Hydrogen production from sodium borohydride: The role of Ni-Ru supported catalysts

***H.X. Nunes*[1], C.M. Rangel[2] and A.M.F.R. Pinto[1]**

[1]*CEFT – Transport Phenomena Research Center, Chemical Engineering Dpt., Faculty of Engineering University of Porto, Porto, Portugal*

[2]*Solar Energy Unit, LNEG – Nacional Laboratory of Energy and Geology, Lisboa, Portugal*

apinto@fe.up.pt

Abstract

Nowadays, the concerns about greenhouse-gas emissions from fossil fuel sources are generating a demand for clean and abundant energy. Since early 2000's the chemical hydrides, in particular sodium borohydride ($NaBH_4$), hydrolysis reaction attracted much attention as a hydrogen carrier due to its high hydrogen storage capacity, safe handling and fast kinetics of hydrogen release. Although, during the last decades, several studies have been focused on sodium borohydride hydrolysis improvement, the reaction kinetics is not fully understood.

Thus, the performance of nickel-ruthenium supported catalysts was studied both in *alkaline* hydrolysis (x = 16) and *alkali-free* hydrolysis (x = 2) reactions. The results present high hydrogen generation rates, at uncontrolled room temperature, that compete directly with the rates previously obtained with a nickel-ruthenium unsupported catalyst, which are advantages for an on-demand low/medium power $NaBH_4$-H_2-PEMFC system.

1. Introduction

Climate change is becoming more remarkable each day and it is the major environmental threat of the 21st century. Together with the fact that in emerging countries, and remote areas, the grids are unreliable, and people lack access to basic electricity services had resulted on a demand for clean energy technologies that could deliver off-grid power.[1]

Therefore, as an alternative energy carrier, hydrogen can be applied in fuel cell systems for power portable supplies. The chemical energy per mass of hydrogen (142 MJ kg^{-1}) is at least three times higher than another chemical fuels. Although hydrogen is the most abundant element on Earth, only less than 1% is presented as molecular hydrogen gas.[2] Nevertheless there are many processes for hydrogen production from both conventional and alternative energy resources.

The process to generate hydrogen through the hydrolysis of sodium borohydride has been attracting interest for hydrogen releasing on-demand.

Sodium borohydride presents a high hydrogen storage capacity (10.8 wt.%) and releases hydrogen with high purity at reasonably low operational temperature and suitable controllability. The hydrolysis reaction of sodium borohydride, presented in Eq. 1, is spontaneous and exothermic and the x represents the hydration factor.[3], [4]

$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 \bullet xH_2O + 4H_2 + heat$ Eq. 1.

Since the Schlesinger and collaborators' findings in 1953, sodium borohydride hydrolysis has been heavily studied, with special attention to the catalysts. Despite the many efforts dedicated to understanding and increase the hydrolysis reaction efficiency through the research and development of a suitable catalyst, the kinetics of sodium borohydride catalytic hydrolysis reaction is not fully understood.[5]
In 2011, the group reported outstanding results with an unsupported nickel-ruthenium based catalyst with a long-life activity – throughout 300 cycles. The durability and reutilization capability studies gave emphasis to the aptitude of the catalyst to be reused during successive loads of fuel without any treatment and minor loss of activity.[6]
Thus, three nickel-ruthenium foams, with different ruthenium concentrations, were developed and several experiments were carried out, at moderate pressure and room temperature, in order to assess the hydrogen storage capacities (gravimetric and volumetric), the reaction yield and the hydrogen generation rate.

2. Experimental

In a collaboration with National Laboratory of Energy and Geology (LNEG), three nickel-ruthenium supported catalysts, with the specifications presented in Table 1, were synthetized. These catalysts were used to performed experiments throughout two different systems of sodium borohydride hydrolysis: *alkaline* hydrolysis (x = 16) and *alkali-free* hydrolysis with stoichiometric amount of water (x = 2). The experiments were carried out with a catalyst/$NaBH_4$ mass ratio range from 0.01 to 0.4 g/g at uncontrolled room temperature. Furthermore, the results were compared with the results previously obtained for sodium borohydride catalytic hydrolysis using a nickel-ruthenium unsupported catalyst.

Table I: Ni-Ru supported catalysts properties

Catalyst	Support	Amount of catalyst (mg)
ESPRU 1	Nickel foam	2.04
ESPRU 2	Nickel foam	0.95
ESPRU 3	Nickel foam	0.44

3. Results and discussion

Figure 1 and 2 present the plot hydrogen generation rates in function of time for both studied systems. The results reveal that nickel-ruthenium supported catalysts showed a great performance. When compared to the results obtained with the unsupported catalyst, for the *alkaline* hydrolysis studies, the supported catalysts present not only similar reaction yields but also hydrogen generation rates in the same order of magnitude of the results previously obtained with a nickel-ruthenium unsupported catalyst at 50°C.[3]

Therefore, the issue related with energy consumption may be overcome. Moreover, it is noteworthy that the experiments with ESPRU 3, which presented higher hydrogen generation rates (5.33 L_{H2} min^{-1} g_{cat}^{-1} for x = 16 and 0.36 L_{H2} min^{-1} g_{cat}^{-1} for x = 2), were performed with a catalyst/$NaBH_4$ mass ratio 8 times lower than the experiments carried out with the unsupported catalyst.
Although the present work gives emphasis to the great performance of nickel-ruthenium supported catalysts, it is important to study a method to increase the durability of theses catalysts since, after 3 experiments, a quick deterioration of the coating in the supported catalysts was observed.

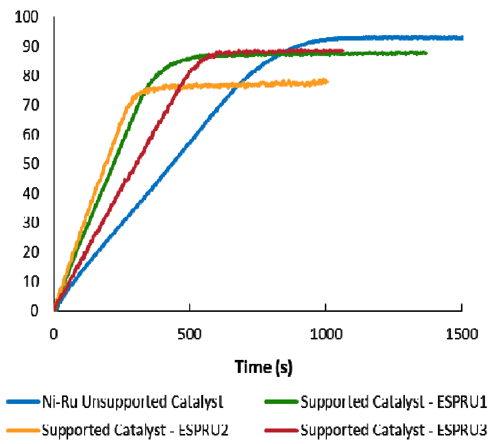

Figure 1: Hydrogen generation plot for $NaBH_4$ *alkaline* hydrolysis using Ni-Ru supported and unsupported catalysts.

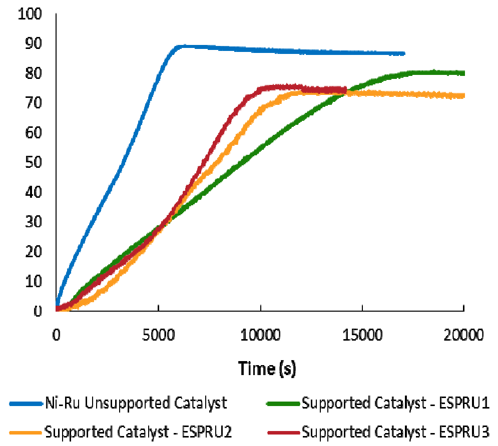

Figure 2: Hydrogen generation plot for $NaBH_4$ *alkali-free* hydrolysis using Ni-Ru supported and unsupported catalysts.

4. Conclusions

The results obtained in the present study revealed that supported catalysts may be the key to improve the hydrogen generation rates in the sodium borohydride hydrolysis reaction.
When compared to the unsupported catalyst, supported catalysts are suitable for an on-demand low/medium power $NaBH_4$-H_2-PEMFC system since, in addiction to great performance, they present the advantage of being easier to handle and clean. Moreover, nickel-ruthenium foams allow to achieve higher hydrogen generation rates, at uncontrolled room temperature, which compete directly with the rates obtained at high temperature.
Nevertheless, it is important to study a method to increase the durability of the supported catalysts to prevent the coating deterioration.

Acknowledgements

The author acknowledges the PhD fellowship funded by Project NORTE-08-5369-FSE-000028, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Social Fund (ESF); and the HYLANTIC Project – Atlantic

Network for Renewable Generation and Supply of Hydrogen to promote High Efficiency (EAPA_204/2016), supported by Interreg Atlantic Area.

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