International Journal of Chemistry and Chemical Engineering.
ISSN 2248-9924 Volume 3, Number 2 (2013), pp. 81-88

http://www.ripublication.com

Studies on Lightweight Complex Borohydrides as Novel Options for Interstitial Hydrogen Storage

Leena V. Bora

Chemical Engineering Department, Institute of Technology,
Nirma University, Ahmedabad, India.

Abstract

Most of the fossil fuels have reached their peak periods and hence there is substantial emphasis on non-conventional and alternative fuel sources. Lots of efforts are being made world-over to not just study them, but also implement them on commercial level. Hydrogen is emerging as the new age fuel due to its several advantages. It burns with oxygen to release just water and energy. But there are issues related with the economic commercialization and usage. Department of Energy (DoE), USA has delineated a few objectives and there are efforts being put to meet the challenges. Hydrogen utilization and safe storage was tried as gas, liquid and metal hydrides, but none of them met commercial success. Hence the research shifted to novel options, one of them is as complex hydrides, such as borohydrides, alanates, aminoboranes, amides, imides, and alanes. This paper discusses the structure, adsorption-desorption kinetics, thermodynamics, capacity and safety issues of lightweight complex borohydrides such as magnesium borohydrides, lithium borohydride, calcium borohydride and sodium borohydride in detail. The improvement in the storage performance due to the addition of relevant catalysts is also discussed. Also a brief comparison has been made with other borohydride options.

Keywords: Hydrogen storage, borohydride, hydrogenation-dehydrogenation.

1. Introduction

One of the major concern in the world today is that of energy crisis. Most of the fossil fuels have crossed the peak periods and are now depleting. Moreover, they harm the environment by releasing pollutants in various forms. Several other alternate options of fuels have been studied and hydrogen has proved to be one of the most promising option. The combustion of hydrogen with oxygen gives water and releases energy.

$$H_2 + O_2 \rightarrow 2H_2O \tag{1}$$

This is an exothermic reaction that releases about 232 kJ of energy per mol of water, which is about three times that of petroleum.

1.2 Challenges

The major gap between the potential and commercialisation of hydrogen as an alternative fuel lies in its economic storage and transportation. On-board hydrogen can be stored in compressed, cryogenic or liquid form, alongwith other options like metal hydrides, high surface area adsorbents, and chemical hydrogen storage media. Compressed hydrogen storage and usage is not a practical option due to low density and safety issues. The solid hydrogen storage options are also not able to fulfil the goals delineated by DoE, USA viz., min. 6.5 wt% gravimetric capacity, 60-120 ^{o}C desorption temperature, safe handling and overall economic usage. Recently, complex hydrides of lithium, sodium, magnesium, calcium have proved to be having a better potential in the form of alanates, borohydrides, amides, imides, alanes, etc. This paper discusses the science and research related to lightweight complex borohydrides such as magnesium, calcium, lithium and sodium.

2. Complex Lightweight Borohydrides

2.1 Magnesium Borohydride

2.1.1 Synthesis.

$Mg(BH_4)_2$ can be synthesized by the reaction of magnesium chloride with either sodium chloride or by mechano-chemical process of ball milling it with lithium borohydride.[1][2]

$$MgCl_2 + 2NaBH_4 \rightarrow Mg(BH_4)_2 + 2\,NaCl \tag{2}$$

There is also a wet process of synthesis in which Mg hydride is reacted with aminoborane as a BH_3 donor.

2.1.2 Structure

Different scientists have proposed different structures based on the different techniques. Initially, two crystalline phases were proposed, viz., tetragonal and cubic. Later, a monoclinic structure was proposed by DFT calculations. Still later, it was proposed that the DFT calculations showed ion arrangement. Recently, it has been proved that $Mg(BH_4)_2$ shows hexagonal symmetry. [3]

2.1.3 Thermodynamics and hydrogenation

It has been proposed that the release of hydrogen from $Mg(BH_4)_2$ takes place in two endothermic steps[4]:

$$Mg(BH4)2 \rightarrow MgH2 + 2B + 3H2 \text{ , } \Delta H= -57 \text{ kJ/mol H2} \qquad (3)$$

$$MgH2 \rightarrow Mg + H2 \qquad (4)$$

The thermogravimetric (TG) and differential thermal analyses (DTA) studies reveal that the dehydridation takes place from about 300 ^{o}C till about 500 ^{o}C. It has been experimentally found that $Mg(BH_4)_2$ shows a release of about 13.7 wt% hydrogen; the rehydrogenation capacity is about 6.1 wt%.[5]

2.2 Calcium Borohydride

2.2.1 Synthesis

Initial synthesis of $Ca(BH_4)_2$ has been from the reaction of calcium hydride with diborane. Another method is the preparation of $Ca(BH_4)_2.(THF)_2$ and later separating $Ca(BH_4)_2$ by heating at about 260 ^{o}C under vacuum. Ball milling of lithium borohydride with $CaCl_2$ can also be used to prepare $Ca(BH_4)_2$. Ball milling CaB_6 with $CaCl_2$ at about 420^{o}C and 70,000 kPa is another option for the synthesis of $Ca(BH_4)_2$. A recent method proposed is to react MgB_2 with CaH_2 at about 400 ^{o}C and 35,000 kPa of H_2.[6]

$$CaB_6 + 2CaH_2 + 10H_2 \rightarrow 3Ca(BH_4)_2 \qquad (5)$$

2.2.2 Structure

A face centered orthorhombic structure was suggested initially by Rietveld analysis. This has also been verified by several other researchers using other techniques[7]. Each Ca^{2+} ion is found to be surrounded octahedrally by six $[BH_4^-]$, each $[BH_4^-]$ surrounded by three Ca^{2+} ion. However, a more recent and indepth study has revealed the structure to be tetragonal.

2.1.3 Thermodynamics and hydrogenation

Dehydrogenation of $Ca(BH_4)_2$ is proposed to be following the following mechanism, which is the exact opposite of reaction number (5):

$$3Ca(BH_4)_2 \rightarrow 2CaH_2 + CaB_6 +10H_2 \qquad (6)$$

This decomposition takes place in the range of 330-450 ^{o}C and 90,000 kPa pressure with an enthalpy change of about 32 kJ/mol of hydrogen, as studied from the P-C isotherm and TG-DTA study. About 3.8 wt% of reversibility has been reported with $TiCl_3$ catalyst. NbF_5 has been proved to be the best catalyst till date catalyzing the rehydrogenation capability to about 5 wt% at 420 ^{o}C and 90,000 kPa pressure[8].

2.3 Lithium Borohydride

2.3.1 Synthesis

Initial synthesis of $LiBH_4$ has been from the reaction of lithium hydride with diborane with diethyl ether as the solvent. $LiBH_4$ can directly be synthesized by reacting lithium metal and boron in hydrogen environment at about 600 ^oC and 80,000 kPa pressure[9]. $LiBH_4$ and $LiBD_4$ can be directly synthesized at 700 ^oC in H_2/D_2 environment at about 150,000 kPa pressure.[10], [11]

2.3.2 Structure

XRD studies revealed the structure of $LiBH_4$ as orthorhombic and each lithium ion surrounded by four borohydride ions. Other results have reproduced the results and also suggested that $LiBH_4$ undergoes a structural transition to hexagonal form at elevated temperatures[12].

2.3.3 Thermodynamics and hydrogenation

DTA results show that about 18 wt% hydrogen can be released within three endothermic peaks in the range of about 110 – 500 ^oC and 10,000 kPa. The first of the three peaks is for structural transition of $LiBH_4$. Second one for formation of $LiBH_2$ and release of hydrogen, and the third one as per equation (9)

$$LiBH_4 \rightarrow Li + B + 2H_2 \qquad (7)$$

$$2LiBH_4 \rightarrow 2LiH + 2B + 3H_2 \qquad (8)$$

$$2LiBH_2 \rightarrow 2LiH + 2B + H_2 \qquad (9)$$

These decompositions takes place with enthalpy and entropy changes of about ΔH= -177 kJ/mol H_2, ΔS= 238 kJ/mol H_2. Use of catalysts like SiO_2, $TiCl_3$, V_2O_3, substitution with Mg, Cu etc. have proved to be fruitful in increasing the gravimetric efficiency and lowering the decomposition temperature. The dehydrogenation kinetics can be significantly increased by mixing $LiBH_4$ with $LiAlH_4$ or with the aid of nanosizing $LiBH_4$ over carbon supports. It has also been reported that the use of Pt catalyst over $LiCoO_2$ can release 100% hydrogen. Hydrolysis of $LiBH_4$ yields hydrogen as well.

$$LiBH_4 + 2H_2O \rightarrow LiBO_2 + H_2 \qquad (10)$$

2.4 Sodium Borohydride

2.4.1 Synthesis

Several reactions have been proposed for the synthesis of $NaBH_4$. Sodium hydride can be reacted with either boric acid or trimethyl borate to yield $NaBH_4$ from the following reactions[13]

$$NaH + 2B_2O_3 \rightarrow NaBH_4 + 2NaBO_2 \qquad (11)$$

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3 \qquad (12)$$

Alternative methods of $NaBH_4$ synthesis include reaction of dehydrated borax with silicon dioxide or reacting sodium hydroxide with diborane.[14]

$$Na_2B_4O_7 + 16\ Na + 8\ H_2 + 7\ SiO_2 \rightarrow NaBH_4 + 2Na_2SiO_3 \quad (13)$$

$$4NaOH + 2B_2H_6 \rightarrow 3NaBH_4 + NaBO_2 + 2H_2O \quad (14)$$

2.4.2 Structure

A face centered tetrahedral lattice structure was suggested initially. Later neutron diffraction studies suggested $NaBH_4$ to possess a structure similar to that of NaCl. $NaBH_4$ was found to become tetragonal below its transition temperature of about 95 °C. It was also found that titanium doping destabilizes the crystal structure of $NaBH_4$ which helps to increase the storage capacity of hydrogen.[15]

2.4.3 Thermodynamics and hydrogenation

About 90 wt% of dehydrogenation has been reported by hydrolysis.

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 + xH_2O + 4H_2 \quad (15)$$

Table 1 below gives the exothermicity of the above equation for different experimental values of x. However, it is suggested to use minimum amount of water for convenience in onboard storage.

Table 1: Enthalpy releases of equation (15) with different amount of water.

x	**ΔH, kJ/mol H_2**
0	-216.7
2	-250.1
4	-272.4

Hence, alternate routes have been studied. One of the methods is to use pure steam as a catalyst and this releases about 95 wt% hydrogen. Sodium hydroxide catalyst has been reported to increase the yield by about 3%. Metal halide catalysts like $NiCl_2$, activated carbon, platinum, Mg doping, Ni, Ru, $CoCl_2$, F, etc have enhanced effect on hydrogen release. Pt-$LiCoO_2$ has been reported as one of the best catalysts for the purpose, which is about 10 times faster than the use of Ru supported on ion exchange resins.

The use of noble catalysts release about 4 wt% hydrogen just at room temperature. Platinum catalysts have proved to serve a dual purpose of electrochemical catalysis of hydrogen with oxygen and catalyzing the hydrolysis reaction to yield hydrogen. Thus it serves as a potential for use in a proton exchange membrane fuel cell (PEMFC). Another catalyst made up with a combination of carbon nanotubes with silicon carbide and Pt and Pd has proved to yield fastest hydrogen from $NaBH_4$. Other effective catalysts include those of Sn-Sb, Ru-Al, $NaBH_4$- $Mg(BH_4)_2$, TiO_2, Zr and TiF_3.

3. Summary, Prospects and Challenges

Hydrogen as an alternative fuel has great potential to tackle today's major demands of energy crisis and pollution. DoE, USA has outlined requirements for onboard storage in terms of gravimetric/volumetric efficiencies, desorption temperature and kinetics and safe and economic storage. Among the various lightweight complex hydrides, this paper has discussed the studies about four potential Borohydrides, viz., lithium, calcium, magnesium and sodium. It is important to understand the synthesis routes and structure prior to studying the hydriding and dehydriding kinetics and thermodynamics. This will aid in cost reduction and selection of proper catalyst dopants. Apart from these, Aluminium borohydride has been investigated recently and is emerging as another potential hydrogen storage medium.

Catalysts doping improves the kinetics to a very large extent and takes the research closer to the DoE requirements. Nanosizing the particles have added effects. Simultaneous addition and size reduction of host and guest particles can be done by mechano-chemical synthesis like ball milling.

Finally, continual researches are on-going all over the globe to address the issues of our mother earth. And with the kind of attention and efforts put in this field of renewable energy, it is expected to fulfil gap.

References

[1] R. Koster, K. Ziegler, Angew, *Chem*. 69, (3), (1957), 94.

[2] Yuko Nakamori, Kazutoshi Miwa, Akihito Ninomiya, Haiwen Li, Nobuko Ohba, Shin-Ichi Towata, Andreas Zuttel, Shin-Ichi Orimo, *Phys. Rev. B*, 74 (2006), 045126.

[3] Krzysztof Chlopek, Christoph Frommen, Aline Leon, Oleg Zabara, Maximilian Fichtner, *J. Matter, Chem*. 33 (2007), 3496-3503.

[4] P. Vajeeston, P. Ravindran, A. Kjekshus, H. Fjellvag, *Appl. Phys. Lett.*, 89 (2006), 071906.

[5] Luci Georage, Vadym Drozd, Surendra K. Saxena, Elisa Gil Bardagi, Maximilian Fichtner, J. Phys. Chem. C, 113 (2009), 486-492

[6] E. Wiberg, H. Noth, R. Z. Hartwimmer, Z. Naturforsch, 10b (1955), 292

[7] Kazutoschi Miwa, Masakazu Aoki, Tatsuo Noritake, Nobuko Ohba, Yuko Nakamori, Shin-Ichi Towata, Andreas Zuttel, Shin-Ichi Orimo, Phys. Rev. B, 74 (2006), 155122

[8] Gagik Barkhordarian, Thomas Klassen, Martin Dornheim, Rudiger Bormann, J. Alloys Comp, 440 (2007), L18-L21

[9] H. I. Schlesinger, C. Brown Herbert, *J. Am. Chem, Soc,* 62 (1940), pp. 3429-3435.

[10] P. M. Harris, E. P. Meibohm, *J. Am. Chem, Soc,* 69 (1947), 1231-1232

[11] Zuttel, Ares. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron, Ch. Emmenegger, *J. Alloys Comp*, 356-357 (2003), 515-520
[12] Yuko Nakamori, Shin-Ichi Orimo, , *J. Alloys Comp*, 370 (2004), 271-275
[13] Yoshitsugu Kojima, Tetsuya Haga, *Int. J. Hydrogen Energy*, 28, (2003), 989-993.
[14] J. M. Adams, *Metal Boron Compounds & Boranes*, Interscience Publishers.
[15] U. Bilici, Second Int. Boron Symposium, vol. 23-25, 2004, pp. 119-125.
[16] R. Lindsay Davis, H. L. Kennard Colin, *J. Solid State Chem*, 59 (1985), 393-396.
[17] B. M. Bulychev, K. N. Semenko, K. B. Bitsoev, Koord. Khim. 4, (1978), 374.
[18] H. Grove, H. W. Brinks, R. H, Heyn, S. M. Opalka, X. Tang, B. I. Laube, B. C. Hauback, *J. Alloys Comp*. 460, (2008), 249-254