnesium–sodium alanate mixture showed a dehydrogenation capacity of 2.7 wt% H₂ from Mg(AlH₄)₂ + 2NaCl, during the first decomposition step at 140 °C, and 1.1 wt% H₂ during second decomposition step, at 280 °C [12]. In the alanate mixture 0.5 Mg(AlH₄)₂ + NaAlH₄ the dehydriding temperature of NaAlH₄ gets lowered by 50 °C (from 190 °C to 140 °C) with 4 times faster desorption kinetics. Nevertheless, the calculated enthalpy of formation suggests that magnesium alanate is metastable at room temperature, and thus not suitable for reversible hydrogen storage [13].

In this work it is studied the assemblage of highly reactive large sized clusters formed by strongly bonded anions of complex hydrides, based on Na and Mg, as well as the energetics of the removal of an H atom from them. These clusters are formed by decorating Na and Mg atoms with AlH₄ and BH₄ groups in number that exceeds the maximal formal valence of the central atom, following the recipe for building up superhalogens, i.e., molecules with electron affinity even higher than that of halogen atoms, as originally proposed by Gutsev and Boldyrev [14]. These are compounds of great relevance in chemistry due to their enormously high electron affinities. In the last decade experimental investigations have successfully confirmed theoretical predictions of superhalogen behavior and vertical electron detachment energies (VDE) of various anions [15–19]. This is the first study on the superhalogen moieties of these alanates as well as on the hydrogen desorption of superhalogens. The results show a significant

decrease in the energy cost for hydrogen release from the superhalogen species as compared with the closed shell clusters.

Method

All calculations based on the density functional theory have been performed with the Gaussian-03 package [20]. For the correlation functional the Becke 3-parameter hybrid exchange and the Lee–Yang–Parr (B3LYP) [21] were adopted. The equilibrium geometries were determined by an optimization procedure of the geometrical parameters of the clusters without any symmetry constraint. The basis chosen is the 6-311++G(3df) set. The use of diffuse functions allow orbital flexibility and relatively stable uncontracted basis set, which is helpful in the description of some diffuse nature of the electronic density, particularly for the anionic form of large sized clusters. In order to determine the ground state geometry several different starting configurations were tried, whose stabilities have been checked by evaluating harmonic vibrational frequencies. Once an imaginary vibrational mode was found, a relaxing procedure along coordinates of imaginary vibrational mode was performed, until the true local minimum is obtained. All geometries used in the total energy calculations were optimized with remanent forces of less than 0.01 eV/Å with total-energy differences better than 10^{−6} eV.

Results and discussion

Sodium alanates

The calculated structure of the hypothetical neutral cluster for the tetrahydroaluminat (AlH₄) is shown in Fig. 1. This has

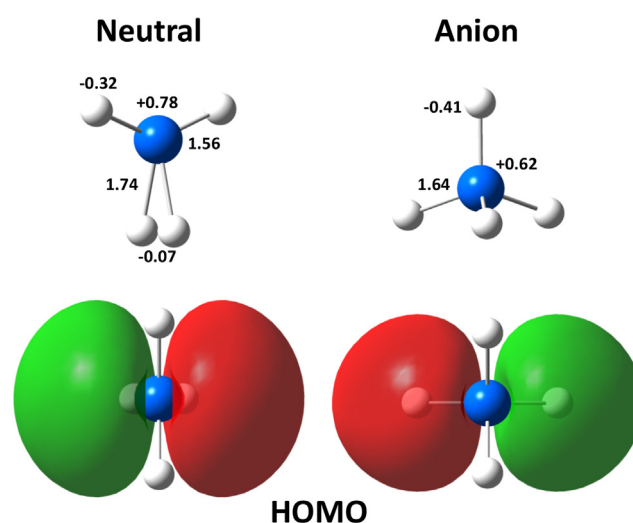


Fig. 1 – Equilibrium geometries for AlH₄ and AlH₄[−] (significant bond lengths (Å) and natural bond orbital (NBO) charges (e) are indicated), and isosurface plots of HOMO (isovalues of 0.001 Å^{−3}, red: +; green: −). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/1271867>

Download Persian Version:

<https://daneshyari.com/article/1271867>

[Daneshyari.com](https://daneshyari.com)