

BATCH SOLID SODIUM BOROHYDRIDE HYDROLYSIS FOR HYDROGEN GENERATION: THE ROLE OF REACTOR BOTTOM SHAPE

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SUMMARY

The present study reports original experimental work on generation of hydrogen, by hydrolysis of solid sodium borohydride with stoichiometric amount of distilled water ($\text{H}_2\text{O}/\text{NaBH}_4$: 2, 2.84 and 3 mol/mol), in the presence of a powder unsupported Ni-Ru based catalyst, reused about 320 times. The experiments, performed in two batch reactors with equal internal volume but with different bottom shapes (flat and conical), revealed - for the conical bottom shape with any excess of water - 8.1 H_2 wt% and 92 $\text{kg H}_2/\text{m}^3$ (materials-only basis), and a H_2 rate of 87.4 $\text{L}(\text{H}_2) \text{min}^{-1} \text{g}^{-1}$ catalyst. The role of reactor bottom geometry on the solid NaBH_4 hydrolysis - with any excess of water - is, as the authors are aware, for the first time here referred.

INTRODUCTION

The quest for abundant energy is the problem of ensuring the sustainability of the world's energy supply as population and the search for affluence continue to grow. Many scientists and engineers agree that the solution to these global problems would be to replace the existing fossil fuel system by the hydrogen (H_2) energy system. Hydrogen is a very efficient and clean energy vector, to be directly converted into electricity by proton exchange membrane fuel cell (PEMFC). Promising PEMFC applications in transportation, stationary and portable electronic devices (laptops, mobile telephones, iPods, iPads, etc) are more over next to reality. However, some drawbacks need to be solve for the plenty usage of H_2 as the main energy carrier, and the H_2 storage has been placed at the top of the schedule (low mass density, usage security, high cost, the need for a distribution network, etc) [1]. Boron and its compounds are considered as most capable candidates to be used as hydrogen storage and production material [2]. Sodium borohydride (NaBH_4), which is a boron chemical, is being studied extensively, because H_2 can be easily and controllably produced by NaBH_4 catalytic hydrolysis, giving no harmful by-products [3]. NaBH_4 reacts with water to generate molecular hydrogen according to the hydrolysis reaction (1):



where x is the hydration factor. Ideal hydrolysis is attained for $x = 0$ [4] where two moles of water are required to react with one mole of solid NaBH_4 to liberate four moles of hydrogen, but in practice excess of water is necessary to account 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 [5]. In fact, most schemes for hydride hydrolysis require a large excess of water ($x \gg 2$) to pre-dissolve the hydride for storage or to keep the by-products in solution. Therefore, this water handling (x) issue, directly related to the H_2 storage system capacity, is of utmost importance, to accepted NaBH_4 -based H_2 generator for fuelling PEMFCs. In truth, the effective gravimetric hydrogen storage capacity (GHSC) of either NaBH_4 or the system $\text{NaBH}_4\text{-H}_2\text{O}$ is well below the ideal value (the theoretical value is 10.8 wt%). This led the US Department of Energy (DOE) recommending no-go for the stabilized solution of NaBH_4 for on-board vehicle applications [6]. However, optimization of effective GHSC could be achieved, using solid NaBH_4 with water vapour or with stoichiometric amount of pure liquid water [7-13] (in the absence of alkali inhibitors), allied to the catalyst efficiency. This latter issue has been extensively studied in the hydrolysis of NaBH_4 , in terms of catalyst performance, but unsatisfactorily with respect to the catalyst durability and operability (in severe conditions).

In a previous work [13], the authors study the activity of a nickel-ruthenium based catalyst (Ni-Ru catalyst/ NaBH_4 : 0.2-0.4 g/g), re-used up to 150 times, in three different batch reactors, with solid NaBH_4 and stoichiometric amounts of pure liquid water of $\text{H}_2\text{O}/\text{NaBH}_4$: 2-8 mol/mol. It was reported 6.3 wt% and 70 kg/m^3 , respectively, for GHSC and volumetric hydrogen storage capacity (VHSC) (materials-only basis), for the compressed H_2 system of 1.26 MPa, in a batch reactor of 229 cm^3 with conical bottom shape (being $x=2$ and H_2 yield=98%). In the present work, the activity and stability of the same Ni-Ru based catalyst is further investigated, also in the topic of hydrolysis of solid NaBH_4 with pure liquid water. The main objective is to exclude any excess of water ($x = 0$), producing H_2 with even higher GHSC to supply on-demand a PEMFC.

EXPERIMENTAL TECHNIQUE/DISCUSSION

A small amount of solid sodium borohydride (NaBH_4) - 1.2 g, is mixed with 0.24 g of the reused powder catalyst (Ni-Ru based/ NaBH_4 : 0.2 g/g), the latter with the impressive long-life cycling of reutilizations between 310 to 320 times. This mixture is placed inside two batch reactors, both with internal volume of 229 cm^3 , but

with different bottom geometries: flat and conical, see Figure 1 (a) and (b). A stoichiometric amount of deionised liquid water, $\text{H}_2\text{O}/\text{NaBH}_4$: 2, 2.84 and 4 mol/mol (or $x = 0, 0.84$ and 1) is rapidly added to the solid mixture inside the reactor, by means of a syringe with a long needle, to ensure that the water is delivered very close to the powder moisture (NaBH_4 plus Ni-Ru catalyst). Then, the catalyzed solid NaBH_4 hydrolysis evolved, in the absence of an inhibitor, at room temperature ($\sim 22^\circ\text{C}$). Specific details of the experimental rig and procedure are explained on earlier work [13]. The temperature of the reactor medium is read by a k-thermocouple (see T.Top in Fig.1) and recorded simultaneously with a data acquisition system using LabView software. To monitor the H_2 generation rate (HGR), the gas pressure inside the reactor is followed with an appropriate pressure probe. The tests with $x = 0$, which are equivalent to 45.2 wt% NaBH_4 , 45.7 wt% H_2O and 9.1 wt% catalyst, performed in batch reactor SRc – with a conical bottom shape, shown the highest experienced HGR of 3.12 bar/s (see Fig.1c) or $87.4 \text{ L}(\text{H}_2) \text{ min}^{-1} \text{ g}^{-1}$ catalyst or $\sim 2958 \text{ L}(\text{H}_2) \text{ min}^{-1} \text{ g}^{-1}$ active metal (the reused catalyst contained 1.42 At% of Ru). This value is the utmost HGR ever reported in the open literature [3].

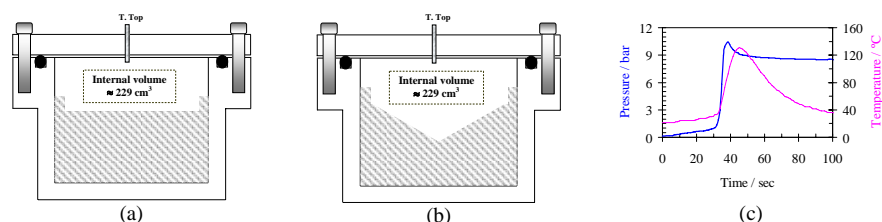


Figure 1: Schematic view of the inside of the two batch reactors: (a) reactor SRf/0.229 L with flat bottom shape, (b) reactor SRC/0.229 L with conical bottom shape and (c) hydrogen evolution in SRC batch reactor for 1.2 g of NaBH_4 and $\text{H}_2\text{O}/\text{NaBH}_4$: 2 mol/mol ($x=0$), and with Ni-Ru catalyst/ NaBH_4 : 0.20 g/g.

Values of 8.1 wt% and 92 kg/m^3 were obtained, respectively, for GHSC and VHSC, on a materials-only basis. The present results, performed in the batch reactor with conical bottom shape, are in conformity with our prior study [13], which shows the positive influence of reactor bottom shape on HGR, induction time and yield, in solid NaBH_4 hydrolysis.

CONCLUSIONS

The present study reveals the catalytic capability of the extreme used Ni-Ru based catalyst (~ 320 times reused) to generate hydrogen with 8.1 wt% (materials-only basis), at $87.4 \text{ L}(\text{H}_2) \text{ min}^{-1} \text{ g}^{-1}$ catalyst, in a batch reactor with a conical bottom shape, with exclusion of any excess of water ($x = 0$; being 80 % de H_2 yield), at room temperature. Decreases of $\sim 40\%$ in these values were observed in the reactor with flat bottom geometry. At the best of authors knowledge, the role of reactor bottom geometry, for H_2 production (and storage), by solid NaBH_4 hydrolysis with any excess of water, is for the first time exposed on the present manuscript. It could be concluded that our compressed H_2 system is a potential energy/hydrogen carrier candidate for portable applications.

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