

## NaOH free hydrolysis of sodium borohydride for hydrogen production

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### Abstract

*An experimental investigation is presented, in a closed pressure vessel, on the reaction of powder sodium borohydride (NaBH<sub>4</sub>) with a stoichiometric amount of pure liquid water for hydrogen production, using an improved reused non-noble nickel-based catalyst (Ni-based/NaBH<sub>4</sub>: 0.2 and 0.4 g/g). No alkali aqueous solution was previously used in this catalytic reaction of NaBH<sub>4</sub>, so we are in the presence of NaOH free hydrolysis of sodium borohydride for hydrogen generation.*

*The experiments were performed in three batch reactors with internal volumes of 646 cm<sup>3</sup>, 369 cm<sup>3</sup> and 229 cm<sup>3</sup>, without magnetic stirring and under uncontrolled temperature (289-295 K). The H<sub>2</sub> generated at moderate pressures was a function of the added water and it was found that the hydrogen yield increases with increasing H<sub>2</sub>O/NaBH<sub>4</sub> ratio. As the H<sub>2</sub>O/NaBH<sub>4</sub> ratio departs from 2 and approaches 8, an increase in the hydrogen yield occurs from 47 up to 98%, for pressures of 0.22-0.45 MPa.*

*The gravimetric and volumetric hydrogen densities attainable in this work at pressure up to 1.26 MPa, respectively 6.3 wt% and 70 kgH<sub>2</sub>/m<sup>3</sup>, were high enough to reach the 2010 FreedomCAR requirements published by the US Department of Energy (DOE).*

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**Keywords:** sodium borohydride; nickel-based catalyst; hydrogen generation; NaOH free; high pressure

### 1 Introduction

The advent of low or carbon-free primary energy sources are of unprecedented interest for a sustainable world's energy economy. In this context, hydrogen is being labelled the energy carrier after the 'petroleum era'. As a combustible fuel, hydrogen produces more energy per kg (12.24×10<sup>4</sup> kJ) than fossil coal, petroleum and natural gas. In addition, hydrogen, as a fuel, has a number of advantages including: minimal environmental pollution; mass transportability comparable to petroleum and natural gas; combustibility in internal combustion engines (Carnot-cycle devices) and rocket engines; and feasibility of electrochemical combination with an oxidant in fuel cells [1].

Proton exchange membrane fuel cells (PEMFC) have been intensively studied in the last decade. This free-energy device takes H<sub>2</sub> and O<sub>2</sub> as input and produces electricity as output. Pure hydrogen is required as the fuel in PEMFC and among many

known vials producing and storing the gas [2], precursor chemicals play an important role in hydrogen-based energy systems, for example various types of hydrides including the chemical hydrides.

Among the chemical hydrides, sodium borohydride (NaBH<sub>4</sub>) has a number of advantages over all other hydrides. It is a compound of known composition which can be made to liberate a stoichiometric amount of hydrogen, is stable under ordinary storage conditions and does not undergo violent reaction [1]. Schlesinger et al. [3] recognized the potential usefulness of NaBH<sub>4</sub> as a hydrogen generator, and the particularly striking catalytic effect of certain transition metals and their salts on its hydrolysis rate. Relevant work was carried out during sixties [1, 4-5], and more recently Amendola [6,7] gave a practical, controlled and portable concept of molecular hydrogen generation using catalytic aqueous sodium borohydride solutions.

$\text{NaBH}_4$  reacts with water to generate molecular hydrogen according to the hydrolysis reaction shown in Eq.(1):



Ideal hydrolysis is attained for  $x = 0$  [3], but in practice excess of water is required accounting for the fact that the solid by-product ( $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ ) can exist with varying degrees of hydration [8-10]. A direct consequence of this is the value of hydrogen storage density. In fact, hydrogen storage capacity can be as high as 21 wt% based on the amount of hydrogen generated per unit mass of sodium borohydride consumed, but the real formation of the hydrated by-product severely compromises the overall storage density, which can be calculated to be close to 4 wt% by taking the amount of hydrogen produced divided by the total weight of the reactants [11].

Lytle et al. [12] observed that commercial borohydride deteriorates rapidly in aqueous solution, but is fairly stable in basic solutions and furthermore the higher the pH the greater the stability. This finding brought the solution pH as the limiting parameter of reaction (1) and forced researchers to find a practical and controlled way of producing hydrogen by the use of catalysts. Heterogeneous catalysis offers a number of advantages: independence of solution pH over a wide range, controllable hydrolysis rate and the reuse of the catalyst.

Several metal catalysts are effective reaction catalysts to enhance hydrolysis of the alkaline sodium borohydride solution. Among them, the catalysts with precious metals most used are: rhodium, platinum, ruthenium [5-7], platinum supported on  $\text{LiCoO}_2$ ,  $\text{CoO}$  and  $\text{TiO}_2$  [13-15] or carbon [16], ruthenium supported on IRA-400 anion resin [17] or alumina pellets [18], ruthenium nanoclusters [19], and Pt/Pd on carbon nanotubes (CNT) paper [20].

The most used high-performance catalysts containing non-noble metals are: nickel [3, 21], nickel and/or cobalt borides [1, 4, 22-29], cobalt boride supported on nickel foam [30, 31] or carbon [32], cobalt boride amorphous alloy powder and Pd/C [33], cobalt on  $\gamma$ -alumina [34], hydrogenphosphate stabilized nickel(0) nanoclusters [35], Co-Mn-B supported on nickel foam [36], and Co-P catalyst [37,38]. A metal alloy catalyst containing a less precious metal:  $\text{Ru}_{60}\text{Co}_{20}\text{Fe}_{20}$  supported on activated carbon fiber, have been reported by Park *et al.* [39], who found high hydrogen release in the reaction given by Eq.(1).

Excluding the works of Kojima et al. [15] and Pinto et al. [25], all the works mentioned reported experiments performed in reaction vessels at ambient pressure. In a previous paper, a nickel-

based catalyst was found to work as a good catalyst for releasing hydrogen by hydrolysis of  $\text{NaBH}_4$  alkali solution in a batch reactor [25].

Since the gravimetric hydrogen density of  $\text{NaBH}_4$  is 4.3 wt% by the conventional alkali solution, that is to say, by the conventional excess of water [15], the present authors try to implement an experimental procedure to produce pure hydrogen gas with higher gravimetric and volumetric densities.

In this paper it is shown that by using powder  $\text{NaBH}_4$ , a stoichiometric amount of water, a reused Ni-based catalyst and moderate  $\text{H}_2$  pressure, hydrogen gas can be produced in large quantities sufficient for use in portable or in situ applications with PEM fuel cells, and meet 2010 FreedomCAR targets published by the US DOE.

## 2 Experimental

### 2.1. Materials

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

The catalyst, characterized by a large specific surface area, was appropriately decanted, washed, filtered, dried and heat-treated at  $110^\circ\text{C}$ . The catalyst was kept in a desiccator until use. In this work, the catalyst is used in powder form, unsupported.

Catalyst samples were analyzed for morphology and elemental analysis on a Phillips Scanning Electron Microscope, Model XL 30 FEG, coupled to EDAX. Figure 1 shows the morphology of the powder exhibiting nanometric particle size and elemental analysis showing nickel as a main constituent.

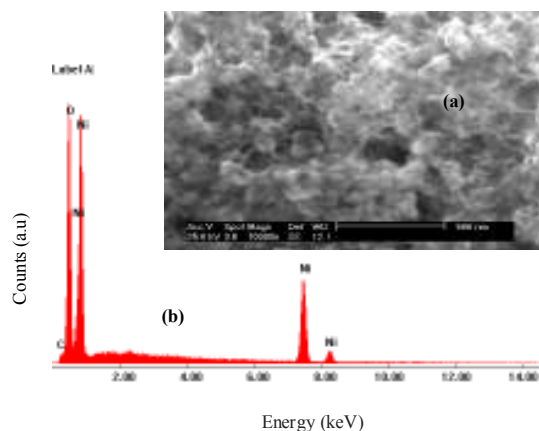


Fig. 1. Scanning electron microscope view of the synthesized catalyst powder (a) and associated elemental analysis EDAX (b).

### 2.1. Hydrogen generation and characterization

Sodium borohydride powder ( $\geq 96\%$  purity) was supplied by MERCK (No.: 1.06371.0100) and was used as received (1.2 g). Deionised water was injected into the reactor by a syringe.  $\text{H}_2\text{O}/\text{NaBH}_4$  (mol/mol) ratios studied were 2-8 mol. Weighed amounts of reused catalyst were in the proportion of Ni-based catalyst/ $\text{NaBH}_4$ : 0.2-0.4 g/g.

Some of the specific details of experimental procedures are explained on an earlier work [25].

Two major improvements were made in the reactor design which allowed an axial installation of O-ring for reactor sealing and the possibility of following the reaction temperature using two k thermocouples positioned at two distinct points inside the reactor: one near its bottom (named T.Bottom) and the other one very close to its top (named T.Top). Figure 2 shows the exposed view of the news reactors.

The three reactors used in the experiments have an internal free volume of  $646 \text{ cm}^3$ ,  $369 \text{ cm}^3$  and  $229 \text{ cm}^3$ , the last two with an inside conical bottom geometry. This configuration enables non-dispersible effects of contacting powdered catalyst and  $\text{NaBH}_4$  with the injected pure water.

Experimental tests were performed without magnetic stirring and without temperature control (289-295 K). A proper quantity of nickel-based powdered catalyst and solid  $\text{NaBH}_4$  were previously measured in an analytical balance and then stored in the bottom of the reactor. After sealing perfectly the reactor, an adequate amount of  $\text{H}_2\text{O}$  was rapidly injected into the reactor by means of a syringe with a very high needle length (150 mm) to ensure that the water is delivered very close to the powder moisture ( $\text{NaBH}_4$  plus catalyst). The temperature of the reactor medium was monitored and recorded simultaneously with a data acquisition system using Labview software. To monitor the rate of hydrogen generation, the gas pressure inside the reactor was followed with an appropriate pressure probe.

In order to determine the remaining species after reaction (1), at  $\text{H}_2\text{O}/\text{NaBH}_4: \geq 2$  mol/mol, the mixture of the by-product and the catalyst was dissolved in pure water. The metaborate by-product was analyzed with X-Ray Diffractometry (XRD). Suitable crystals were obtained by slow evaporation of water solution and were orthorhombic, space group  $Pca2_1$ , cell volume  $V=364.62(4) \text{ \AA}^3$ . Unit cell parameters  $a = 10.7252(7) \text{ \AA}$ ,  $b = 5.2525(3) \text{ \AA}$ ,  $c = 6.4724(4) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  (uncertainties in parentheses). There are four molecules per unit cell, calculated density of  $2.237 \text{ g/cm}^3$ . Diffraction data were collected at 293 K with a Gemini PX Ultra equipped with  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). A total of 562 independent reflections were measured, of which 501 were observed ( $I > 2\sigma(I)$ ). The structure was solved by direct methods using SHELXS-97 [40] with atomic positions and

displacement parameters refined with SHELXL-97 [41]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined freely with isotropic displacement parameters. The refinement converged to  $R$  (all data) = 3.93% and  $wR^2$  (all data) = 9.92%.

## 3 Results and discussion

The hydrogen yield in reaction (1) was calculated by the following equation

$$\text{Hydrogen yield} = n(\text{H}_2)_{\text{exp}}/n(\text{H}_2)_{\text{theoretical}} \quad (2)$$

where  $n(\text{H}_2)_{\text{exp}}$  is the number of moles (mol) of generated  $\text{H}_2$  and  $n(\text{H}_2)_{\text{theoretical}}$  is the theoretical amount of generated  $\text{H}_2$  assuming 100% conversion of  $\text{NaBH}_4$  by applying the ideal gas law to the final volume of gas inside the reactor. Special care was taken to correct the free varying volume of gas inside the reactor due to the consumption of  $\text{NaBH}_4$  and water.

Figure 3 shows the course of hydrogen generation in terms of  $\text{H}_2$  pressure as a function of time, for the batch reactor with internal volume of  $646 \text{ cm}^3$ , by changing the amount of  $\text{H}_2\text{O}/\text{NaBH}_4$  (mol/mol) ratio from 2 to 8 mol and Ni-based catalyst/ $\text{NaBH}_4$ : 0.4 g/g.

In all the experiments reported in this work it was used an amount of approximately 1.2 g of  $\text{NaBH}_4$  (equivalent to the mass of  $\text{NaBH}_4$  existing in  $\sim 10 \text{ cm}^3$  of an alkali solution of 10 wt%  $\text{NaBH}_4$ , 7 wt%  $\text{NaOH}$ , 83 wt%  $\text{H}_2\text{O}$ , [25]).

These results show an improvement in the performance of the Ni-based catalyst used in this work, comparing with the similar trend published by Pinto et al. [25], the latter with a larger particle size. In fact, the nano-powdered Ni-based catalyst gives high  $\text{H}_2$  yield in a relatively short reaction time until the 'plateau' is achieved with a few moles of molecules of water by excess (for  $\text{H}_2\text{O}/\text{NaBH}_4$ : 8 mol/mol).

Kojima et al. [15] reported an  $\text{H}_2$  yield of about 80% with  $\text{H}_2\text{O}/\text{NaBH}_4$ : 2 mol/mol and Pt- $\text{LiCoO}_2/\text{NaBH}_4$ : 0.5 g/g, after 400 s, at 0.68 MPa and 296 K. The same authors reported, for the same experimental conditions but at atmospheric pressure, only 37%, with the plateau reached on 330 s.

As shown in Fig.3, the hydrogen yield found in this work in a similar experiment with  $\text{H}_2\text{O}/\text{NaBH}_4$ : 2 mol/mol and Ni-based/ $\text{NaBH}_4$ : 0.4 g/g at 0.22 MPa and 295 K, was about 47 %, reached in 125 min.

The substantial lower value obtained by the present authors may be due to the different catalyst used – Kojima et al. [15] used a noble one, and also by a lower hydrogen pressure (0.22 MPa instead of 0.68 MPa [15]).

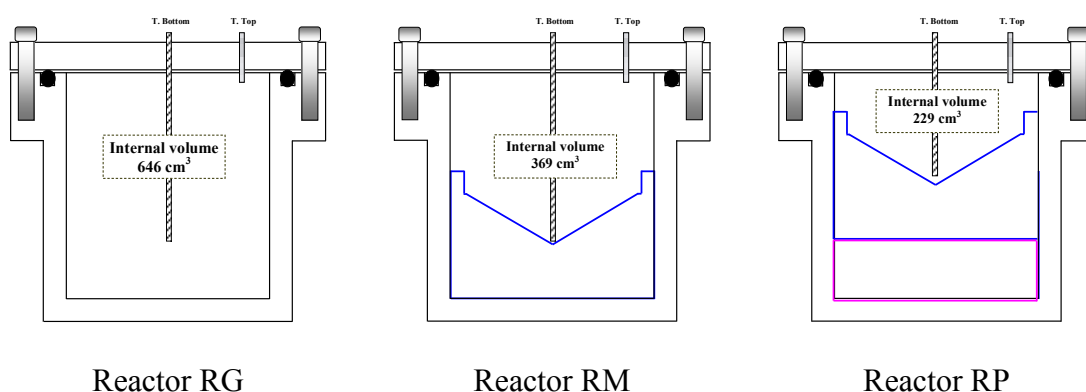


Fig. 2. Schematic view of the inside of the reactors: reactor RG – flat bottom, and reactors RM and RP – conical bottom.

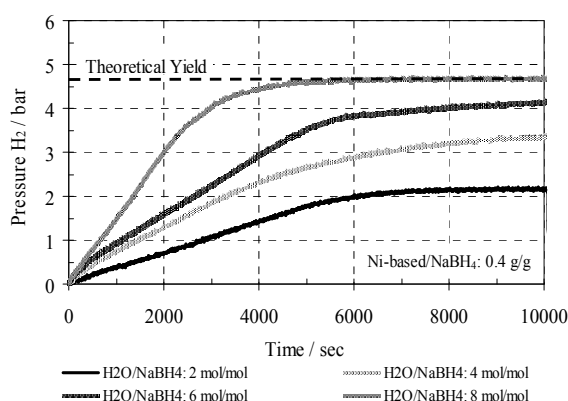


Fig. 3. Hydrogen generation in the flat bottom batch reactor (646 cm<sup>3</sup>) for experiments with Ni-based/NaBH<sub>4</sub>: 0.4 g/g and H<sub>2</sub>O/NaBH<sub>4</sub>: 2-8 mol/mol.

To solve this apparent incomplete reaction (1) by H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol, we decided to open the closed pressure vessel and injected a second loading of pure water with the same H<sub>2</sub>O/NaBH<sub>4</sub> (mol/mol) ratio.

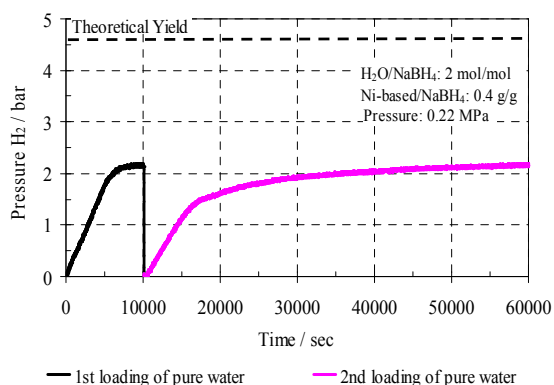


Fig. 4. Hydrogen generation in the batch reactor (646 cm<sup>3</sup>) with Ni-based/NaBH<sub>4</sub>: 0.4 g/g and H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol, after two successive individual loadings of pure water.

This new mass of water reacts with the unreacted NaBH<sub>4</sub> present inside the batch reactor after the first loading of water, for which the experimental H<sub>2</sub> yield was 47 %. As expected, the amount of hydrogen gas that was generated is approximately the same that was generated in the first loading of water. Figure 4 shows the results of the experimental procedure mentioned above.

The cumulative amount of hydrogen generated gave an absolute H<sub>2</sub> pressure of 4.33 bar, with a total H<sub>2</sub> yield of 94 %. Accounting to this fact and to experimental rig design characteristics, the nature of the unsupported and non-noble reused catalyst, and for the fact that the experiments were performed at uncontrolled room temperature and at moderate pressures, up to 12.6 bar, it was decided that the minimum ratio H<sub>2</sub>O/NaBH<sub>4</sub> (mol/mol) needed to be 4 mol instead of 2 mol, to ensure that sodium borohydride in reaction (1) is the limiting reagent. The following figures and tables correspond to the use of H<sub>2</sub>O/NaBH<sub>4</sub>: 4 mol/mol. Figure 5 shows the hydrogen yield versus the pressure at the stoichiometric amount of water using Ni-based catalyst (Ni-based/NaBH<sub>4</sub>: 0.4 g/g). The experimental results found in the present work are compared with those of Kojima et al. [15].

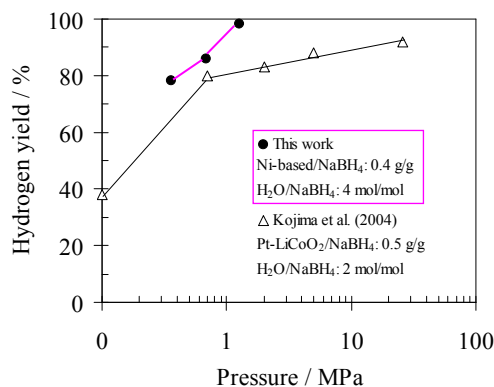


Fig. 5. Influence of pressure on H<sub>2</sub> yield (this work at 289-295 K).

For moderate pressures (0.36-1.26 MPa), H<sub>2</sub> yields up to 78-98% are obtained. Kojima et al. [15] reported 80-93% for hydrogen yield under high pressures (0.7-25 MPa) at H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol. Figure 5 shows the important finding that the 150 times reused Ni-based catalyst (Ni-based/NaBH<sub>4</sub>: 0.4 g/g) has high activity under moderate pressure and that results in a significant increase in the amount of hydrogen generated. Kojima et al. [15] conclude the same trend at H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol but with a noble catalyst (Pt-LiCoO<sub>2</sub>/NaBH<sub>4</sub>: 0.5 g/g) and at much higher H<sub>2</sub> pressure (up to 25 MPa).

Figure 6 shows the influence of added water, H<sub>2</sub>O/NaBH<sub>4</sub> (mol/mol), on hydrogen yield.

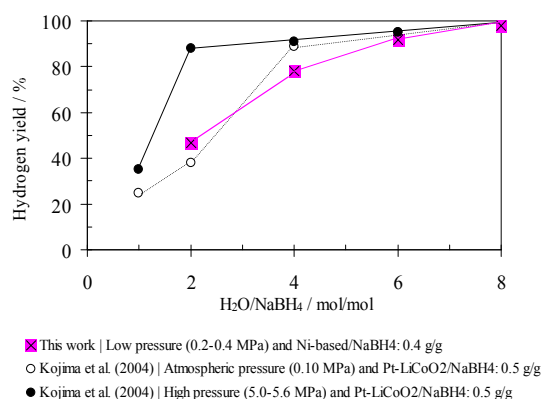


Fig. 6. Hydrogen yield as a function of added water, H<sub>2</sub>O/NaBH<sub>4</sub> (mol/mol).

Comparing this work results (at 293-295 K with a Ni-based/NaBH<sub>4</sub>: 0.4 g/g) with those of Kojima et al. [15] (at 296 K with Pt-LiCoO<sub>2</sub>/NaBH<sub>4</sub>: 0.5 g/g), plotted in the same figure, we observe that the H<sub>2</sub> yield increases with increasing H<sub>2</sub>O/NaBH<sub>4</sub> ratio. That tendency was found more moderate in the present work. For a molar ratio H<sub>2</sub>O/NaBH<sub>4</sub> of 2 to 6 mol/mol, a H<sub>2</sub> yield of 47-92% was obtained at low pressure (0.22-0.45 MPa). Kojima et al. [15] reported a strikingly sharp increase in hydrogen yield as H<sub>2</sub>O/NaBH<sub>4</sub> departs from 1 to 2, with values of 35 up to 87%; for 6 mol/mol a 95% yield was reported, all values obtained at high pressure (5.0-5.6 MPa). For atmospheric and moderate pressures, high values of H<sub>2</sub> yield are obtained (≥ 80%) only for H<sub>2</sub>O/NaBH<sub>4</sub>: ≥ 4 mol/mol.

The crystal structure of reaction (1) by-product reveals that the boron atoms are in a triangular configuration with three oxygen atoms, with B-O bond lengths between 1.27 and 1.29 Å. The BO<sub>3</sub> triangular arrangement was already found in the crystal structure of orthorhombic [42] and monoclinic [43] metaboric acid, although in the title crystal structure the oxygen atoms are bound to just one B atom. The BO<sub>3</sub> triangles form layers 3.238 Å apart that sandwich a layer of sodium and water molecules (see Fig. 10). For each boron atom

there are three bound oxygen atoms and one water oxygen. Half of the sodium atoms have their valence strength distributed between six Na-O bonds and the other half between seven Na-O bonds (as already determined in other sodium metaborate structures [44]). The water molecules are involved in a net of interactions with the sodium atoms (see Fig. 7).

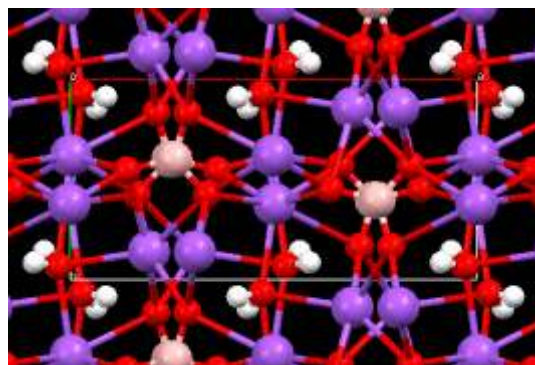


Fig. 7. View along the *c*-axis of the crystal structure of sodium metaborate dehydrate, showing the BO<sub>3</sub> triangular arrangement and the Na bound network. Na in violet, O in red, B in pink and H in white.

It was found that the reaction (1) by-product at H<sub>2</sub>O/NaBH<sub>4</sub>: ≥ 2 mol/mol, is a sodium metaborate dehydrated, NaBO<sub>2</sub>·2H<sub>2</sub>O.

Thus, the reaction of powder NaBH<sub>4</sub> with a stoichiometric amount of water in the presence of a reused Ni-based catalyst at moderate H<sub>2</sub> pressure, is written as follows



Kojima et al. [15] found that the by-product, at H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol, is an amorphous sodium metaborate, NaBO<sub>2</sub> (*x* = 0 in eq.(1)).

The time required for an increase in hydrogen generation is defined as the induction period [15]. Table 1 reports the H<sub>2</sub> yield as a function of induction period and compares the values of this work with those of Kojima et al. [15]. The latter found that the induction period is approximately independent of pressure, for H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol. In our study, we found an enormous difference in induction period: 20,000 → 100 s as pressure increases from 0.36 → 0.69 MPa. Maybe a good explanation for this result resides in the shape of the reactor bottom: the induction period of 100 s was observed in the reactor with a conical bottom, for H<sub>2</sub>O/NaBH<sub>4</sub>: 4 mol/mol. Consequently, a sharp increase in the temperature of hydrolyzed NaBH<sub>4</sub> was registered, as shown in Fig. 8 (295 → 428 K).

We may conclude that when the temperature of hydrolyzed hydride increased the induction period decreased. A similar trend was found by Kojima et al. [15].

The temperature in the batch reactor (with a conical bottom), at 0.69 MPa, shows the maximum value of

428 K after the induction period, and decreases rapidly with time.

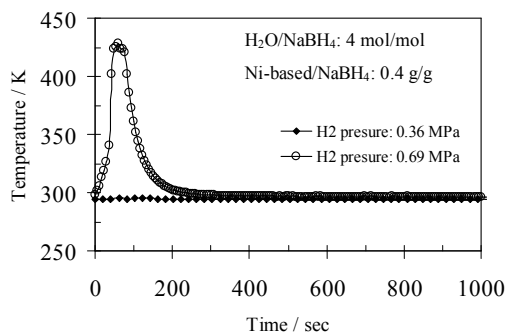


Fig. 8. Temperature of the hydrolyzed  $\text{NaBH}_4$  as a function of time by different pressure.

Kojima et al.[15] reported that the structure of the by-product produced from the reaction of  $\text{NaBH}_4$  and water using  $\text{Pt-LiCoO}_2$ , is  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$  at atmospheric pressure and  $\text{NaBO}_2$  at high pressure. Consequently the temperature of the hydrolyzed  $\text{NaBH}_4$  is higher in the catalyzed reaction at 0.10 MPa compared to the reaction at 0.68 MPa. One possible explanation for this increase in the reaction temperature was the energy required for the addition of two water molecules in the heat of formation of  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ . In fact, the lower exothermic reaction temperature increased the yield of  $\text{H}_2$  probably because the  $\text{H}_2$  is not consumed to hydrate  $\text{NaBO}_2$ . A similar behaviour was found in this work in the experiments performed on reactors RM and RP (see Fig.1). A decrease in the temperature from 295 to 289 K increased the  $\text{H}_2$  yield from 86 to 98% on  $\text{H}_2\text{O}/\text{NaBH}_4$ : 4 mol/mol and  $\text{Ni-based}/\text{NaBH}_4$ : 0.4 g/g experiments, respectively, in RM and RP reactors. The amount of catalyst is another variable that influences the induction period. As can be seen in the plot of Fig.9, increasing the amount of the catalyst decreased the induction period: 27,300  $\rightarrow$  21,200 s for  $\text{Ni-based catalyst}/\text{NaBH}_4$ : 0.2 g/g  $\rightarrow$  0.4 g/g; but the hydrogen generated was similar (0.36 MPa) and independent of the temperature (295 K).

Since the main purpose of the experimental study reported in this work is to produce pure hydrogen gas with very high gravimetric and volumetric densities, and following closely the results of Kojima et al. [15], we conclude that the ability to produce anhydrous sodium borate is the key to increasing the overall storage density of systems based on sodium borohydride as the storage media. The US Department Of Energy (DOE) has published FreedomCAR requirements for automotive hydrogen storage systems. Two of the principal technical targets, based on system mass and volume, are the gravimetric hydrogen density

and the volumetric hydrogen density. Table 2 shows these FreedomCAR two specifications [10].

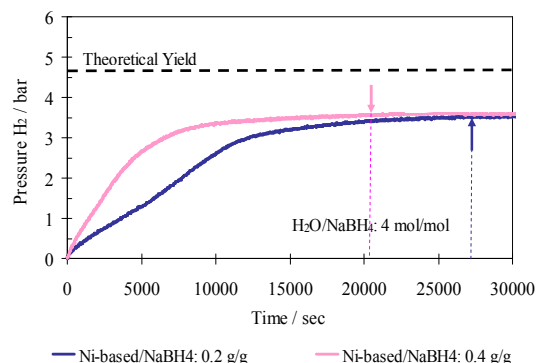


Fig. 9. Influence of the amount of catalyst in the induction time.

Table 3 shows the influence of  $\text{Ni-based catalyst}/\text{NaBH}_4$  on gravimetric hydrogen density and hydrogen yield for  $\text{H}_2\text{O}/\text{NaBH}_4$ : 4 mol/mol. A prediction of the volumetric hydrogen density is also presented. The density of our materials ( $\text{H}_2\text{O}/\text{NaBH}_4$ : 4 mol/mol;  $\text{Ni-based}/\text{NaBH}_4$ : 0.2-0.4 g/g) was calculated by an addition relationship of the densities of  $\text{NaBH}_4$  (1.07 g/cm<sup>3</sup>), water (1.00 g/cm<sup>3</sup>) and  $\text{Ni-based catalyst}$  (3.17 g/cm<sup>3</sup>) [15].

It was found that our system of compressed hydrogen generation by moderate pressure of 1.26 MPa is currently capable of meeting 2010 FreedomCAR targets published by the US DOE. Results published by Pinto et al. [25], using the conventional excess of water method ( $\sim 10 \text{ cm}^3$  of an alkali solution of 10 wt%  $\text{NaBH}_4$ , 7 wt%  $\text{NaOH}$ , 83 wt%  $\text{H}_2\text{O}$ ) and performed also at moderate pressures (up to 0.49 MPa), gave a gravimetric hydrogen density of 4.1%. Working with  $\text{NaOH}$  free hydrolysis of a chemical hydride ( $\text{NaBH}_4$ ) using stoichiometric amount of water and low cost efficient catalysts (capable of releasing large quantities of  $\text{H}_2$ ), is the path to find a new  $\text{H}_2$  storage technology for fuel cell vehicle.

It is worthwhile to notice that sustainable methods to recycle  $\text{NaBO}_2$  or  $\text{NaBO}_2 \cdot \text{H}_2\text{O}$  back to  $\text{NaBH}_4$  would be a very important obstacle to overcome for the adoption of  $\text{NaBH}_4$  as an energy carrier of choice for automotive  $\text{H}_2$  fuel cell applications.

The  $\text{H}_2$  generated in this work, at pressures below hydrogen critical pressure, was supplied to a PEMFC fuel cell that was housed in a bus like shape mobile platform, used for didactic proposes – the “MicroBoro Bus” [26].

Table 1  
Hydrogen yield as a function of time by different pressure

H <sub>2</sub> yield / %	Time / sec	Pressure /MPa		Reactor bottom
78	20000	0.36	<b>This work</b>	H <sub>2</sub> O/NaBH <sub>4</sub> : 4 mol/mol flat
86	100	0.69		Ni-based/NaBH <sub>4</sub> : 0.4 g/g conical
40	400	0.10	Kojima	H <sub>2</sub> O/NaBH <sub>4</sub> : 2 mol/mol
80	500	0.68	et al. (2004)	Pt-LiCoO <sub>2</sub> /NaBH <sub>4</sub> : 0.5 g/g

Table 2  
FreedomCAR targets published by US Department of Energy [10]

Year	2007	2010	2015
Gravimetric H <sub>2</sub> density / wt.%	4.5	6.0	9.0
Volumetric H <sub>2</sub> density/ kgH <sub>2</sub> /m <sup>3</sup>	36	45	81

Table 3  
Influence of Ni-based/NaBH<sub>4</sub> on gravimetric hydrogen density and hydrogen yield for H<sub>2</sub>O/NaBH<sub>4</sub>: 4 mol/mol.  
Prediction of the volumetric hydrogen density\*.

Ni-based/NaBH <sub>4</sub> / g/g	Gravimetric H <sub>2</sub> density / wt.%	H <sub>2</sub> yield / %	Volumetric H <sub>2</sub> density* / kgH <sub>2</sub> /m <sup>3</sup>	Pressure / MPa
0.2	5.3	78	57	0.36
0.4	5.0	78	56	0.36
0.4	5.3	86	59	0.69
0.4	6.3	98	70	1.26

\* It was assumed that the average value of the density of our materials, by addition relationship of densities of NaBH<sub>4</sub> (1.07 g/cm<sup>3</sup>), H<sub>2</sub>O (1.00 g/cm<sup>3</sup>) and Ni-based catalyst (3.17 g/cm<sup>3</sup>) is:

**1.07 g/cm<sup>3</sup>**, for H<sub>2</sub>O/NaBH<sub>4</sub>: 4 mol/mol, Ni-based catalyst/NaBH<sub>4</sub>: 0.2 g/g; and

**1.11 g/cm<sup>3</sup>**, for H<sub>2</sub>O/NaBH<sub>4</sub>: 4 mol/mol, Ni-based catalyst/NaBH<sub>4</sub>: 0.4 g/g

## 4 Conclusions

The unsupported and reused Ni-based catalyst, offered in a finely divided powder having a large specific surface area, shows a high activity under moderate pressure up to 1.26 MPa and produced nearly the theoretical H<sub>2</sub> yield using a stoichiometric amount of water (H<sub>2</sub>O/NaBH<sub>4</sub>: 4 mol/mol). A similar finding was reported elsewhere, with a noble catalyst (Pt-LiCoO<sub>2</sub>/NaBH<sub>4</sub>: 0.5g/g and H<sub>2</sub>O/NaBH<sub>4</sub>: 2 mol/mol, [15]).

The compressed hydrogen generation using chemical hydride may lead to a new H<sub>2</sub> storage technology for portable or in situ applications and meet 2015 FreedomCAR targets published by the US DOE.

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