Generation of Hydrogen from Chemical Hydrides under Pressure up to 70 Bar

V.R. Fernandes[1], A. Esteves[1], M. J.F. Ferreira[2], A.M.F.R.Pinto[2], C.M. Rangel[1]

[1]Laboratório Nacional de Energia e Geologia – LNEG, Fuel Cell and Hydrogen Unit,
Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal
carmen.rangel@lneg.pt

[2]Centro de Estudos de Fenómenos de Transporte - CEFT, Departamento de Engenharia Química , Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Porto
apinto@fe.up.pt

Abstract

Hydrogen production by sodium borohydride through hydrolysis in alkaline solutions has been extensively studied as a production/storage option. The potential application of this option is dependent on an easily controllable catalysed hydrolysis reaction at significant rates to comply with fuel cell feeding but also on the increase of the gravimetric density being of paramount importance, the design and implementation of compact and efficient reactors and the reaction characterization under pressure. In this work, hydrogen generation by the catalyzed hydrolysis of sodium borohydride was studied under pressure up to 70 bar with excellent results.

Keywords: *chemical hydrides, catalysed hydrolysis, hydrogen generation*

1 Introduction

Chemical hydrides, particularly borohydrides, are currently being developed as storage options, since they exhibit good energy densities.

Sodium borohydride ($NaBH_4$) is currently being studied as a promising hydrogen storage option due to its high gravimetric capacity (10.73 wt%), well within DOE targets for 2015. Its good stability in alkaline solution, easy control of hydrogen generation rate, moderate operation temperatures and environmentally benign hydrolysis product has prompted numerous research works contemplating catalysed hydrolysis as a means to produce meaningful reaction rates [1-3].

It is to be noticed that the chemical hydride system, based on the hydrolysis of sodium borohydride, looses efficiency of storage due to the fact that the reaction needs excess water to account for the solubility of $NaBH_4$ and the borate by-products; furthermore the latter capture water reducing even further the efficiency of the reaction, equation (1). This has become a critical issue in the developing of an efficient generator. Furthermore, with the by-products species being alkaline, the reaction medium promotes a low yield of the reaction making it necessary to use a catalyst to take the reaction to its full extent. In practice, four moles of water are necessary for full hydrolysis of 1 mol of borohydride (equation 1).

$$NaBH_4 + (2+ x)\ H_2O \rightarrow NaBO_2.x\ H_2O + 4H_2\uparrow\ (-218\ kJmol^{-1})\quad (1)$$

In spite of a no-go recommended by US DOE for NaBH4 for on-board automotive hydrogen storage, interest continues to find solutions for portable applications [3].

Recently work in our group has found that the gravimetric efficiency of the system can be improve to over 6 wt% (material-only basis) by working in alkali free solutions and specific stoichiometric water to borohydride ratio under pressures up to 1.26 MPa [4].

Kojima *et al.* [5] published experimental work on compressed H_2 generation using $NaBH_4$ at pressures up to 5.6 MPa.

In fact, work concerning borohydride hydrolysis under pressure are scarce [5,6], the majority of works are performed under atmospheric conditions.

In this work, the generation of hydrogen from sodium borohydride under pressure up to 70 is reported for the first time.

2 Experimental

The hydrolysis in alkaline solutions of sodium borohydride has been studied as a production/storage option. A cheap, non-noble nickel based non-commercial nanostructured catalyst, was developed having proved to be efficient in the hydrolysis of sodium borohydride. The quantity of hydrogen generated is 100 % stoichiometric. The catalyst has been demonstrated to have been re-used by more than 200 times without significant degradation, fact already reported in previous publications [4].
The developed catalyst has been used in the present study of the hydrolysis reaction of sodium borohydride, under pressure, which was conducted in a 300Parr reactor composed of a type 316 stainless steel pressure vessel equipped with several head fittings such as, a magnetic drive, a gas inlet valve, a thermocouple, a liquid sampling valve, a gas release valve, a safety rupture disc and a pressure gage. The reactor is connected to a Parr 4842 temperature control unit when required.

Fig.1 Stainless steel (type 316) reactor used for the study of sodium borohydride catalysed hydrolysis, under pressure up to 70 bar.

A study of the hydrolysis reaction was also conducted at ambient pressure in a glass reactor, in order to determine reaction rates for comparison. In this case the volume of generated gas was measured by a water displacement method rendering values at standard pressure and temperature. The produced gas volumes were measured as a function of time at controlled temperature, till complete exhaustion of the reactant.

3 Results

Figure 2 shows the hydrogen generation from sodium borohydride in 10wt% stabilized solutions with 3 wt% sodium hydroxide.

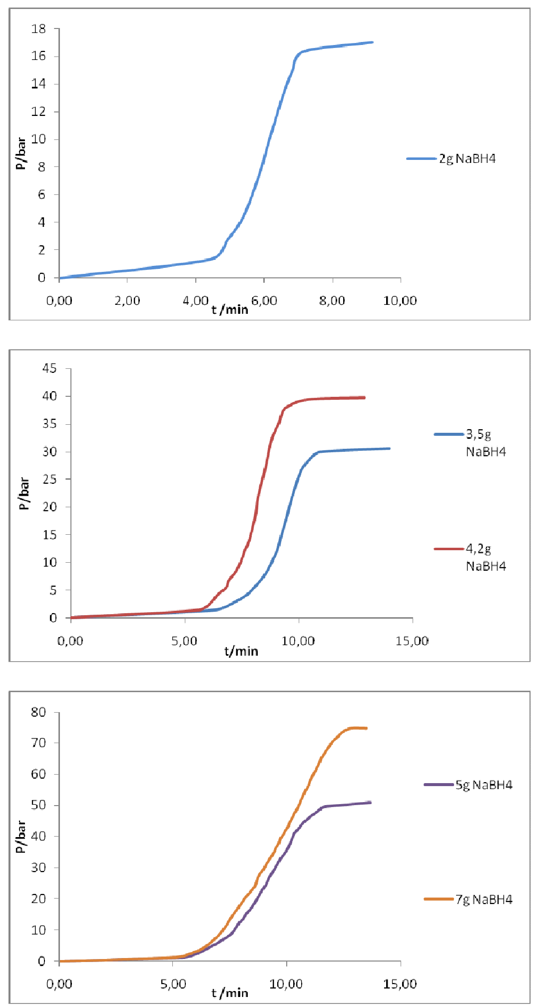

Fig. 2 Hydrogen generation from NaBH4 expressed as the reactor pressure as a function of reaction time, for various initial amount of sodium borohydride compliant with 10wt% in the reactant in the working solution.

Various initial amounts of borohydride and solution volumes were used, in order to have a 10 wt% solution.
Pressures from 17 to ~75 bar were obtained with production efficiencies higher than 98% for the higher pressures.

Hydrogen production rates are 3 times higher, in comparison with those obtained in the same conditions but at atmospheric pressure.
Table 1 summarizes results obtained in this work and compares with other Ni-based catalyst available in the open literature.

Table 1. Normalized hydrogen production rates obtained in this work.

Catalyst	**Solution composition/ Amount of catalyst**	**H_2 generated ($Lmin^{-1}g^{-1}$) / T**	**Observation**
Ni-based bimetallic	10wt% NaOH;3 wt% NaBH4 / 100 mg	10 (45ºC)	Atmospheric pressure
Ni-based bimetallic / under pressure	10wt% NaOH;3 wt% NaBH4 / 100 mg	30 (no temperature control)	Under pressure up 70 bar

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