Chemical Engineering Science 84 (2012) 70–79

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

A sodium borohydride hydrogen generation reactor for stationary applications: Experimental and reactor simulation studies

T. Sousa [a], V.R. Fernandes [a], P.J.R. Pinto [a], Y. Slavkov [b], L. Bosukov [b], C.M. Rangel [a,*]

[a] LNEG/Fuel Cells and Hydrogen Unit, Paço do Lumiar 22, 1649-038 Lisboa, Portugal
[b] Labtech Ltd, 12 Asen Yordanov, Sofia 1784, Bulgaria

HIGHLIGHTS

- Ru/Ni-foam catalyst was prepared by electrodeposition.
- Langmuir–Hinshelwood kinetic model proved to be the suitable kinetic model.
- The reaction rate was particularly affected by mass transport resistance.
- Reactor design played an important role on performance.

ARTICLE INFO

Article history:
Received 18 June 2012
Received in revised form
31 July 2012
Accepted 1 August 2012
Available online 10 August 2012

Keywords:
Kinetics
Sodium borohydride
Hydrolysis
Numerical simulation
Modelling
Hydrogen storage

ABSTRACT

Ruthenium on nickel-foam catalyst was prepared for hydrogen production from the hydrolysis reaction of an alkaline $NaBH_4$ solution. Experiments were carried out at five temperatures (30, 40, 45, 50 and 60 °C) in a 0.1 dm^3 small batch reactor. To understand the kinetic behaviour of the hydrolysis reaction in the presence of this catalyst, the experimental data were fitted to three kinetic models (zero-order, first-order and Langmuir–Hinshelwood) using the integral method. Results showed that Langmuir–Hinshelwood model described fairly well the reaction for all tested temperatures and for the entire time range. Zero-order could be applied only at low temperatures or until the concentration of $NaBH_4$ remained high in the solution; first-order could be only applied efficiently at 60 °C.

In addition to the kinetic study, a dynamic, three dimensional and non-isothermal model was developed to describe a pilot scale reactor for stationary use. The experimental data was used to validate the numerical model which was developed using a commercial solver software. All relevant transport phenomena were treated in detail and the kinetic model developed previously was introduced into the algorithm. Results showed that the reaction rate was extremely affected by the mass transport resistance of sodium borohydride from the bulk to the catalyst surface.

1. Introduction

During the last two decades chemical hydrides have been considered as promising hydrogen storage materials. In particular, sodium borohydide ($NaBH_4$) has been widely studied due to its high gravimetric capacity (10.73 wt%). In 2001 Daimler Chrysler demonstrated successfully the Millennium Cell's $NaBH_4$ system in a minivan (Hyde, 2001). However, in 2007 the U.S. Department of Energy (DOE) recommended a no-go for $NaBH_4$ for on-board automotive hydrogen storage applications (DOE, 2007). This decision was based on the following observations (Demirci et al., 2009): (1) too low gravimetric hydrogen storage capacity ($NaBH_4$ solution is a convenient storage way but has a huge limitation, the low solubility of the $NaBH_4$ and by-products implies the use of excess water, which leads to a massive decrease of the gravimetric capacity); (2) inefficiency of hydrolysis by-product ($NaBO_2$) recycling; (3) cost. This no-go decision was only based on specifications for on-board vehicular storage; for portable and niche applications there are not any specific targets, yet several authors believe that $NaBH_4$ can be a suitable storage material for this kind of applications (Demirci et al., 2009; Liu et al., 2008; Principi et al., 2009).

Typically, in $NaBH_4$ systems the chemical hydride is premixed with water to form a solution. To avoid auto-hydrolysis a small amount of NaOH is added to stabilise the solution. This solution in contact with a heterogeneous catalyst reacts rapidly according to Eq. (1).

$$NaBH_4+(2+x)H_2O \xrightarrow[\text{catalyst}]{} NaBO_2\cdot xH_2O+4H_2\uparrow(-210\ \text{kJ mol}^{-1}) \quad (1)$$

where x is the hydration factor. Much work has been done in order to understand and increase the efficiency of this reaction

* Corresponding author. Tel.: +351 210924664.
E-mail address: carmen.rangel@lneg.pt (C.M. Rangel).

0009-2509/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2012.08.001