Borohydrides for hydrogen storage. Thermolysis or hydrolysis advantages and disadvantages.

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Introduction

Borohydrides are the highest hydrogen containing compounds. However the recovering of hydrogen is not simple and easy. Two main ways of hydrogen generation are possible:

- Thermal decomposition,

- Hydrolysis using various oxo compounds.

For on board application the ratio between the total weight of the hydrogen generation system and the useful energy is a key problem. In this balance, the required energy to evolve hydrogen from the storing material must be taken into account, specially because this energy must be subtracted from the available store hydrogen.

The two hydrogen production manners will be discussed taking into account the mobile duties for on board utilization specially for automobile application.

Literature and State of Art

The more common values for physical properties:

Borohydride	$LiBH_4$	$NaBH_4$	KBH_4	$Be(BH_4)_2$	$Mg(BH_4)_2$	$Al(BH_4)_3$
Mol. weight	21.8	37.8	53.9	38.62	53.9	71.4
Melt Point °C	268	505	585			- 64.5
Decomp. Temp°C	380	314	584	123	320	
Density	0.68	1.08	1.17			0.57
$\Delta H^{f}_{298.15}$ kJ.mol-1	-184.5	-183.3	-242.3			- 301.8
$S°_{298.15}$ J.mol-1.deg-1	128.7	126.2	162			289
Hydrogen total weight %	18.3	10.6	7.4	20.7	14.8	16.8

From BD James& MGH Wallbridge Prog in Inorg Chem 1970 Vol 11 p99-N N Greenwood Pergamon text in Inorg. Chem. Vol 8

Hydrogen recovering using thermal decomposition

Widely studied to evolve hydrogen **- Main problems encountered**

Melting of the borohydride → lowering of the surface area → solution : dilution with silica (Züttel 28 % W) Hydrogen content 13 %

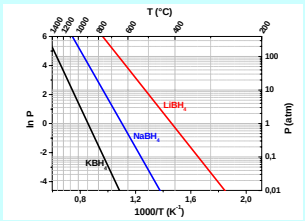
Alkaline metal decomposition (high temperature leading to gaseous alkaline metal).

Difficult solution → decomposition never performed and storage is lower.

	$LiBH_4$	$NaBH_4$	KBH_4
Simple hydride	LiH	NaH	KH
Dec temp/ met melt (°C)	450 /180	250/97	255/63
Hydrogen weight %	13.7	7.9	5.5

Impossibility to use borohydrides in a reversible storage process :
Couple temperature and pressure impossible to manage for on board utilization.

The Van t'Hoff diagrams show high pressure and temperature to be used in a reversible process.

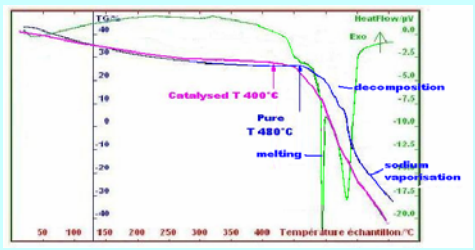


** Efficiency of catalysis*

Thermogravimetric decomposition of sodium borohydride under 10 mBar of hydrogen. Comparison between

- **pure $NaBH_4$ TG (bleu) and DTA (green)**
- **and 1% Pd containing sample (violine)**

The decomposition temperature lowering is very small.



Hydrogen recovering using hydrolysis

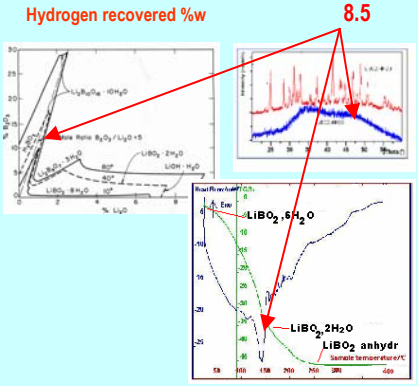
** Water becomes a reactant → the storing properties are fixed by the hydrolysis relations;*

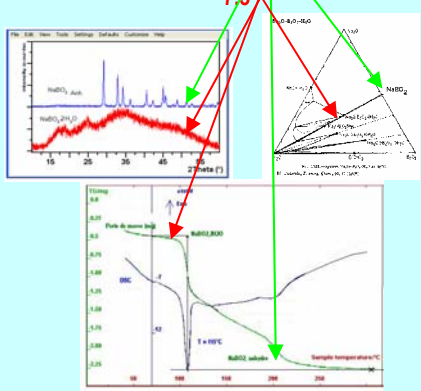
** Water storing possibilities are related to the the hydration of by products 11.1 for anhydrous borates, 5.55 if hydrated*

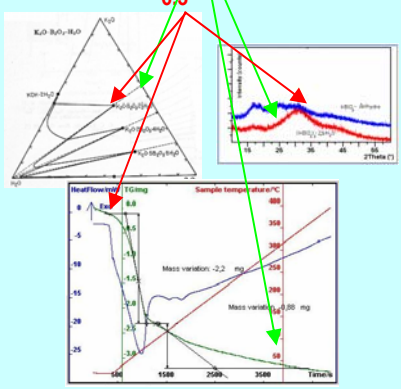
$MBH_4 + 2\,H_2O \rightarrow MBO_2 + 4\,H_2$ *or* $MBH_4 + 4\,H_2O \rightarrow MB(OH)_4 + 4\,H_2$

Under standard conditions, hydrolysis of borohydrides never yield anhydrous borates.

	$LiBH_4$	$NaBH_4$	KBH_4
Theoretical Hydrogen wt%.	18.3	10.6	7.4
Solution 2xH_2O Mol Weight	57.8	73.8	89.9
Hydrogen recovered wt %	13.8	10.8	8.9
Solution 4xH_2O/ Mol Weight	93.6	109.8	125.8
Hydrogen recovered %w	8.5	7.3	6.3







CONCLUSIONS

In spite of their high hydrogen content, the utilizations of borohydrides appeared difficult to manage especially for on board applications.

Thermal decomposition of borohydrides **occurred at high temperature and the melting of the salts before or during the decomposition required the dilution of the borohydrides that lower the storage capacities. The last step of hydrogen recovering is never performed to avoid alkaline metal sputtering into the system. However the Van t'Hoff plotting are not precise, the decomposition of borohydrides could not be considered as reversible under domestic conditions. This storage way seems to be impossible for the moment.**

Hydrogen production through hydrolysis **: this technique is more promising specially for on board applications. Using solutions of borohydrides, several industrial developments are under progress. The role of water in the hydrogen storage is preponderant. The temperature of the reaction is a key of the water role as discussed above. If the reaction temperature is kept at a higher value than the dehydration of the more stable hydrate of the formed borate, very high hydrogen contents can be reached.**

An other important key is the possibilities of recover the hydrolyzed products. Using stabilized solutions of sodium borohydride and hydrolysis known process (Millenium Cell) , a new opportunity has been patented claiming metastable solution of metaborate. That seems to be a real opportunity to fit this storage way to automobile restricting conditions. Patent has been deposed in this way recently in France.

LITERATURE

Non exhaustive list of participants ! more than 200 references, Millenium Cell, Merit, H.I. Schlesinger, H.C. Brown, E. Wiberg, H. Nöth, V.I. Mikheeva, J. Plesek, A. Züttel, S. Suda, S. Amendola, Y. Wu, E. Foulkes etc……..