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HYDROGEN PRODUCTION BY CATALYTIC HYDROLYSIS OF SODIUM BOROHYDRIDE IN BATCH REACTORS: NEW CHALLENGES

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ABSTRACT

The present manuscript faces the study of H_2 generation and storage from catalytic hydrolysis of sodium borohydride ($NaBH_4$) under pressure. We revisit several works on this topic developed (or under development) by our team in the last four years on some of the most critical issues in this research area, namely catalyst durability/reutilization, gravimetric hydrogen storage density and recyclability. New results are also presented.

Hydrogen generation rates and yields and hydrogen storage capacities can be augmented to reach ≈ 6 wt%, by adding small amounts of an organic polymer (CMC) to the *classic* $NaBH_4$ hydrolysis, performed with stoichiometric amount of water in a batch reactor with a conical bottom shape and in the presence of Ni-Ru based catalyst, reused from 300 times.

Sodium tetrahydroxoborate, $NaB(OH)_4$), was produced in the presence of CMC additive, and did not show crystalline water in its crystal structure. This latter finding has potential to reduce recycling costs of $NaBO_2$ back to $NaBH_4$ and also increase the overall storage density of systems based on $NaBH_4$ as hydrogen carrier.

1. INTRODUCTION

Hydrogen (H_2) has been recognized as a clean energy carrier of the future. To promote the *fuel* hydrogen on the road to a sustainable and climate-friendly energy economy, the commitment of industry, societal support for innovation and market launch strategies for H_2 and fuel cells are essential. Important challenges related to production, storage and distribution must be overcome to reach a, for the moment utopian, Hydrogen economy. Produced hydrogen needs to be effectively and safely stored with high gravimetric/volumetric storage capacities. Reversibility of hydrogen storage and durability and cost of fuel cells are also important technological barriers.

Chemical and metal hydrides have a very high volumetric H_2 storage density on a materials basis [1,2]. Complex hydrides, such as some boron hydrides, are among the most promising hydrogen storage systems. In particular, sodium borohydride ($NaBH_4$) and ammonia-borane (NH_3BH_3) have been considered as the *chosen* hydrogen carriers for mobility due to their high theoretical gravimetric and volumetric hydrogen storage capacities [3,4]. Unfortunately, the effective values of these storage densities are well below those maximum values due to inefficiency: both hydrides exhibit low storage densities in aqueous solutions, there is hydrogen spent in recycling the by-products and loss of performance related to catalyst durability [4]. These and other difficulties led to a no-go recommendation from the U.S. DOE concerning the use of $NaBH_4$ in on-board automotive hydrogen storage [5]. However, the intense published literature on sodium borohydride as energy/hydrogen carrier has definitively shown its potential for portable or niche applications [5,6].

Some critical problems in the development of hydrogen generation technology from $NaBH_4$ hydrolysis have been generally stated [7,8]. Catalyst degradation is a very well known difficulty. Agglomeration of catalyst particles, surface oxidation of catalyst and catalyst component dissolution in alkaline $NaBH_4$ solutions are common reasons for catalyst deterioration. The strong generation of hydrogen bubbles in the liquid phase promotes shocks between catalyst particles that can contribute to damage the material, particularly for high H_2 production rates [7]. Sodium borohydride reacts with water (H_2O) to generate molecular hydrogen according to the hydrolysis reaction:

$$NaBH_4 + (2+x)\ H_2O \rightarrow NaBO_2.xH_2O\ +\ 4\ H_2 + \text{heat}, \qquad (1)$$

where x represents the excess hydration factor [8]. A critical issue in the development of an efficient hydrogen generator from $NaBH_4$ is the amount of water needed for reaction completion. For person-portable and transportation applications, the amount of water required for complete hydrolysis must be minimized in order to minimize the system volume and mass. Ideal hydrolysis is attained for $x = 0$ [9], where two moles of water are required to react with one mole of solid $NaBH_4$ to release four moles of hydrogen. In practice, excess of water is necessary to guarantee that the by-product $NaBO_2$ remains in the liquid phase avoiding degradation of catalytic performances. Another reason for the use of excess water is the fact that the stable form of reaction by-product is $NaBO_2.xH_2O$ with various degrees of hydration [8].

The hydrolysis reaction for production of hydrogen from sodium borohydride is nonreversible. Sodium borohydride utilization on a large scale will requires a low energy intense method of recycling the reaction by-products back to $NaBH_4$ [10]. Researchers keep looking for an efficient approach that will decrease the cost and energy consumption of the recycling process such as the conversion of $NaBO_2$ to borax. It seems that a more energy efficient route is possible if borax is used as the starting material for $NaBH_4$ production [11].

In the present paper we revisit several works on the sodium borohydride hydrolysis developed (or under development) by our team in recent years [12-16] on some of the most critical issues in this research area. Three different types of catalytic hydrolysis of sodium borohydride were considered, two of them in the presence of an inhibitor (sodium hydroxide, NaOH), namely *alkali* hydrolysis and *less Polar Organic Polymeric Solutions (lPOPS)* and the other, in absence of NaOH, designated by *alkali free* hydrolysis (or solid $NaBH_4$ hydrolysis). New results are now presented.

2. EXPERIMENTAL PROCEDURE

2.1. Catalyst

Most of the hydrolysis experiments related in references [12-16] occurred in the presence of a nickel-based bimetallic catalyst of Ni-Ru, in the form of a finely divided powder and unsupported, 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, has been used since its synthesis in many of our studies with the purpose of studying reutilization and aging (still running at the present time), and reached the impressive number of almost 300 reutilizations. Weighted amounts of catalyst in the proportion of Ni–Ru based catalyst/$NaBH_4$ varying from 0.1 to 0.6 g/g (or 4.2 and 6.2 wt% of catalyst) were selected. Between the experiments, the used Ni–Ru based catalyst was separated by sedimentation from the by-product slurry, washed five times with deionised water, dried at 80 ºC for

3 hours and re-used. A detailed study of textural properties and morphology of the catalyst can be found on a separate publication [15].

2.2. Hydrogen generation experiments

Typically, in the alkali hydrolysis experiments (with and without polymer additives), a volume of 10 cm^3 of stabilized sodium borohydride aqueous solutions (the water being in excess: x equal to 16 or $H_2O/NaBH_4$: 18 mol/mol), with 10 wt% $NaBH_4$ (Rohm and Haas, ≥ 98% purity) and 7 wt% NaOH (Eka, ≥ 98% purity), was injected into the tested batch reactors by means of a syringe. In the most recent works [14-16], three batch reactors - the *large reactor*, LR, with internal volume of 0.646 L, the *medium reactor*, MR with internal volume of 0.369 L and the *small reactor*, SR, with internal volume of 0.229 L (see Fig.1) – made of stainless-steel and positioned vertically, were carefully designed, with optional flat and conical bottom shapes.

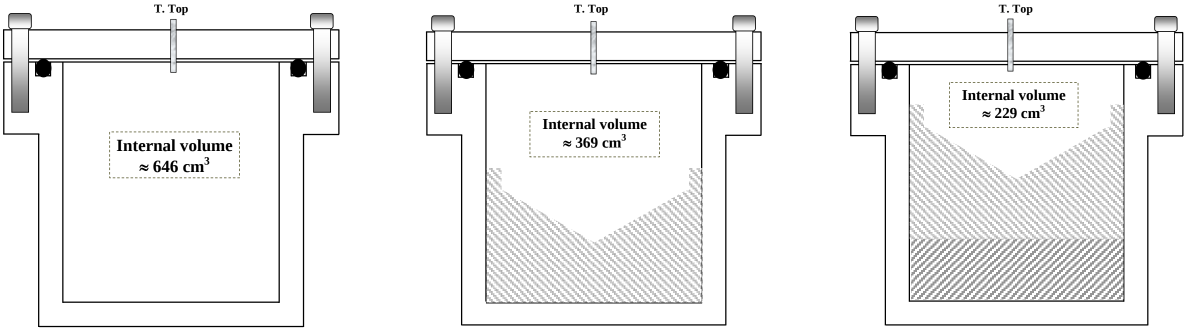

Figure 1. Schematic view of the inside of the three batch reactors: (a) reactor LR/0.646 L with flat bottom shape, (b) reactor MR/0.369 L and (c) reactor SR/0.229 L, the later two with conical bottom shapes.

In the *alkali free* hydrolysis (or solid $NaBH_4$ hydrolysis) the reactant blend was produced without adding NaOH aqueous solution to solid $NaBH_4$. Hence, the proper quantity of powder catalyst and solid $NaBH_4$ were mixed together in the solid state, forming a solid powder mixture. Next, this mixture was stored at the bottom of the reactor and the reaction vessel was closed and after proper sealing, an adequate amount of deionised water was rapidly injected into the reactor.

The effects of temperature, sodium borohydride concentration, sodium hydroxide concentration, catalyst concentration and system pressure, on the hydrogen gas generation rate, were investigated for the different types of hydrolysis. Particular importance was given to the effects of the reactor bottom geometry on hydrogen generation yields, rates and induction times.

More specific details of the experimental rig and procedure are explained elsewhere [12-16].

3. RESULTS AND DISCUSSION

3.1. *Alkali free* hydrolysis (or solid $NaBH_4$ hydrolysis)

This type of hydrolysis is excellent from an environmental point of view because it does not involve strongly caustic solutions. Experiments were performed in the three batch reactors. The effects of ratios $H_2O/NaBH_4$ (mol/mol) were studied and the H_2 generated was found to be a function of the added water. Completion was achieved with $H_2O/NaBH_4 = 8$ mol/mol (see Fig. 2). The results showed that hydrogen yields and rates increase remarkably increasing both system temperature and pressure. As can be observed from the plot of Figure 3, the reactor bottom shape deeply influences H_2 generation: the conical bottom shape greatly enhances the rate and practically eliminates the reaction induction time.

Our system of compressed hydrogen generation up to 1.26 MPa showed an effective maximum of 6.3 wt% and 70 kgm^{-3}, for gravimetric and volumetric hydrogen storage capacities (materials only-basis), respectively, with $H_2O/NaBH_4 = 4$ mol/mol [15].

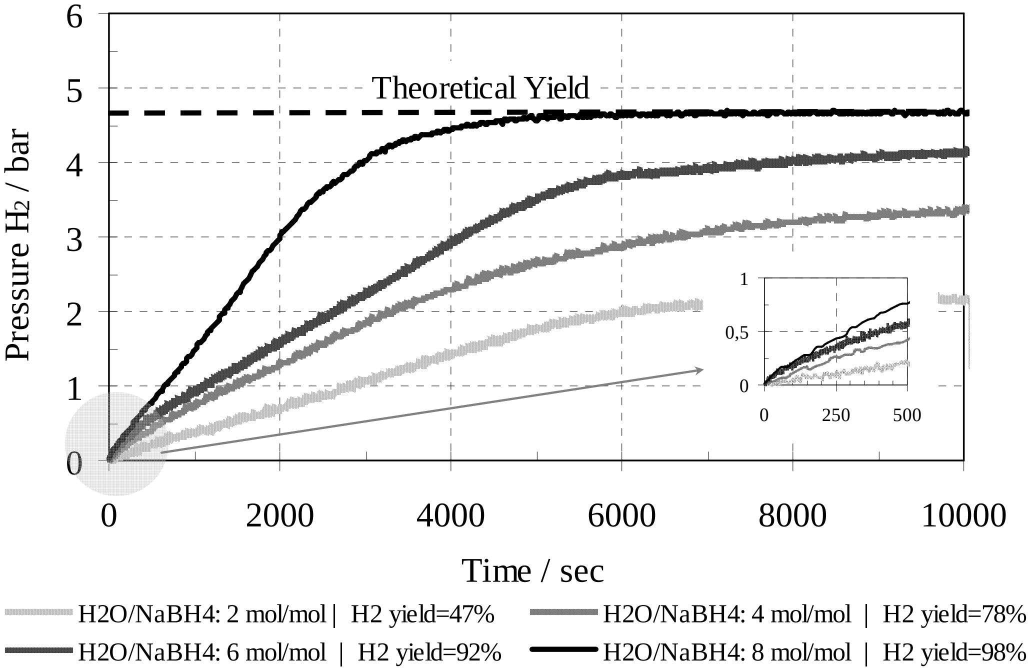

Fig. 2. Hydrogen generation in the flat bottom batch reactor LR (646 cm^3) for experiments with Ni – Ru based catalyst/$NaBH_4$: 0.4 g/g and $H_2O/NaBH_4$: 2-8 mol/mol.

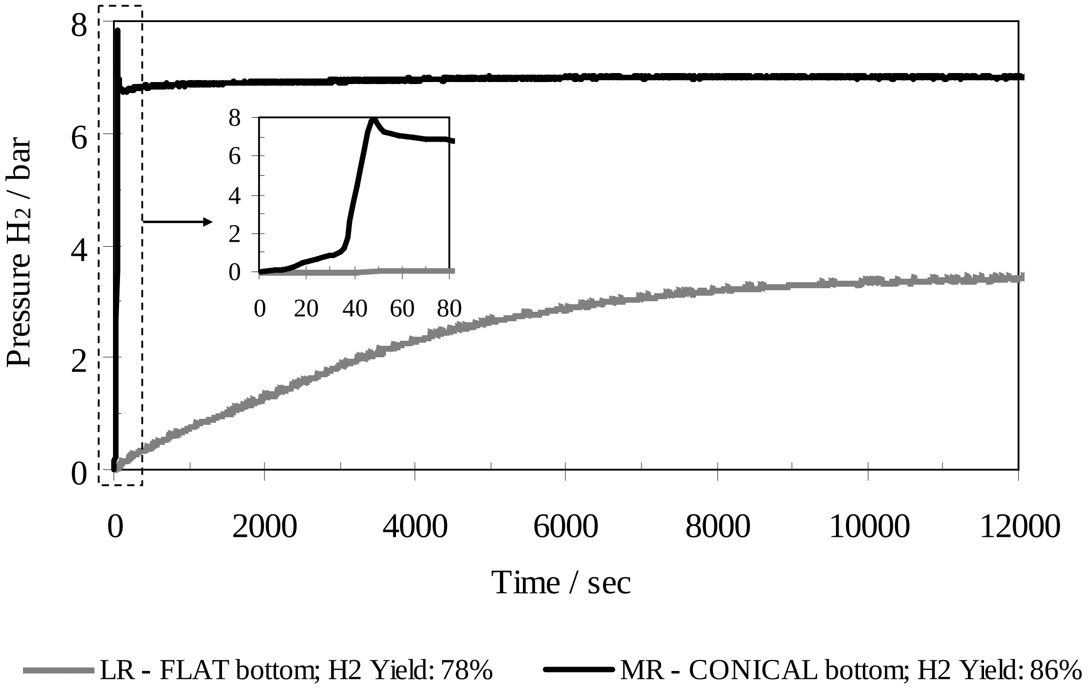

Fig. 3. Influence of reactor bottom shape on H_2 yield, rate and lag time (experiments performed in batch reactors LR (646 cm^3) and MR (369 cm^3), with flat and conical bottom shapes, respectively; at temperature range of 289-295 K, with catalyst reused ≈150 times and $H_2O/NaBH_4$= 4 mol/mol).

3.2. *Alkali* hydrolysis

In an earlier work, the first developed nickel-based catalyst was found to work as a good catalyst for releasing hydrogen by hydrolysis of $NaBH_4$ *alkaline* solution in a batch reactor up to 3 MPa [12]. The catalyst was further developed and in April of 2008 an enhanced powder nickel based bimetallic catalyst (Ni-Ru) was prepared. As already referred, very few papers studied the catalyst durability which is a mistake from an application point of view. Aiming at studying the catalyst durability – it is still under way – we have reused the developed catalyst more than 300 times. Figure 4 shows examples of H_2 generating curves for three catalyst «ages». The catalyst slowly looses performance but still exhibits hydrogen generation rates within the higher values found in the open literature [16].

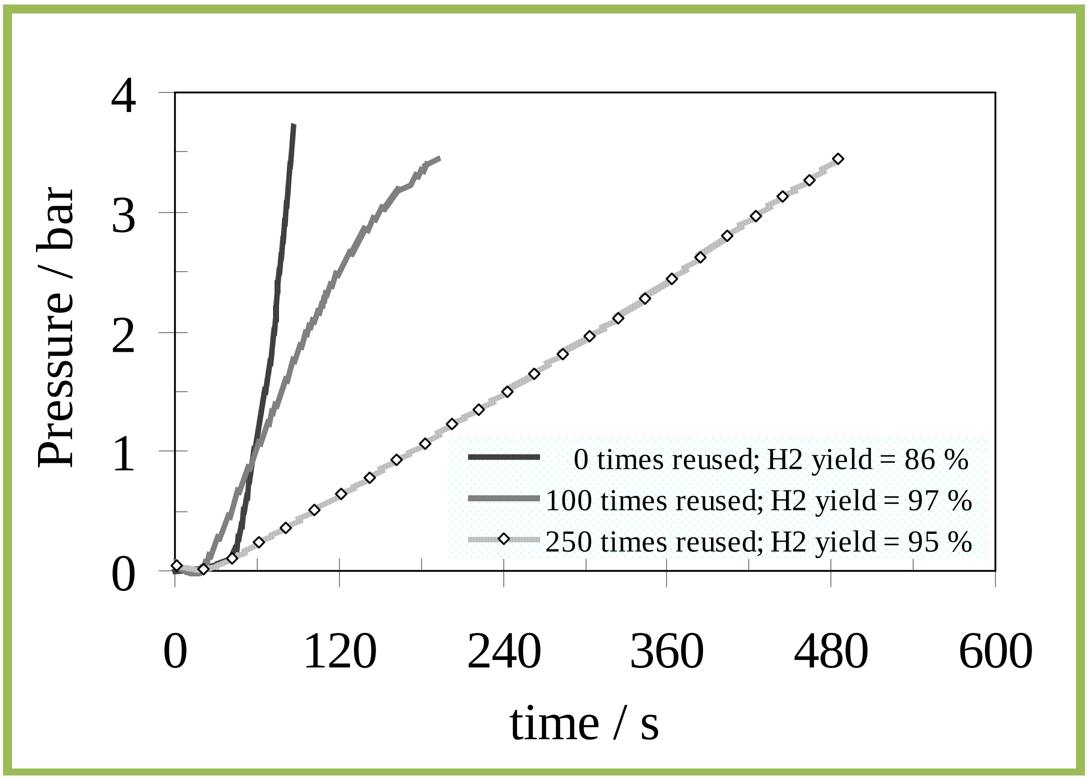

Fig. 4. Hydrogen generation plots with a $NaBH_4$ concentration of 10 wt%, an inhibitor concentration of 7 wt%, for three different stages of catalyst reutilization (0, 100 and 250 times reused). The reactions were performed using 10 cm^3 of reactant solution performed in LR batch reactor with a proportion of Ni-Ru based catalyst/$NaBH_4$: 0.4 g/g and at room temperature of $\approx$ 25 ºC.

Studies on the possibility of refuelling the reactor with $NaBH_4$ fresh solution (successive loadings) without recharging the reactor with fresh catalyst have also been conducted with the reused bimetallic catalyst [14]. In addition, magnetic stirring was allowed to investigate possible mass transfer limitations between the reacting solution and the reused catalyst.

Experiments, performed in vessels LR and MR, without controlled reaction temperature, put in evidence the large quantities of H_2 generated proving the good performance of the re-used catalyst. The activity of the catalyst seems to increase under high pressure after successive loadings. This effect was more intense in the reactor MR due once again to the positive influence of the conical bottom shape.

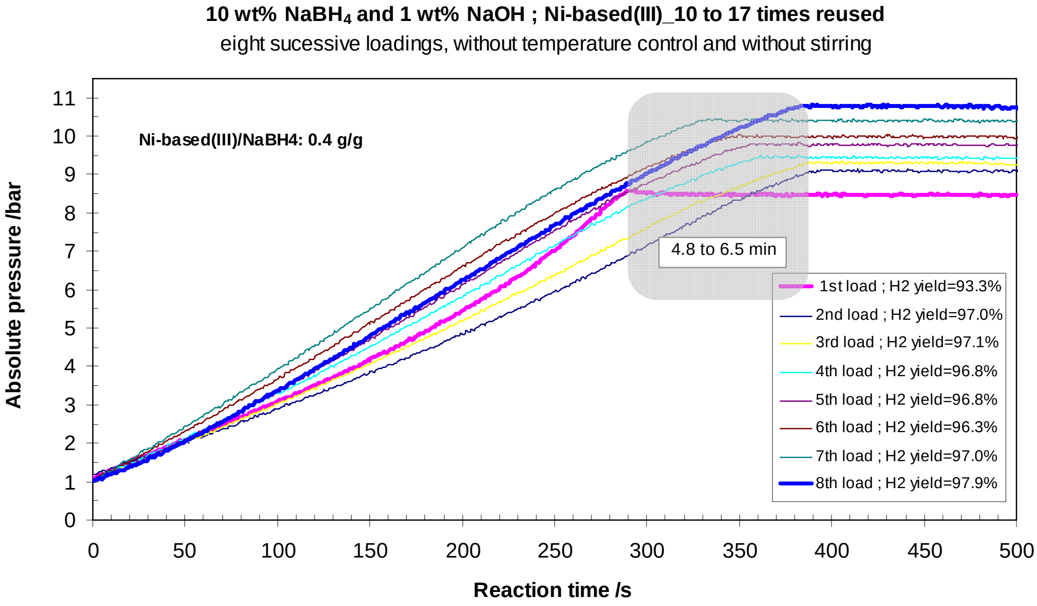

Fig. 5. Hydrogen generation in reactor MR concerning eight successive loadings of the reactant solution, with Ni-Ru based/$NaBH_4$: 0.4g/g (10-17 times re-used): 10 wt.% $NaBH_4$, 1 wt.% NaOH, 89 wt.% H_2O

The increase of the dynamic behaviour of reactants and products inside the reactor by the rise of the internal pressure probably enhance the release of hydrogen in the liquid phase even in the absence of mechanical stirring. The catalyst keeps very good activity in the successive reactions, the induction times are low and the hydrolysis reaches almost completion in short times. The same type of experiments was preformed for different catalyst «ages» with similar results.

The capability of re-use a constant amount of catalyst during successive loadings of *fuel*, without any treatment and without loss of activity, is a major finding if we having in mind the possible applications of this concept for hydrogen generation and storage.

3.3. *less Polar Organic Polymeric Solutions (lPOPS).*

Recently, an experimental study was presented both on the generation and storage of molecular hydrogen (H_2) by small additions of an organic polymer – *carboxymethyl cellulose* (CMC) - to sodium borohydride ($NaBH_4$), through the catalytic alkaline hydrolysis [16]. The main inspiration behind this route was the expected influence of colloids on the solubility of gases in water and the possibility of enhancing that positive impact when increasing the operating pressure, according to Henry's law. The results showed that working at moderate pressures, up to 2.7 MPa, even with reused catalyst around 280 times, increases slightly the H_2 dissolution in the liquid phase, enhanced by the changing of the polarity of the remained solution inside the reactor [16].

In order to study the effect of the molar ratio $H_2O/NaBH_4$ (mol/mol), some experiments using $NaBH_4$ in the solid phase were performed, this time adding to the solid mixture (catalyst and $NaBH_4$) the amount of $H_2O/NaBH_4$ (mol/mol) ratio from 2 to 18. The liquid water was provided from an aqueous stabilised solution with 0.25 wt% CMC. The molar ratio $H_2O/NaBH_4$ strongly affects the H_2 yield and rates. Growing from 2 to 18 in the number of moles of water, the H_2 yield increases from 59% to reaction completion (for example, for x equal to 16 or $H_2O/NaBH_4$: 18 mol/mol, a yield of 100% was achieved), whereas the H_2 generation rate diminishes from 48 to 2.3 $L(H_2)min^{-1}gcat^{-1}$ [16].

3.4. The influence of pressure and reactor bottom geometry on H_2 yields and storage capacity

The plots of Figure 6 put in evidence that the H_2 yield increases with increasing hydrogen pressure. The higher yield was obtained for experiments performed in the smaller batch reactor, SR. Kojima and co-workers reported that, for x=0 and under very high pressures (0.7-25 MPa), H_2 yields up to 80-93% were obtained [17]. Remarkable values for the gravimetric and volumetric hydrogen storage capacity values (6.8 wt% and 74 kgH_2/m^3, GHSC and VHSC, respectively) were obtained at relatively low pressure for the system $H_2O/NaBH_4$: 2 mol/mol, performed in batch reactor SR with bottom conical shape and with Ni-Ru based catalyst 260 times reused.

The results showed as before that hydrogen yields and rates increase remarkably with increasing pressure. The reactor bottom shape influences deeply H_2 generation in solid $NaBH_4$ hydrolysis: the conical bottom shape greatly enhances the rate and practically eliminates the reaction induction time

3.5. The $NaBH_4$ hydrolysis by-products

Analysis of reaction by-products, by X-Ray Diffractometry (XRD), revealed the presence of sodium metaborate di-hydrated in the *alkali* hydrolysis. In the *lPOPS* hydrolysis, sodium tetrahydroxoborate, $NaB(OH)_4$ by-product was produced in the presence of CMC additive, showing the absence of crystalline water in its crystal structure ($NaB(OH)_4$ presents structural water, with boron atoms linked to four hydroxyl groups). This new finding never reported to form at < 50 ºC, has a positive impact in recyclability costs of $NaBO_2$ back to $NaBH_4$ due to the elimination of two energy consuming steps in the metaborate dehydration kinetics.

During the entire experimental studies, the H_2 generated by the catalytic hydrolysis of $NaBH_4$ was successfully used to fuel a PEM fuel cell to evaluate the capabilities of an integrated solution/application [13].

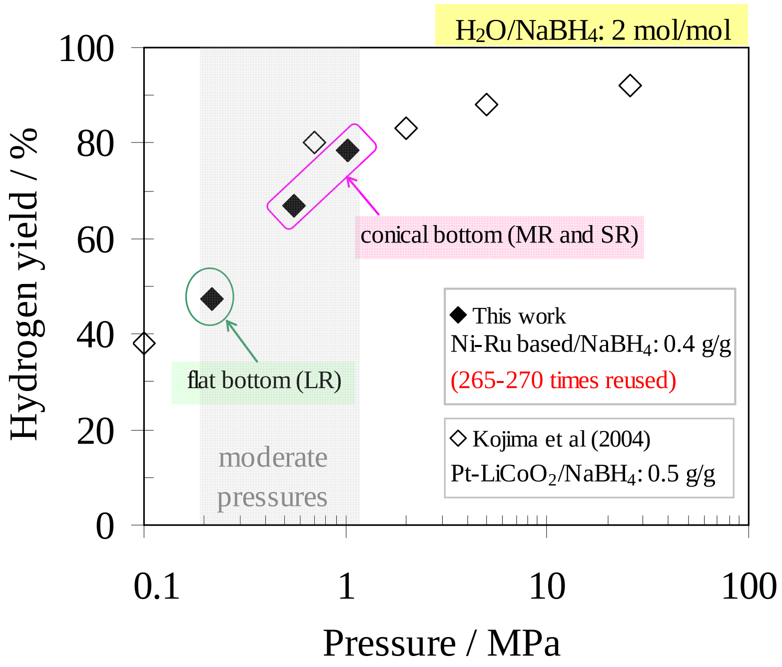

Fig. 6 Influence of pressure on H_2 yield (experiments done in the batch reactors: LR, MR and SR, at room temperature with catalyst Ni-Ru based/$NaBH_4$ = 0.40g/g, reused between 265 to 270 times, for the system $H_2O/NaBH_4$ = 2 mol/mol).

4. CONCLUSIONS

Promising results with potential to overcome some of the critical issues on catalytic hydrolysis of sodium borohydride are here presented. The catalytic abilities of a Ni-Ru based catalyst in H_2 generation rates, even when reused around 300 times, and summarized in the present work, are above the range of the greatest values reported so far in the open literature. The capability of re-use a constant amount of catalyst during successive loadings of *fuel*, without any treatment and without loss of activity, is also a very important finding.

We may conclude that our system of compressed hydrogen at moderate pressures, shows that both H_2 generation rates and yields and hydrogen storage capacities can be augmented, the latter to reach more than 6 wt%, by adding stoichiometric amounts of water (x = 0-2) to the catalytic hydrolysis of solid $NaBH_4$, performed in a reaction vessel with a conical bottom shape, without stirring and at room temperatures.

The *novel route* of adding small amounts of an organic polymer (CMC) to the *classic* $NaBH_4$ hydrolysis, performed with stoichiometric amount of water and up to 2.7 MPa, shows a slightly increased in the H_2 dissolution in the liquid phase, enhanced by the changing of the polarity of the remained solution inside the reactor. Sodium tetrahydroxoborate, $NaB(OH)_4$ by-product was produced in the presence of CMC additive, showing the absence of crystalline water in its crystal structure ($NaB(OH)_4$ presents structural water, with boron atoms linked to four hydroxyl groups). This new finding, never reported to form at < 50 ºC, has a positive impact in recyclability costs of $NaBO_2$ back to $NaBH_4$ due to the elimination of two energy consuming steps in the metaborate dehydration kinetics.The eventual success of this *new route* will depend upon developing a advantageous method of converting borates into tetrahydroborate and also finding materials (chemicals) which enhance the solubility of H_2, promoting its reversible storage in the liquid phase. A deep investigation on this subject is presently under way.

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