HYDROGEN STORAGE USING BOROHYDRIDES.

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ABSTRACT:
The possibilities of hydrogen storage using borohydrides are presented and discussed specially in regard of the recoverable hydrogen amount and related to the recovering conditions. A rapid analysis of storage possibilities is proposed taking in account the two main ways for hydrogen evolution: the dehydrogenation obtained through thermal decomposition or the hydrolysis of solids or solutions. The recoverable hydrogen is related to the dehydrogenation conditions and the real hydrogen useful percentage is determined for each case of use. The high temperature required for dehydrogenation even when using catalyzed compounds lead to poor outlooks for this storage way. The hydrolysis conditions direct the chemical yield of the water consuming, and this must be related to the experimental conditions which rule the storage capacity of the “fuel” derived from the borohydride.

KEYWORDS : Hydrogen, Storage, Borohydrides, Dehydrogenation, Hydrolysis.

INTRODUCTION.

Hydrogen is considered as the most promising energy vector which should be developed in the near future to replace hydrocarbon derivatives. In fact hydrogen is not an energy source but it appears to be the easiest way to store energy whatever the original primary source is. When converted into hydrogen, energy can be stored and used when needed. However, huge differences in the storage tools should be considered, taking in account the great varieties of hydrogen uses so that the chemicals used for storage and the energy restoration mechanism chosen must be very different. The requirements for mobile applications are surely opposed to those of fixed installations and for this kind of application, the chemicals and the recovering system chosen must answer to specific duties. The most difficult problems are encountered for on-board applications including high storage performance, safety, simplicity of refueling and low cost.

Among the high hydrogen containing chemicals, tetrahydroborates are the highest hydrogen containing compounds and among them the simpler anion family, MBH₄, usually called borohydrides, are the more known compounds. A brief comparison between the more usual and commercially available borohydrides is proposed in this study, focusing on the more convenient applications through the hydrogen recovery processes.

ABOUT BOROHYDRIDES, COMMON PROPERTIES

The chemistry of the compounds containing boron and hydrogen is not very old and metal tetrahydroborates and their derivatives have been extensively studied since LiBH₄, BeB₂H₆ and Al(BH₄)₃ were first reported 60 years ago in the work of A. Stock [1], H.I. Schlesinger [2] and E. Wiberg [3]. Numerous reviews are available updating earlier compilations [4,5] but the great development of borohydride chemistry must be related to the work of H.C. Brown [6] leading to the Nobel Prize for the hydroboration of organics. The better known borohydrides are the alkali metal salts which are produced on a very large scale for the industry and very little have been reported on the alkaline earth and aluminum derivatives.
Out of the lithium and beryllium borohydrides whose crystalline and bonding systems are more complexes, the borohydrides are essentially ionic solids which slowly hydrolyze in air. Hydrolytic stability decreases with an increase in the atomic weight of the cation. The BH$_4^-$ anion which is isoelectronic with methane has been shown to be tetrahedral by spectroscopic studies. If the bonding of the more common borohydrides is mainly ionic, the beryllium, and aluminum derivatives are described as the first three center bonding compounds studied [7,8]. Some of their chemical and physical properties are summarized in Table I [1,2].

Table I. : Physical and chemical constants of borohydrides considered for hydrogen storage [1,2].

The mark * corresponds to a lack of information but also to a high reactivity.

<table>
<thead>
<tr>
<th>Property</th>
<th>LiBH$_4$</th>
<th>NaBH$_4$</th>
<th>KBH$_4$</th>
<th>Be(BH$_4$)$_2$</th>
<th>Mg(BH$_4$)$_2$</th>
<th>Al(BH$_4$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>21.8</td>
<td>37.8</td>
<td>53.9</td>
<td>38.62</td>
<td>53.9</td>
<td>71.4</td>
</tr>
<tr>
<td>Density (g.cm$^{-3}$)</td>
<td>0.68</td>
<td>1.08</td>
<td>1.17</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Enthalpy of formation $\Delta H_{f}^{\circ}$ (kJ.mol$^{-1}$)</td>
<td>-184.5</td>
<td>-183.3</td>
<td>-242.3</td>
<td>-301.8</td>
<td>-301.8</td>
<td>-301.8</td>
</tr>
<tr>
<td>Entropy $S_{f}^{\circ}$ (J.mol$^{-1}$.deg$^{-1}$)</td>
<td>128.7</td>
<td>126.2</td>
<td>162</td>
<td>289</td>
<td>289</td>
<td>289</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>275</td>
<td>505</td>
<td>585</td>
<td>123*</td>
<td>320</td>
<td>-64.5</td>
</tr>
<tr>
<td>Decomposition Temp (°C)</td>
<td>380</td>
<td>565</td>
<td>584</td>
<td>123</td>
<td>320</td>
<td>44.5</td>
</tr>
<tr>
<td>Solubility (g/100g solvent)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>1.6(-45°C)</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Diglyme</td>
<td>5.5</td>
<td>0</td>
<td>complex</td>
<td>54</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>THF</td>
<td>24.3</td>
<td>0.1</td>
<td>complex</td>
<td>54</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Liquid NH$_3$</td>
<td>48</td>
<td>104</td>
<td>20</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>*</td>
<td>55</td>
<td>19</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Hydrogen content W%</td>
<td>18.3</td>
<td>10.6</td>
<td>7.4</td>
<td>20.7</td>
<td>14.8</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Hydroborates are among the rare hydrides which can be dissolved in water without any danger. This remarkable property is related to their stability. This has been one of the reasons for the intensive development of the use of borohydrides in organic and nanoparticle chemistry. Moreover potassium and sodium borohydrides form numerous solvates and specially hydrates. The compounds NaBH$_4$,2H$_2$O, KBH$_4$,H$_2$O and KBH$_4$,3H$_2$O have been reported and their formation usually modifies the reactivity of anhydrous borohydrides.

The alkali metal borohydrides have been prepared using a large variety of reactions. Usually, boron is provided as an oxide and the hydrogenation is performed through a transfer of hydrogen from an alkali metal hydride. The direct synthesis of borohydrides, even if reported in literature [9], has never been developed on an industrial scale. The most common method for the commercial production of sodium borohydride is based on the use of a mineral oil suspension of sodium hydride for hydriding reagent. Sodium dispersions may be hydrogenated directly in the mineral oil and the oil provides a heat sink which facilitates temperature control of the exothermic reaction with methyl borate [10]. The new outlooks given to the borohydrides as important chemicals for hydrogen storage have renewed the interest for these compounds and specially for the recycling of the borates formed when hydrolysis is used to generate hydrogen. Numerous patents have been taken out but the principle of the synthesis has been kept the same however the hydriding transferring chemicals were only changed leading to diborane [11] or magnesium hydride [12] utilization.

From these basic considerations, the ability of borohydrides to be vectors for hydrogen storage can be clearly defined. Some hydroborates have to be considered as able to be used in the solid state to generate hydrogen through thermal decomposition or hydrolysis and the others can lead to stable hydrolysable solutions which can be used as a "liquid fuel".
HYDROGEN GENERATION THROUGH THERMOLYTIC DEHYDROGENATION OF BOROHYDRIDES

As reported in the Table 1, borohydrides can be dehydrogenated, or decomposed, at relatively moderate temperatures and the reaction proceeds through several steps [13]. Until recently, the dehydrogenation could be summarized by the following reactions:

\[ M(BH_4)_n \rightarrow n \text{MH} + n \text{B} + \frac{3}{2} n \text{H}_2 \]  

(1)

The second step corresponds to the alkali metal hydride dehydrogenation

\[ n \text{MH} + n \text{B} \rightarrow n \text{B} + n \text{M} + \frac{1}{2} n \text{H}_2 \]  

(2)

Hence the stability and the dehydrogenation conditions of these hydrides, gathered in Table II, show clearly that their thermolysis leads through reaction 2 to liquid or gaseous alkali metals. These alkali metals would be spread into the whole hydrogen generation system, conditions which are not possible to develop. So the storage will exclude the dehydrogenation of the alkali metal hydride which induces a drastic decrease in the storage properties. Recently, for LiBH₄, a new decomposition scheme has been proposed, the mechanism taking in account the phase transition in the solid state and the melting of the borohydride [14,15]. A non stoichiometric phase seems to be induced during the solid state phase transition leading to symetrisation of the crystal. The hydrogen lost was about 0.3 % by weight when the crystallographic structure changed from orthorhombic to fcc. The melting of LiBH₄ at 268 °C does not lead to decomposition when the sample is pure, an important hydrogen evolution being obtained at about 420°C. Attempts have been made successfully to enhance the decomposition and favor a low temperature dehydrogenation by using a dilution phase. For instance, silica added to lithium borohydride enhances the first step of the dehydrogenation and the poor hydrogen production in the range 300-400°C when pure LiBH₄ is dehydrogenated is clearly increased. This can be related to the surface area increase of the molten borohydride. This first step is followed by a sharp hydrogen evolution which has been interpreted in terms of the existence of a sub-hydride corresponding to the crude formula "LiBH₂" and the dehydrogenation scheme proposed becomes:

\[ \text{LiBH}_4 \rightarrow \text{LiBH}_4^- + \varepsilon \frac{1}{2} \text{H}_2 \rightarrow \text{LiBH}_2 + \left(1-\frac{\varepsilon}{2}\right)\text{H}_2 \rightarrow \text{LiH} + \text{B} + \frac{1}{2} n \text{H}_2 \]  

(3)

Referring to the alanates, no BH₆⁻ structured compounds have been clearly characterized like Na₃AlH₆ in the hydroaluminates [16]. This decomposition scheme seems to be enhanced when catalyzed using silica powder in a proportion of 25 % by weight borohydride and 75 % silica but no specifications are given for the employed silica and the inertness of this adduct [14,15]. An important point must be outlined: the hydrogen storage capacity of the "catalyzed" borohydride drop drastically due to the great "catalyst" addition. The enhancing of the dehydrogenation properties using silica lowers the storage down to 34.3 % by weight. Table II gathers the possibilities of hydrogen storage taking into account the impossibility to recover the hydrogen bound to the alkaline metal.

Table II. Recoverable hydrogen from thermolysis process.

<table>
<thead>
<tr>
<th></th>
<th>LiBH₄</th>
<th>NaBH₄</th>
<th>KBH₄</th>
<th>Be(BH₄)₂</th>
<th>Mg(BH₄)₂</th>
<th>Al(BH₄)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple hydride decomposition</td>
<td>LiH</td>
<td>NaH</td>
<td>KH</td>
<td>BeH₂</td>
<td>MgH₂</td>
<td>AlH₃</td>
</tr>
<tr>
<td>T°C for PH₂ = 1 bar</td>
<td>980</td>
<td>420</td>
<td>427</td>
<td>240</td>
<td>270</td>
<td>158</td>
</tr>
<tr>
<td>Melting point of alkali metal</td>
<td>179</td>
<td>97.8</td>
<td>63.5</td>
<td>1278</td>
<td>651</td>
<td>659</td>
</tr>
<tr>
<td>Hydrogen content Weight%</td>
<td>18.3</td>
<td>10.6</td>
<td>7.4</td>
<td>20.7</td>
<td>14.8</td>
<td>16.8</td>
</tr>
<tr>
<td>Recoverable hydrogen</td>
<td>137</td>
<td>79</td>
<td>55</td>
<td>155</td>
<td>11.1</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Taking into account the important technological improvement obtained with metal catalyzed alanates leading to an important increase of the kinetic of storage, sodium borohydride has been activated by deposition of metal nanoparticles using a classical method often described for catalysts preparation [17]. Several noble metals were tested: platinum, palladium, ruthenium but also nickel and cobalt with different metal amounts.
XPS measurements confirm the presence of native metal on the surface of borohydride for noble metals but an important part of borides (30% in atoms) were characterized for nickel and cobalt. The metal nanoparticles were smaller than 10 nm and uniformly scattered on the borohydride surface as characterized by the XRD pattern (Fig. 1) recorded on the 5% nickel activated sample where no diffraction line corresponding to nickel appeared.

Figure 1. XRD spectrum of 5 w% nickel catalyzed NaBH₄.

The dehydrogenation of activated NaBH₄ have been performed under low pressure (1 mbar) using TGA with a 5°.mn⁻¹ heating rate. The temperatures of the beginning of the decomposition of the catalyzed samples were given in Table III. No spectacular changes occurred even when increasing of the catalyst amount (here ruthenium) and the dehydrogenation temperatures were only 40°C lowered.

Table III: Dehydrogenation temperature lowering of catalyzed NaBH₄ obtained from TGA.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>None</th>
<th>0.5 % Pd</th>
<th>1 % Pt</th>
<th>1 % Ru</th>
<th>10 % Ru</th>
<th>5 % Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydrogenation T°C</td>
<td>465</td>
<td>440</td>
<td>455</td>
<td>420</td>
<td>435</td>
<td>430</td>
</tr>
</tbody>
</table>

An important point has to be outlined: if borohydrides are used as hydrogen storage material and if the recovery of hydrogen is performed by thermal dehydrogenation, borohydrides could never be considered as reversible compounds, opposite to alanates, even if the storage materials were efficiently catalyzed. A Van T’Hoff plot of the equilibrium of hydrogen pressure versus temperature for the alkaline borohydrides following reaction 1 is given in Figure 2 from the values of the literature [17].

Figure 2. Equilibrium conditions of dehydrogenation of alkali metal borohydrides.
The values of the hydrogen pressure related to the temperature are too important to be applied in a large scale, even if direct synthesis of sodium borohydride has been early reported [9]. The alkali metal borohydrides must be considered as a non reversible system for hydrogen storage because the equilibrium conditions are not compatible with on-board absorption-desorption conditions.

**HYDROGEN GENERATION BY HYDROLYSIS OF BOROHYDRIDES**

To generate hydrogen, the hydrolysis of solid borohydrides [19] or borohydrides in aqueous solutions is presently under industrial development and several ventures propose hydrogen generators [20] or direct electricity generators [21] from sodium borohydride solutions. In fact when a borohydride reacts with water or alcohol, the hydrolyzing species becomes a reactant. In the case of water, which contains more than 11 % by weight of hydrogen, if all the hydrogen of the water can be reacted, for low hydrogen containing borohydrides, the hydrogen amount of the mixture borohydride-water, the "fuel", is clearly enhanced.

Alkaline earth borohydrides can be dissolved into water or protic solvents without or with a light hydrolysis as given in Table 1. The beryllium, magnesium and aluminum borohydrides react violently with water and the dissolution of lithium borohydride is very exothermic, which favors the hydrolysis. The solutions of sodium borohydride can be stabilized by addition of sodium hydroxide [22] however the addition of the stabilizing compound (1 to 10 % by weight) lowers the amount of stored hydrogen and leads to more difficult conditions to recover hydrogen. A balance must be chosen between the stabilization of the "fuel", the loss of stored hydrogen and the suitable hydrolysis conditions. The stability of soda-added solutions has been widely studied and several companies commercialize sodium borohydride solutions [23] for example "Hydrifin C" composed of 20 % NaBH₄, 20 % NaOH and 60 % water.

The storage properties of borohydrides were clearly related to the stoichiometry of the reaction of hydrolysis. The reaction can be written with the quantity of water just required to evolve the hydrogen.

\[
\text{MBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{MBO}_2 + 4 \text{H}_2. \quad (4)
\]

This can only be performed using solid borohydride and the obtained sodium borate must be anhydrous. In fact, even when using solid borohydride, the borates formed are usually hydrated and reaction 4 must involve more water [19]. The yield of the storage of hydrogen will be fixed by the amount of water included in the reaction, which means that it is the hydration of the borate which will determine the percentage of hydrogen from the borohydride-water mixture. Usually the obtained borates are not anhydrous and the more stable hydrate depends upon the nature of the cation and the reaction conditions. An example is given by sodium borohydride whose hydrolysis yields sodium borate hydrated with two molecules of water at room temperature. Reaction 4 becomes:

\[
\text{NaBH}_4 + 4 \text{H}_2\text{O} \rightarrow \text{NaB(OH)}_4 + 4 \text{H}_2. \quad (5)
\]

The reactive fuel which generates hydrogen will be composed of 34.4% weight sodium borohydride and 65.6% water. This fuel will store 8 g hydrogen for 100 g fuel, which is a not so bad value, but very different from the claimed 10.6 %! To give useful values and storage possibilities of borohydrides, Table IV gathers the storage capacities of the "fuel" needed for hydrolysis.

### Table IV. Hydrogen storage properties of the "fuels" borohydride-water solutions.

<table>
<thead>
<tr>
<th></th>
<th>LiBH₄</th>
<th>NaBH₄</th>
<th>KBH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical hydrogen wt%</td>
<td>18.3</td>
<td>10.6</td>
<td>7.4</td>
</tr>
<tr>
<td>Fuel Solution 2xH₂O Mol.Weight</td>
<td>57.8</td>
<td>73.8</td>
<td>89.9</td>
</tr>
<tr>
<td>Hydrogen recovered wt%</td>
<td>13.8</td>
<td>10.8</td>
<td>8.9</td>
</tr>
<tr>
<td>Fuel Solution 4xH₂O/Mol.Weight</td>
<td>93.6</td>
<td>109.8</td>
<td>125.8</td>
</tr>
<tr>
<td>Hydrogen recovered % wt</td>
<td>8.5</td>
<td>7.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Stable borate hydrate</td>
<td>LiBO₂·4H₂O</td>
<td>NaBO₂·2H₂O</td>
<td>KBO₂·1.5H₂O</td>
</tr>
<tr>
<td>Dehydration temperature °C</td>
<td>320</td>
<td>190</td>
<td>250</td>
</tr>
</tbody>
</table>
An important point is also the stability of the hydrates formed and the conditions leading to anhydrous borate. A rapid study of the dehydration conditions of the borates can fix the conditions yielding to anhydrous borate which correspond to the highest yield for hydrogen storage. The data have been limited to the water-soluble borohydrides, the other ones, more reactive, are more difficult to be employed. From Table IV, the conditions to obtain the best hydrogen storage percentage are easy to determine. Using lithium borohydride, if the hydrolysis is performed at a temperature higher than 350°C, only little water is required and the storage properties are not too affected by the hydrogen recovery process. If the hydrolysis is performed at room temperature, the storage properties drop drastically. If potassium borohydride is used, if the water is totally decomposed, the storage properties of the pure hydride are enhanced because the hydrogen recovered from water is higher that the hydrogen stored in the borohydride. These possibilities of storage are summarized on figure 4, were the different domains of stability of oxides are reported.

Figure 4 : different stability domains of oxides after hydrolysis.

The amounts of recoverable hydrogen are higher than the values required in many reports. However other problems can occur in the exploitation system but the storage of hydrogen using borohydride under solid state or in "fuel" solution is possible.

An important point in this system of storage is the hydrolysis of the solutions which have been stabilized [22]. Transition element compounds are known to react with tetrahydroborate ions in solution [24,25]. Frequently, transition metal hydride complexes are obtained and borides or borane derivatives may likewise be formed. Transition metal ions often enhance the rate at which BH₄⁻ is hydrolyzed in aqueous solution. Half times for hydrolysis have been measured for a large number of compounds and a reactivity schedule shows that ruthenium or rhodium compounds are more than 100 times more efficient than palladium. This hydrolysis enhancement rate is an important point in storage systems using borohydrides. The most efficient results have been obtained using ruthenium metal [26], platinum nano particles or ruthenium coated lithium cobalt oxide [27].

The regeneration of the borohydride after hydrolysis must be performed off board. The recovery of borates and the chemical re-treatment must be performed in plants but no essential difference exists in the chemistry between the boron ores, usually borax, and the recovered hydrolyzed wastes. This regeneration is not technically difficult but is energy consuming and the last patents devoted to the borohydrides synthesis have made accurate energy evaluations in order to propose realistic solutions.
CONCLUSIONS

Borohydrides, however high hydrogen containing compounds, are not very simple compounds to be involved in hydrogen storage. Whatever the solution chosen for stored hydrogen recovery, the regeneration of the borohydride must be operated out of the site of hydrogen utilization. Borohydrides would never be considered as reversible compounds for hydrogen storage.

Hydrogen recovery using thermal dehydrogenation is highly energy consuming because borohydrides, especially alkaline earth compounds, require high temperatures to evolve hydrogen. Moreover the multistep thermolysis of borohydrides leads to very stable intermediates such as alkaline hydrides whose dehydrogenation is impossible due to the volatility of the alkaline metal. The announced hydrogen content must be lowered by 25 % at least. The regeneration of the thermolyzed borohydrides residues, composed from a mixture of alkaline metal hydride and boron, involves a specific chemical treatment which has not been studied up to now.

More promising are the developments of borohydrides through hydrolysis processes. If the hydrogen stored percentage must take into account the hydrolysis chemical reactions, the technical conditions of the hydrolysis directed the storage capacity. The hydrogen recovery process involves water as a reactant and a key of the "fuel" efficiency is the conditions of the reaction of hydrolysis. The amount of hydrogen is fixed by the stoichiometry of the reaction but the ultimate state of the formed borate after hydrolysis controls the yield of the reaction. Water and the hydrates obtained from borohydrides become the most important key of the storage capacity. If all the hydrogen of water can be recovered, the high hydrogen content of water allows high "fuel" efficiency. If the dehydration conditions of the side products formed after hydrolysis are not possible or require too hard conditions, the storing fuel yield will be lowered.

The option of hydrolyzing borohydride-water solutions has to face two antagonist conditions: the solution must be as stable as possible to avoid any hydrogen leaking but the hydrolysis reaction must be as fast as possible to feed the fuel-cell with hydrogen. This balance is difficult and choices must be made to favor technical solutions.

The recycling of the borate resulting from the hydrolysis must be done out of the hydrogen consuming zone and technical points are presently not yet resolved, especially for on board applications.

REFERENCES