

Can small additions of an organic polymer or surfactant to sodium borohydride show the way to high hydrogen storage systems for portable applications?

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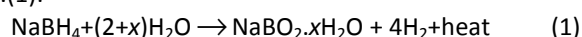
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1 Introduction

Currently, there is a great interest in the use of solid state materials for the storage of hydrogen. Hydrides of light elements may represent the only viable method of achieving a high weight percent and high volume density of stored hydrogen; sodium borohydride (NaBH₄) has such features [1].

NaBH₄ reacts with water to generate molecular hydrogen according to the hydrolysis reaction shown in Eq.(1):



Ideal hydrolysis is attained for $x = 0$, but in practice excess of water is required accounting for the fact that the by-product (NaBO₂·xH₂O) can exist with varying degrees of hydration [2]. Ferreira et al. [3-4] show that at moderate pressures and temperatures below 335 K the value of x is 2.

In this work we report original data on high gravimetric hydrogen density when a small amount of an organic polymer or a surfactant is added to the reactant solution before its injection in the reactor. An organic polymer, Carboxyl Methyl Cellulose (CMC), and a surfactant, Sodium Dodecyl Sulphate (SDS), both in the form of fine powder, were added to the reactant solution before its injection in the reactor. The obtained results emphasize the potential of the chemical hydride for use in portable applications. As far as the authors are aware, this effect has not been described in the literature.

2 Experimental procedure

2.1 Materials and experimental set-up

A nickel based bimetallic catalyst (patent pending) in the form of a finely divided powder was prepared from a mixture of precursors - impregnating small quantities of ruthenium in the nickel salts (Riedel-de Haën) - by chemical reaction with 10 wt% borohydride solution (Rohm and Haas), as the reducing environment.

A volume of 20 mL of reactant solution, prepared with 10 wt% NaBH₄ (Merck) and stabilized with 7 wt% NaOH (Eka), were injected into one of the reactors (0.369 L and 0.229 L), by a syringe. Another two solutions were as well prepared by addition of 0.25 wt%

CMC and 0.25 wt% SDS. Weighed amounts of reused catalyst were in the proportion of bimetallic Ni-based catalyst/NaBH₄: 0.4 g/g and had been previously stored in the conical bottom of the two reactors tested (the adopted reactor bottom configuration – conical - enables non-dispersible effects of contacting powdered catalyst and the injected reactant solution). More specific details of experimental procedures are explained on an earlier work [5].

All the experimental tests were performed with temperature control (318 K) and after reaction completion; magnetic stirring inside the reactor was allowed for 30 minutes to promote complete saturation of H₂ with the remaining by-product solution.

3 Results and discussion

3.1 Effect of pressure in hydrogen generation

Plots in Figure 1 show a typical course of a hydrogen generation reaction presented in terms of the operating pressure as a function of time, for one single loading *fuel* solution in the smaller reactor.

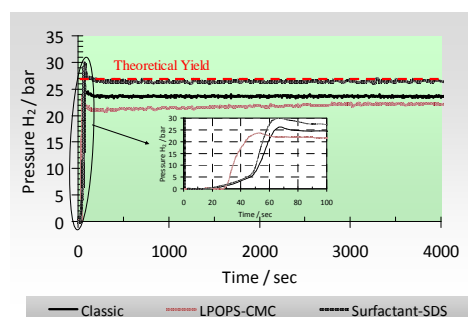


Fig. 1. Hydrogen generation by a single loading of 20 cm³ of reactant solution, with bimetallic Ni-based/NaBH₄: 0.4g/g.

Table 1 reports the hydrogen yield for the three studied solutions, in the two batch reactors. Assuming 100% efficiency conversion, the maximum hydrogen generated (evaluated by the maximum reached pressure inside the batch reactor) was found to be lower than that predicted by the ideal gas law; this effect was more pronounced in the smaller reactor. A very reasonable explanation for this behaviour was related with solubility effects [5].

Table 1. Hydrogen yield for the studied reactant solutions in the two batch reactors and prevision of respective H₂ solubility effects.

REACTOR	H ₂ yield, %	10 wt% NaBH ₄ and 7 wt% NaOH		
		without polymer	CMC, 0.25 wt%	SDS, 0.25 wt%
0.369 l	H ₂ yield, %	97	98	99
	Solubility effects, %	3	2	1
0.229 l	H ₂ yield, %	89	95	99
	Solubility effects, %	11	5	1

The addition of polymer CMC and surfactant SDS results in a *less Polar Organic Polymeric Solution (IPOPS)* changing the overall conductivity of the remaining solution; see table 2 for data before and after the reaction.

Table 2. Values of conductivity and pH of the studied reactant solutions.

20 mL reactant solution 10 wt% NaBH ₄ , 7 wt% NaOH	before the reaction		after the reaction	
	Conductivity (mS/cm)	pH (-)	Conductivity (mS/cm)	pH (-)
Classic - no polymer addition	80,3	13,4	64,5	13,4
plus 0.25 wt% CMC	80,5	13,6	67,5	13,4
plus 0.25 wt% SDS	87,1	13,4	23,0	13,5
temperature	298 K			

3.2 Finding structures of NaBH₄ hydrolysis by-products

By-product suitable crystals of the hydrogen generation reaction for the three studied reactant solutions were obtained by slow evaporation of water solution, and were analyzed by X-Ray Diffractometry (XRD). *i)* For *classic* reaction (1), the by-product is a metaborate dehydrate, NaBO₂·2H₂O, see Fig. 2; *ii)* For the reactants presented in reaction (1) plus addition of 0.25wt% CMC, the crystal structure of the by-product is a borate anhydrous, NaBO₄ (with boron atoms in a tetrahedral configuration with four oxygen atoms), schematically presented in Fig.2; *iii)* For the reactants presented in reaction (1) plus addition of 0.25wt% SDS, the crystal structure of the by-product reveals that the oxygen atoms adopt a tetrahedral conformation around half of the boron atoms and a triangular conformation around the other half. Hence, a tetraborate anhydrous structural unit, Na₂B₂O₉, schematically presented in Fig.2, shows the BO₃ triangles and the BO₄ tetrahedra sharing oxygen atoms so as to produce endless zigzag chains.

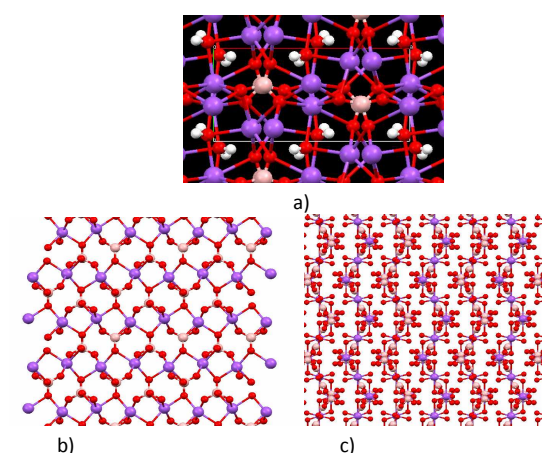


Fig. 2. View along the *c*-axis of the crystal structure Na in violet, O in red, B in pink and H in white; a) sodium metaborate dehydrate. b) adding CMC to the reacting solution; c) adding SDS

Adding just 0.25 wt% of CMC and 0.25wt% of SDS to the reactants described in equation 1, results in the formation of an anhydrous crystalline borates. Unexpectedly,

it seems that both CMC polymer and SDS surfactant behave like desiccators of the NaBH₄ by-product hydrolysis. Maybe the low value, 1%, found for H₂ solubility in the remaining solution (with 0.25 wt% SDS) can now be explained by the capability of forming micelles enclosing water instead of hydrogen gas, in a way similar to a clathrate.

It is though that the presented results are significant findings in terms of:

- NaBH₄ by-product hydrolysis recyclability. In fact, the inexistence of H₂O in the crystalline borates mentioned in *(ii)* and *(iii)*, marks effectively a cost reduction in the process of recycling these by-products back to NaBH₄, comparing the same stage of the process but with the traditionally NaBO₂·H₂O.

- Gravimetric H₂ density. Actually, the ability to produce anhydrous sodium borate (or metaborate) is the key to increase the overall storage density of systems based on sodium borohydride as the storage media [1,2,6]. For 2015, automotive hydrogen storage systems targets for gravimetric H₂ density (FreedomCAR/DOE) point toward 9.0 wt% [2]. The gravimetric hydrogen density for the experiments reported in this work can be *ideally* found, assuming H₂O/NaBH₄: 4, and 2 mol/mol, respectively, for items *(i)*, *(ii)* and *(iii)*, mentioned above. The obtained results indicate that the gravimetric H₂ density is 6.0 wt% for the *classic* reactant system; 8.8 wt% for reactant systems with 0.25 wt% CMC and 0.25 wt% SDS, representing a remarkable improvement from previous work by the authors [5].

4 Conclusions

Results presented in this work showed that gravimetric density of the hydrolysis of borohydride can be improved to reach targets imposed by the DOE for 2015 giving ~9 wt%, by adding small amounts of surfactant or polymer to the *classic* reactant solution.

5 Acknowledgements

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6 References

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