HYDROGEN PRODUCTION FROM CATALYTIC HYDROLYSIS OF SODIUM BOROHYDRIDE IN BATCH REACTORS

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Abstract. *The catalytic hydrolysis of alkaline NaBH$_4$ solution was studied using a non-noble, nickel based powdered catalyst exhibiting strong activity even after long time storage. This easy to prepare catalyst showed an enhanced activity after being recovered from previous use. The effects of temperature, NaBH$_4$ concentration, NaOH concentration and pressure on the H$_2$ generation rate were investigated. Particular importance has the effect of pressure, since the maximum reached pressure of hydrogen is always substantially lower than predictions (considering 100% conversion) due to solubility effects. The solubility of hydrogen is greatly enhanced by the rising pressure during reaction, leading to storage of hydrogen in the liquid phase. This effect can induce new ways of using this type of catalyst and reactor in the construction of hydrogen generators and even containers for portable ant in situ applications.*

Keywords: Hydrogen generator; Sodium borohydride; Chemical Hydride; Fuel cell; Hydrogen storage.

1. Introduction

There is a common vision for a new sustainable energy economy, which will be in place in the coming decades and fundamentally based on a diverse spectrum of low or carbon-free primary energy sources. The hydrogen is being focused as the energy source, which will replace the current fossil fuel and be used in the wide application range at the 21st century. H$_2$ can be used directly in internal combustion engines or be oxidized efficiently in fuel cells where the energy obtained in the reaction is converted to electric energy. Fuel cells are alternative power sources for providing clean energy for transportation and personal electronic applications where low system weight and portability are important. Hydrogen has a great number of attractive advantages as an active anodic material such as high energy density, non toxic reaction products and abundant natural resources.

Recently, hydrogen application as a fuel in vehicles has been largely promoting the improvement of conventional physical storage devices (tanks containing gas under pressure or liquefied) and the research and development of more advanced concepts and materials: absorption or adsorption, metallic alloys, metal hydrides, chemical compounds and carbon nanostructures. Since the intermetallic hydrides contain transition or rare earth metals, their hydrogen storage capability in terms of specific energy density is still to low to meet the requirements of various applications. In the last few years, there are numerous attempts to use nanometric materials such as carbon and boron nitride nanotubes but their great hydrogen absorption capacity occurs only at extreme operation conditions.

Hydrogen can also be stored in a chemical hydride such as NaBH$_4$ (Schlesinger *et al.* 1953; Levy *et al.* 1960; Kaufman *et al.* 1985; Kong *et al.* 1999; Aiello *et al.* 1999; Amendola *et al.* 2000a and Amendola *et al.* 2000b), NaH (Dipietro and Skolnik, 2000), LiH (Mclaine *et al.* 2000) or NaAlH$_4$ (Bogdanovic *et al.* 2000). Among these, attention has been given to the hydrolysis of a chemical hydride such as NaBH$_4$ because of the large theoretical H$_2$ content of

10.9%. Sodium borohydride is stable when compared with other chemical hydrides and easy to handle. At room temperatures, only a small percentage of the theoretical amount of hydrogen is released by hydrolysis reaction of $NaBH_4$ and H_20 (Kong *et al.* 1999), but the reaction can be enhanced by using catalysts. Conventionally known catalysts are metal halides, colloidal platinum, activated carbon, fluorinated Mg-based hydride (Suda *et al.* 2001) or ruthenium supported on anion exchange resin (Amendola *et al.* 2000a and Amendola *et al.* 2000b) as well as cobalt and nickel borides (Levy *et al.* 1960; Kaufman *et al.* 1985 and Hua *et al.* 2003). All these works reported experiments performed in reaction vessels at ambient pressure (open systems).

In the present paper, results are reported of studies on the catalyzed hydrolysis reaction of $NaBH_4$ in alkaline solutions by using a non noble nickel based catalyst in batch reactors. The effect of the pressure on the reaction was, as the authors are aware, for the first time referred.

2. Experimental

2.1. Materials
Sodium borohydride (Panreac Química SA) was used for the reaction with water. The reaction of $NaBH_4$ and H_2O is shown as follows:

$$NaBH_4 + 4H_2O \rightarrow NaBO_2 + 4H_2$$
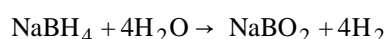
It is well known that the sodium borohydride undergoes self-hydrolysis when stored as aqueous solution. This hydrolysis can be greatly inhibited by addition of NaOH. Detailed discussion on the mechanism of borohydride hydrolysis has been given by Amendola *et al.* 2000a and Amendola *et al.* 2000b. In this work the generation of hydrogen was conducted using stabilized solutions of the sodium hydride using different NaOH concentrations.

2.2. Preparation and activity of the catalyst

A nickel based catalyst in the form of a finely divided powder was prepared from nickel salts by chemical reaction with borohydride solution, in a reducing environment. The catalyst characterized by a large specific surface area, was appropriately decanted, washed, filtered, dried and heat treated before use. Typical experiments involved a 10 wt % sodium borohydride stabilised solution, using 3 wt % NaOH. Concentrations up to 10% NaOH were also used.
The catalyst activity was characterized by the study of the hydrolysis reaction, first conducted using small volumes of the reacting solution, in order to determine reaction rates in different conditions. The produced hydrogen volumes were measured as a function of time at controlled temperature till complete exhaustion of the reactant.
For the catalyst used in this work, a proportion of 0.05 g catalyst/ml (reacting solution) was found suitable.

2.3. Experimental rig

An overview photograph of the experimental rig is presented in Fig. (1). The borohydride batch reactors were two stainless steel cylinders: one with an internal volume 0.444 **l**, for the experiments at lower pressures and the other with an internal volume of 0.213 **l**, for the experiments at higher hydrogen final pressures.
Typical hydrogen generation experiments involved the preparation of the reacting solution adding the appropriate amount of $NaBH_4$ to a certain volume of aqueous solution of the inhibitor NaOH, with the chosen hydroxide concentration. The adequate volume of reacting solution was rapidly injected into the reactor with a syringe. The proper quantity of nickel powdered catalyst had been previously stored in the bottom of the reactor and the perfect sealed H_2 generator introduced in the thermostatic bath for about 15 minutes. After injecting the solution and closing the inlet valve, the reactor was again submersed as shown in the photograph of Fig. (1-a). The generation of hydrogen was followed using the data acquisition system until attaining a constant pressure inside the reactor. For experiments with an expected maximum pressure of hydrogen lower than 10 bar, a pressure probe allowed the acquisition of this parameter along the reaction (Fig. 1-c). For the experiments with higher hydrogen final pressure, this variable was read by means of a bourdon manometer with an appropriate range. For both types of experiments the reaction temperature was followed using a thermocouple and the bath temperature was efficiently controlled at the desired value.
The catalyst used in most of the reported experiments was prepared as described and stored for around two months in an uncontrolled ambient. Before use, the catalyst was heat treated in an oven at 60 ^{0}C for around four hours. With the objective of studying the capability of reuse the catalyst, in some experiments the used nickel powder was recovered from the remaining solution in the reactor after previous use, by washing, filtrating and drying in an oven at 60 ^{0}C.
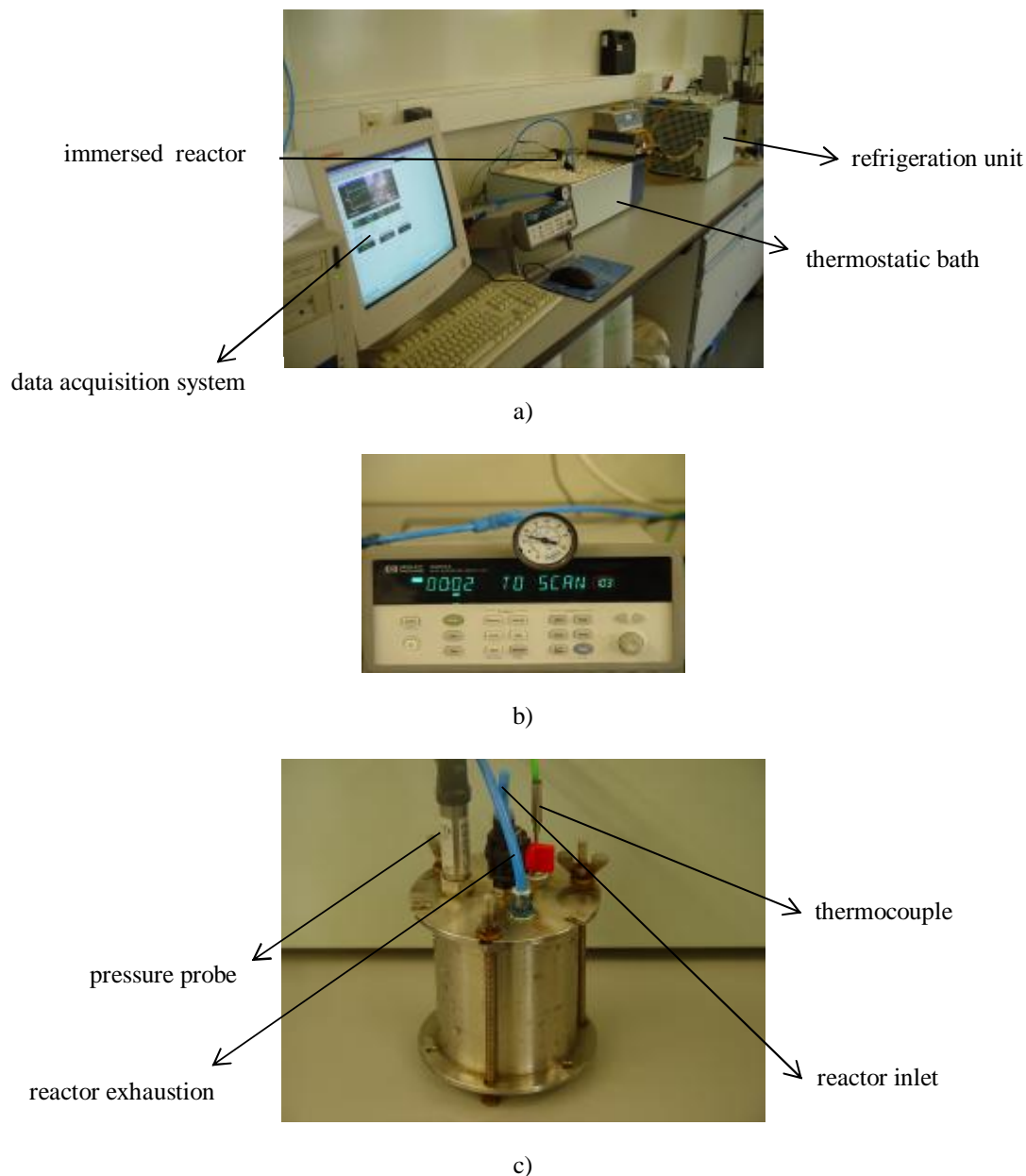
a)

b)

c)

Figure 1. Experimental set-up a) general view; b) pressure reading c) batch reactor (internal volume 0.444 **l**)

3. Results and Discussion

As already referred, hydrogen was generated from the hydrolysis of sodium borohydryde solutions. The effects of temperature, $NaBH_4$ concentration, NaOH concentration and pressure on the H_2 generation rate were studied. The experimental conditions studied are summarized in Tab (1).

The volume of reacting solution used in each experiment was calculated for a given predicted maximum H_2 pressure, (Tab. 1), assuming 100% conversion efficiency, by applying the ideal gas law to the final volume of gas in the reactor. This final gas volume was corrected adding to the initial volume of gas, the extra volume corresponding to the reacted moles of water. In the calculation procedure, care was always taken to use the appropriate specific weight of the aqueous NaOH solution with different values of wt%.

It is well known that the hydrolysis reaction is exothermic. The temperature control system used was efficient since the temperature elevation during reaction was less than 2 ^{o}C for all the studied conditions.

Table 1. Experimental conditions

| Temperature (°C)	Wt% NaBH$_4$	Wt% NaOH	H$_2$ predicted maximum pressure (kPa)	H$_2$ maximum pressure obtained (kPa)	Reactor volume (l)	Reacting solution volume (l)	Reused catalyst (Y/N)
45	10	7	700	469	0.444	0.0098	N
25	10	7	700	548	0.444	0.0104	N
55	10	7	700	622	0.444	0.0095	N
45	10	3	700	495	0.444	0.0095	N
45	20	3	700	469	0.444	0.0005	N
45	10	10	700	604	0.444	0.0098	N
45	20	7	700	513	0.444	0.0005	N
45	20	10	700	520	0,444	0.0005	Y
45	10	7	700	497	0,444	0.0098	Y
45	10	10	2000	1380	0.213	0.0123	Y
45	10	10	2600	1960	0.213	0.0153	Y
45	10	10	3100	2500	0.213	0.0187	Y
45	10	10	3600	2910	0.213	0.0215	Y

3.1. Effect of the reaction temperature
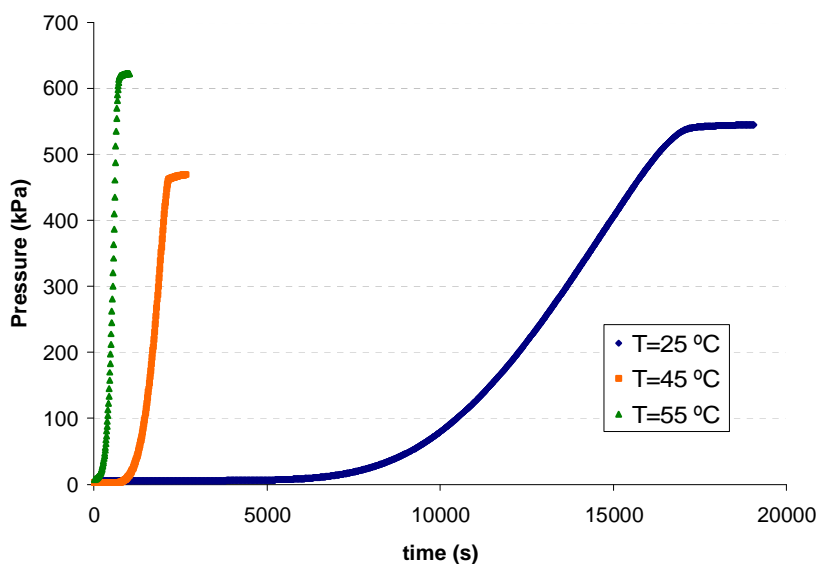
Figure 2. Hydrogen generation with a NaBH$_4$ concentration of 10%, an inhibitor concentration of 7% for a maximum H$_2$ predicted pressure of 700 kPa at different temperatures

The influence of temperature on the velocity of the H$_2$ generation is put in evidence in the plots of Fig. (2). The reaction rate is very sensitive to this variable. As expected, the rate rises with the increase in temperature and the hydrogen pressure demonstrates a nearly linear variation with reaction time. The reaction rate remains practically constant when, during reaction, the NaBH$_4$ concentration decreases, demonstrating zero order reaction as was also found by Kaufman and Sen (1985) and Hua *et al.* (2003). The time needed for the reaction to begin is substantially higher for the lower temperature.

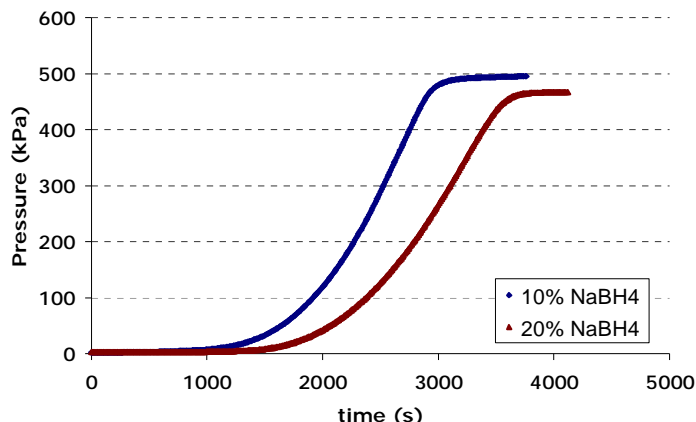### 3.2. Effect of NaBH$_4$ concentration on H$_2$ generation rate

Figure 3. Hydrogen generation with an inhibitor concentration of 7%, at 45°C for a maximum H$_2$ predicted pressure of 700 kPa with different NaBH$_4$ concentrations.

Figure (3) shows the influence of the NaBH$_4$ concentration on the H$_2$ generation rate. As the borohydride concentration increases the reaction rate tends to decrease. Accordingly, the reaction starting time is higher for the higher NaBH$_4$ concentration.

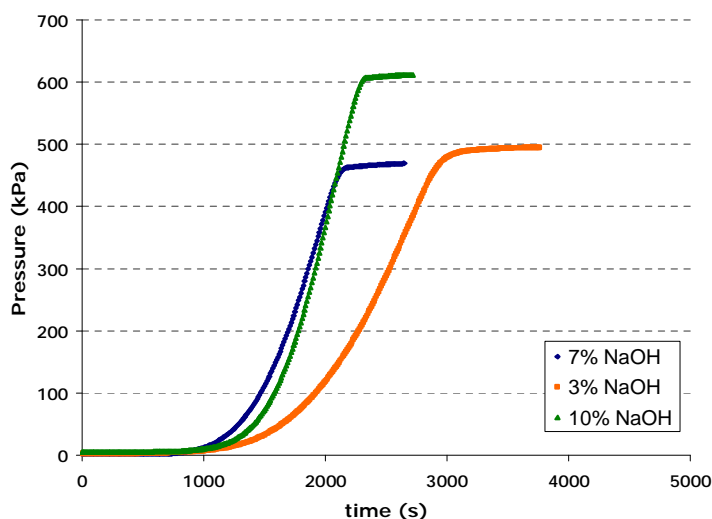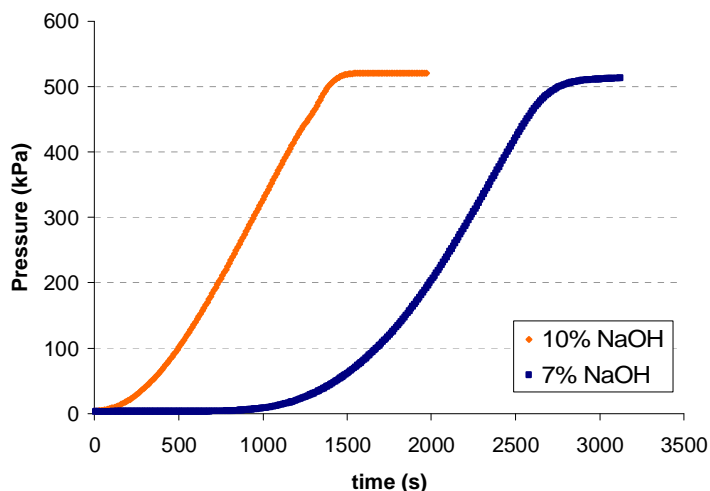### 3.3. Effect of NaOH concentration on H$_2$ generation rate

Figure 4. Hydrogen generation with a NaBH4 concentration of 10%, at 45°C for a maximum H$_2$ predicted pressure of 700 kPa with different NaOH concentrations.

Figure 5. Hydrogen generation with a NaBH$_4$ concentration of 20%, at 45°C for a maximum H$_2$ predicted pressure of 700 kPa with different NaOH concentrations.

Figures (4) and (5) show the dependence of the hydrolysis reaction rate on the NaOH concentration. The reaction rate is enhanced by the increase of the NaOH concentration. This result was already reported by Hua *et al.* (2003), which used a nickel boride catalyst but is at contrast with the results of Kaufman and Sen (1985) with a Ru catalyst. These contradictory effects are not easy to explain. Probably the reaction with the nickel based catalyst used in this work involves complicated surface reactions with the hydroxide ions. The accelerating effect of NaOH is quite interesting since it ensures during reaction a good efficiency for the hydrogen generator, compensating a possible negative effect caused by reduced activity of water and lowered solubility of the reaction product at higher hydroxide concentration.

The reported enhancing effect is more significant for the lower NaBH$_4$ concentration (Fig.4) as expected from the results analyzed in the previous section.
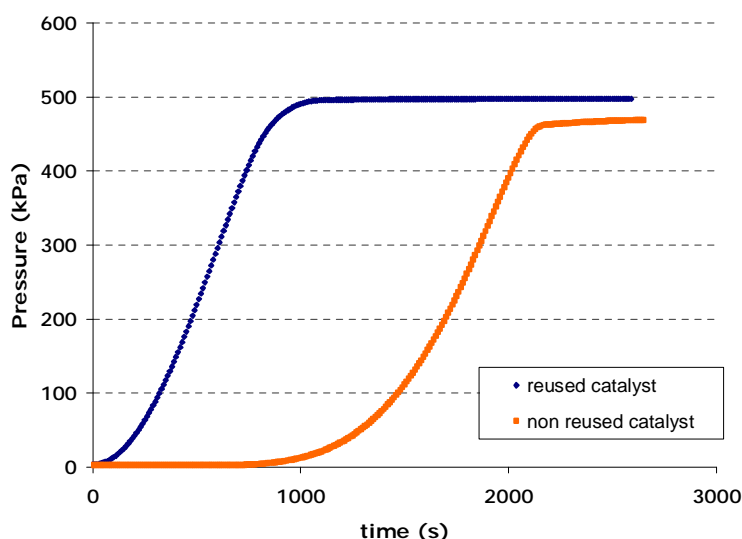
3.4. Effect of catalyst reuse

Figure 6. Influence of the catalyst reutilization on the hydrogen generation with a NaBH4 concentration of 10%, an inhibitor concentration of 7%, at 45°C for a maximum H$_2$ predicted pressure of 700 kPa.

The results of the two experiments plotted on Fig. (5), show an interesting feature: the reaction starting time for the higher hydroxide concentration is much lower than the obtained values for all the results already presented. As can be verified in Tab. (1), the only difference in the conditions of these two experiments, besides the NaOH concentration, is the fact that in that experiment the catalyst had been reused. To confirm this finding, another experiment was repeated with catalyst powder recovered from previous experiments by washing, filtrating and drying in an oven. The results are compared in Fig. (6), putting in evidence the clear advantage of reusing the catalyst, corresponding to lower starting times and higher slopes in the linear zone. A more detailed study of this increase of catalyst activity is required to optimize conditions of reutilization.

3.5. Effect of the pressure on H_2 generation efficiency

Finally, the effect of the pressure in the H_2 generation efficiency was analyzed. In fact, in all the experiments performed, a curious result was found: the maximum reached hydrogen pressure is substantially lower than the maximum predicted (100% efficiency conversion) H_2 pressure, as can been seen by the values presented in Tab. (1) and in Figs (2) – (6). At first, the hypothesis of conversion by reaction lower than 100% was considered. To verify if the supposition was correct, a second type of experiment was performed, as soon as the final (constant) pressure of hydrogen was reached. A quick purge was done evacuating the hydrogen through the reactor exhaustion becoming the pressure inside the reactor equal to ambient pressure. After closing the reactor outlet, the pressure and temperature were followed for several hours and a very slow increasing of the H_2 pressure was detected without any temperature increase. This H_2 releasing process lasted long suggesting that it could not correspond to a reacting process. It was concluded that the difference between maximum predicted hydrogen pressure and the maximum final pressure for all the experiments was not due to a conversion lower than 100%. A very reasonable explanation for this behavior was then considered. The obtained pressure of hydrogen is lower than expected due to solubility effects in the liquid solution. As far as the authors are aware, this effect has not been described probably because the works found in literature report experiments performed at ambient pressure. As it is well known, the effect of increasing the gas pressure enhances strongly the gas dissolution in the liquid phase and increasing temperature is favorable to the solute releasing from it. The increasing pressure of the gas phase forces the hydrogen dissolution. An interesting result was obtained since gaseous hydrogen was generated but also stored in the liquid phase. A new set of experiments was designed to further verify our proposed explanation using a second reactor prepared to work under higher pressures but without pressure probe. The results of this second set of experiments, complemented with the information from Tab. (1) are presented in Fig. (7), showing the same effect, now even more markedly.
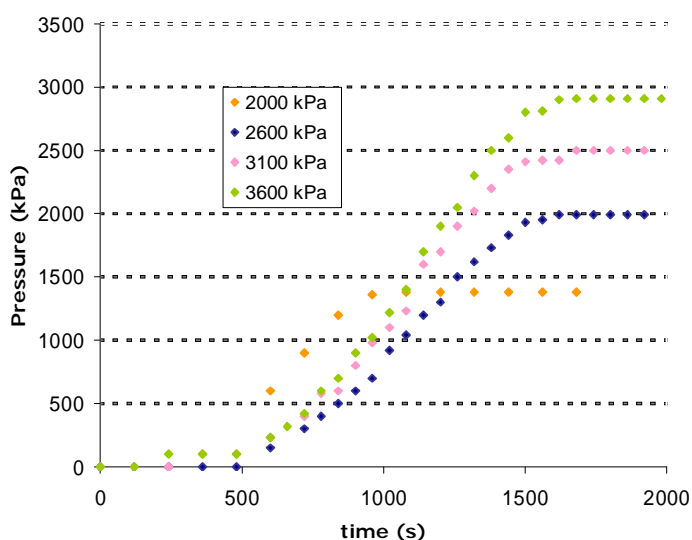

Figure 7. Hydrogen generation with a NaBH$_4$ concentration of 10%, 10% of NaOH concentration, at 45°C for different maximum H$_2$ predicted pressures.

4. Conclusions

The hydrolysis of sodium borohydride using a non-noble nickel based catalyst was studied in batch reactors. The effects of temperature, $NaBH_4$ concentration, NaOH concentration and pressure on the H_2 generation rate were studied.
The main conclusions of the investigation are:

- The prepared catalyst presents good activity for the hydrogen generation even after storage for several months in an uncontrolled ambient. This inexpensive and easy to prepare catalyst showed an enhanced activity after being recovered from previous use. These findings suggest that the catalyst is capable for practical application as a hydrogen generator coupled to fuel cells.
- The reaction rate increases with an increase in temperature and a decrease of the $NaBH_4$ concentration. The hydrogen generation rate is enhanced by the increase of the NaOH concentration being this effect quite interesting since it ensures during reaction a good efficiency for the hydrogen generator.
- The influence of the pressure of hydrogen during reaction was investigated and a curious behavior is described: the maximum reached pressure of hydrogen is always substantially lower than predictions (considering 100% conversion) due to solubility effects. The solubility of the solute H_2 is greatly enhanced by the rising pressure during reaction, leading to storage of hydrogen in the liquid phase. This effect is at present under deep investigation since it can shed new ways of using this type of catalyst in the construction of hydrogen generators and even containers for several applications.

5. Acknowledgement

6. References

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