PRODUCTION OF HYDROGEN BY BOROHYDRIDES: IN SEARCH OF LOW COST NON-NOBLE EFFICIENT CATALYST

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Abstract: Hydrogen production by sodium borohydride through hydrolysis in alkaline solutions has been extensively studied as a production/storage option due to the high volumetric and gravimetric efficiency exhibited. The potential application of this option is based on an easily controllable catalysed hydrolysis reaction, non-toxic and recyclable by-products, and the high purity hydrogen produced can be used in fuel cells.
This work reports on a comparative study of own-developed, supported and non-supported, non-noble catalyst. Ru based catalysts are taken as reference. Characterization of the catalyst was accomplished using a FEG-SEM scanning electron microscope and FTIR analysis. Obtained values amount to 10 $NLmin^{-1}g^{-1}$ for Ni-based catalyst while Ru-based catalyst amount to twice as much in the same experimental conditions. Typical solutions contain sodium borohydride of concentrations between 2 and 10 wt%, stabilized with 3 to 10 wt % NaOH. Produced hydrogen is measured at ambient pressure as a function of catalyst exposure time at controlled temperatures till completion of the reaction. A thorough study of the open literature rendered normalized values for the reaction rate with different catalyst, making comparisons valuable.

1. Introduction

Chemical borohydrides emerge as potential hydrogen carriers and media for storage due to their high volumetric and gravimetric efficiency. In the case of sodium borohydrides as much as 10.8 wt% hydrogen might be obtained, taking into account the reactants stoichiometric ratio [1-8].

Through catalysed hydrolysis, high purity hydrogen can be produced at low temperature; the reaction is exothermic and does not need energy input and the reaction products are non-toxic. Another advantage is that sodium borohydride dissolved in water is non-flammable, even though the option of using solutions as a storage media is impaired by self-hydrolysis that occurs even in stabilized solutions [9]. Cost effective recycling methods of the reaction products are also needed.
Furthermore, the development of compact and efficient reactors is limited by the availability of low cost catalysts that present high conversion rates. A number of supported catalysts are being proposed in the literature [1, 6, 9] since their use allows the recirculation of the working solution as well as water management, reaction products separation and the injection of borohydride for the repeated generation of hydrogen with minimal catalyst deactivation, as well as catalyst recovery.
This work reports on a comparative study of own-developed, supported and non-supported, non-noble catalyst. A comparison of the results with those available in the open literature is made.

2. **Experimental**

In this work a number of non-noble metal catalysts, active in the hydrolysis of borohydride have been prepared by:

reactive sol-gel
Co-based catalysts were prepared by forming a cobalt acetylacetonate complex followed by decomposition under reductive conditions.

ball milling
Ni and Ru catalyst were prepared from metal chlorides using ball milling with solid $NaBH_4$ in order to produce pre-catalysed samples and avoid long induction times at the beginning of the hydrolysis.

wet chemistry: A Ni-based catalyst in the form of a finely divided powder was prepared from nickel salts in a reducing environment, the catalyst is bimetallic with small amounts of ruthenium. For comparison Ru nanoparticles have been also produced using the same method.

Some of the best performing catalysts were fixed on different support and their effect on reaction rate tested:

catalyst supported on α-Al_2O_3 and α- α-Al_2O_3 /SiO_2
Ni, Co and Ru catalysts were used with loadings of 5 wt% metal loadings. Particle size of the metal powder varied between 19 and 34 nm.

catalyst supported on metallic foams
Ni foams with a density of 380 gm^{-2} and a thickness of 1.6 mm, using doctor blade technique [6].

Typical experiments used 0.1g of catalyst in solutions containing 2 to 10 wt % sodium borohydride (from either Rohm and Haas or Aviabor) stabilised solution with either 3 or 10 wt % NaOH, as indicated. Concentrations up to 20% NaOH were also used to ascertain the effect of NaOH as stabiliser of the self-hydrolysis of sodium borohydride.

The catalysts have been characterised using XPS, FTIR and SEM.

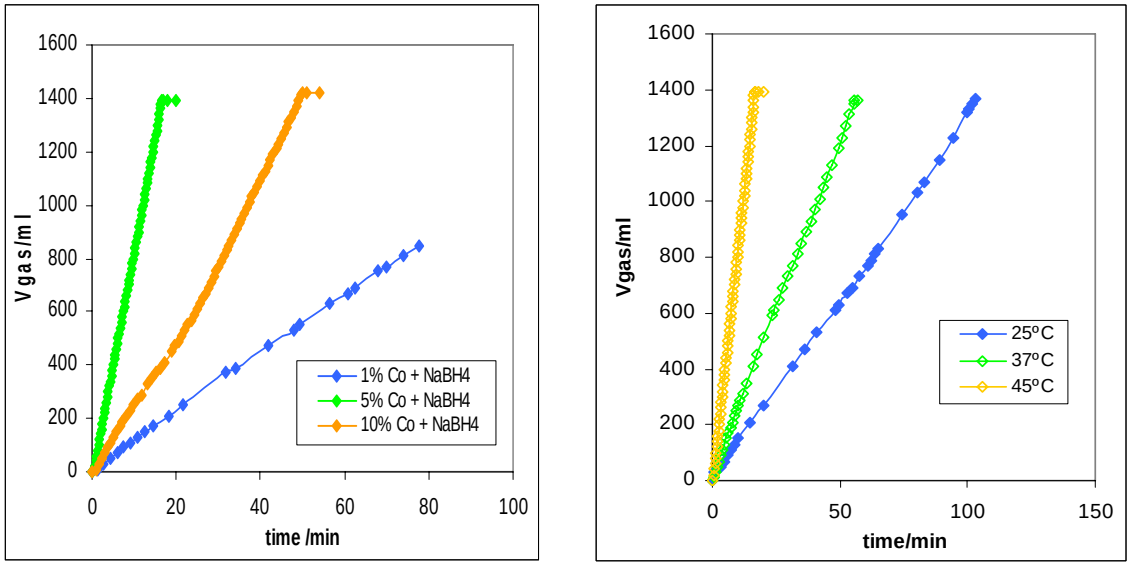
A study of the hydrolysis reaction was first conducted at ambient pressure in order to determine reaction rates in different conditions. The volume of generated gas was measured by a water displacement method rendering values at standard pressure and temperature. Some experiments were also conducted in a batch type reactor. The produced gas volumes were measured as a function of time at controlled temperature, till complete exhaustion of the reactant.

3. Results and Discussion

Non-supported catalyst

Pre-catalysed samples prepared by reactive sol-gel were tested using a 10 wt% $NaBH_4$ solution stabilized with 3 wt% of NaOH. Figure 1a) shows the amount of generated gas which exhibits a linear relationship with exposure time and increases with Co concentration in the samples for concentrations up to 5 wt% Co. An increase in the amount of Co brings about a drop in the reaction

rate, furthermore, the production rate is variable slightly increasing after the first 20 minutes of exposure but never reaching or surpassing the generation rate for sample with 5 wt% Co. It is noticeable that the borohydrides present in the catalyst is also reacted to produce hydrogen. For the case of the catalyst containing 1 wt% Co the reaction was slower and was not allowed to proceed till the end.
Since the sample containing 5 wt %Co showed the best results, the effect of temperature was studied with this catalyst concentration. Results are shown in figure 1b).
Borohydride from the solution and that incorporated in the catalyst reacted to full extent to produce hydrogen.



(a) (b)

Figure 1. The effects of concentration of the catalyst (a) and temperature for the pre-catalysed 5 wt % Co catalyst powder (b) in a 10 wt % $NaBH_4$ solution stabilised with 3 wt% of NaOH. (All sodium borohydride present reacted to form hydrogen gas, when the reaction was slow as in the case of 1% Co catalyst, the measurements were interrupted after 80 minutes).

Using the Ni-based nanopowder prepared by wet chemistry, the variation of the hydrogen production rates exhibited a maximum at 10 wt% NaOH [9]. Variation with the temperature up to 60ºC give more than 10 L gas per minute per gram of catalyst, see figure 2.
Ruthenium nanoparticles were also tested in the same conditions giving a rate of 26 $Lmin^{-1}g^{-1}$.

Supported Catalyst

On α-Al_2O_3 and α-Al_2O_3 / SiO_2

Co, Ni catalysts supported on α-Al_2O_3 and α-Al_2O_3 / SiO_2 were also tested both at ambient pressure and in a small batch reactor. Ru catalyst was supported only on α-Al_2O_3.

Ru presented the highest reaction rates. The catalyst support was observed to dissolve in the reaction media, as suggested by EDAX analysis of the powders, before and after use of the catalyst in the hydrolysis of $NaBH_4$, see figure 3. In the case of the alumina /silica support, the silica appears preferentially lost. The powder preparation for observation under the scanning electron microscope,

included coating of the powder with gold justifying the observed corresponding peak. Na and B are also identified.

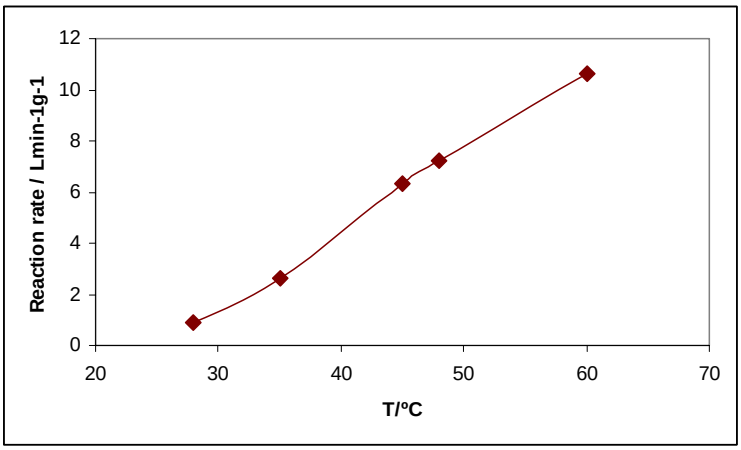


Figure 2. Reaction rates as a function of temperature for Ni-based catalyst for 10 wt% NaOH.

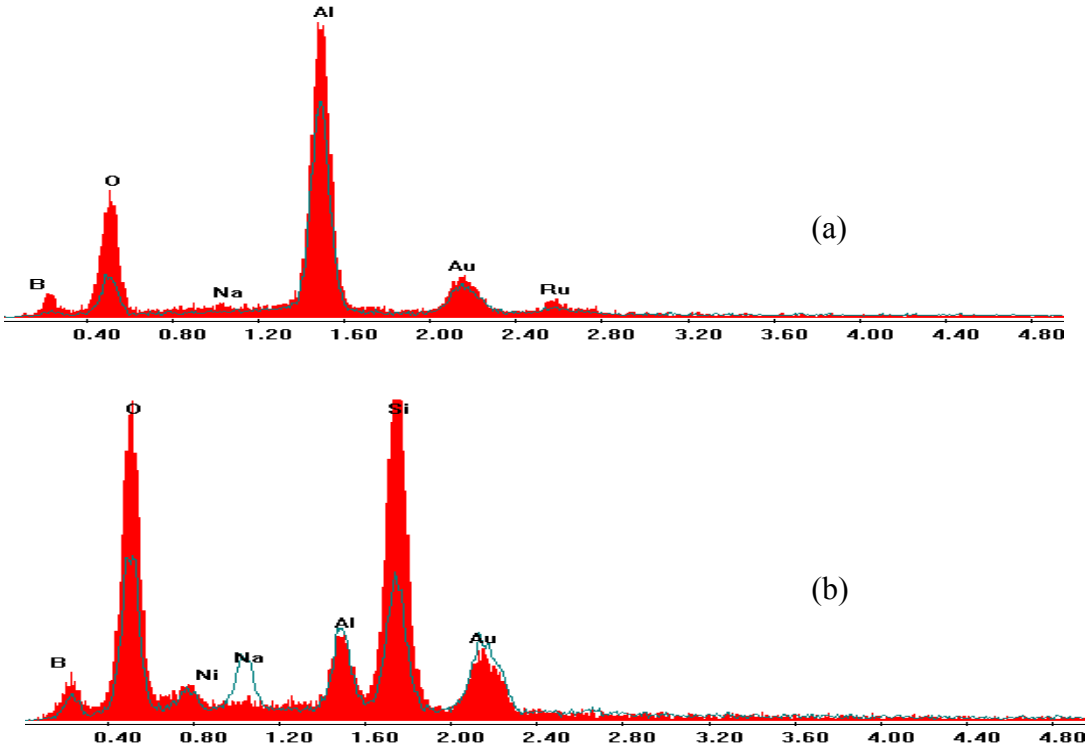


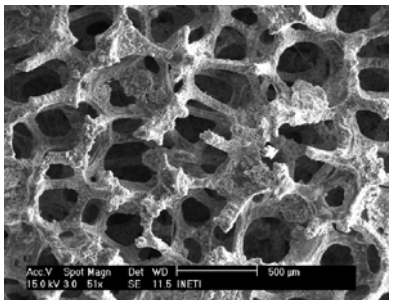
Figure 3. Typical EDAX spectra for supported catalyst before and after testing in sodium borohydrides. Ru catalyst supported on Alumina (a); Ni catalyst supported in Alumina – Silica (b), showing Aluminium loss in the first case and Si loss in the second case. The blue line represents the spectrum recorded for the sample after reaction.

On Ni metallic foam

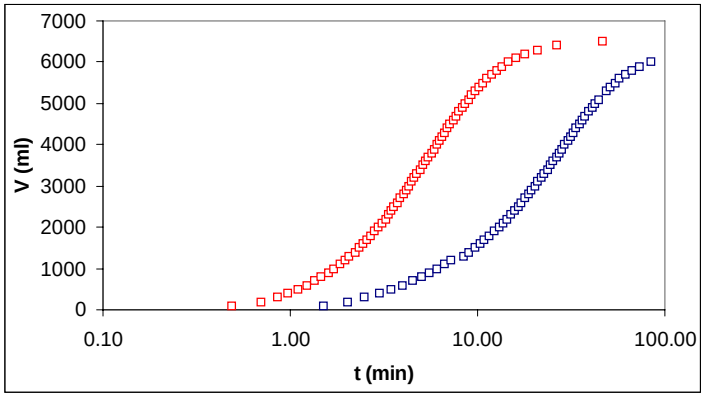
Ni-based catalyst formulations were fixed on a Ni metallic foam with a density of 380g.m^{-2} and a thickness of 1.6 mm.

Figure 4a) shows a SEM picture of the used foam with applied catalyst. Figure 4b) shows the volume of gas produced as a function of time in a 2 wt % sodium borohydride solution at 45 and 65ºC. Three different regions were identified: a region of adsorption of species where there is no hydrogen production, which represents a reaction induction time; this region is activated by temperature. A second region, associated to a linear variation of the volume of produced gas with time and a third region where the rate of H_2 decreases before it stops due to total consumption of sodium borohydride.

Even though a comparative analysis of data obtained from the open literature revealed itself difficult, due to the different experimental conditions used, an attempt was made to collect relevant results that could be compared with the data obtained in the present work, see table 1.



(a)



(b)

Figure 4. SEM view of Ni-based catalyst supported on a Ni foam (a). Hydrogen volume produced using a Ni based supported catalyst at room temperature and 65ºC using a 2 wt % $NaBH_4$ solution stabilised with 10 wt% NaOH.

It is observed that the data obtained in this work compare well with the highest rates obtained by other authors when using own synthesised Ru powder or with supported Ni-based catalyst. Regarding Ru catalyst high surface area powders were reported to reach 60 Lmin^{-1}g^{-1} [10].

FTIR analysis of the catalyst indicate characteristics band for groups Ni--OOH and Ni—OH at 463 and 651 cm^{-1}, respectively as well as a wide band at 3640-3250 cm^{-1} and peaks between 1430-980 cm-1 and 1633 cm^{-1} attributed to stretching and deformation vibrations of OH groups and bending vibrations of H--O—H.

More comprehensive results accounting for the characterisation of the catalyst used will be the subject of publication elsewhere.

Table1. Data on supported and non-supported catalyst used for the production of hydrogen from sodium borohydride solutions stabilised with NaOH in various experimental conditions.

Catalyst	**Solution composition/ Amount of catalyst**	**H_2 generated ($Lmin^{-1}g^{-1}$) / T**	**Reference**
Ru/IRA400	10wt% NaOH;10wt% NaBH4 / 250 mg (5 wt%Ru)	12 (45ºC)	**Amendola 2000**
Ni/B	10wt% NaOH, 1,5 wt% NaBH4;	0.29 (40ºC)	**Hua 2003**
	10wt% NaOH, 1,5 wt% NaBH4 / 200 mg (2 wt%Ru)	0.83 (60ºC)	
Ni Filaments	10wt% NaBH4, KOH 0,01M, / Ni Filaments, 1g	0.057 (RT)	**Kim 2004**
Ni Filaments 20wt% Co	10wt% NaBH4, KOH 0,01M, / Ni Filaments 20 wt% Co 1g	0.089 (RT)	
Co/B	2wt% NaBH4, 5wt%NaOH / 100 mg	1.4 (without T control)	**Wu 2005**
Ru	5wt% NaOH;20wt% NaBH4/ 50 mg	1.6 (20ºC)	**Jeong 2005**
Co/B	5wt% NaOH;20wt% NaBH4/ 50 mg	0.88 (20ºC)	
Pt- $LiCoO_2$	5wt%NaBH4, 5wt%NaOH / 239 mg (Pt 10 wt%)	16 (25ºC)	**Krishman 2005**
Ru- $LiCoO_2$	5wt%NaBH4, 5wt%NaOH / 125 mg (Ru 10 wt%)	9.6 (25ºC)	
PtRu-$LiCoO_2$	5wt%NaBH4, 5wt%NaOH,/ 125 mg (PtRu 10 wt%)	3.8 (25ºC)	
Ru em IRA-400	5wt%NaBH4, 5wt%NaOH / 185 mg (Ru 6.78 wt%)	3.3 (25ºC)	
Ru	10wt% NaOH; 10wt% NaBH4 / 50 mg	26 (45ºC)	**This work**
Ni-based bimetallic		8.5 (45ºC)	
Ni-based bimetallic / Ni foam	10wt% NaOH;2wt% NaBH4 / 60 mg	10 (60ºC)	

CONCLUSIONS

A number of catalysts have been synthesised and tested in sodium borohydride stabilized solutions in a search for cheap, stable and efficient catalyst for hydrogen production. Ni-based catalyst performed well at temperatures up to 60ºC. Supporting on Ni foams gave excellent results allowing re-use of the catalyst and repeated injection of the borohydride solution with no catalyst de-activation.
Ru catalysts were taken as a reference both from literature data and own-synthesized powder giving always higher rates.

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