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A dynamic two phase flow model for a pilot scale sodium borohydride hydrogen generation reactor

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ABSTRACT

A two-dimensional, non-isothermal and dynamic model was developed to describe a sodium borohydride/hydrogen reactor for stationary use. All relevant transport phenomena were treated in detail and the kinetic model developed previously by the authors was introduced into the algorithm. In this paper the reactive solution was modelled as a two phase flow; with this approach the impact of the hydrogen production on the solution stirring could be observed and quantified.

Results showed that not all ruthenium deposited on the nickel foam was used efficiently as catalyst. In fact, most of the reaction occurred in the surface of the catalyst foam and around 70% of the deposited catalyst was not used. The influence of the catalyst foam position in the solution and the design of the perforated plastic support were analysed in order to find the optimum experimental conditions. It was also demonstrated the importance of the two phase flow approach for a correct simulation of the solution stirring and heat transfer.

1. Introduction

There is no doubt that hydrogen will be a major clean energy carrier in the near future. However, the establishment of a sustainable hydrogen-based economy has been delayed due to several unsolved problems in the supply chain. In particular, storage of appropriate hydrogen amounts has been proven to be a challenge for the scientific community. In addition to the traditional and well established methods to store gases (high pressure gas tanks and liquefied gas tanks) several other storage methods and materials have been studied extensively over the last years in order to meet the requirements of specific applications where the traditional methods cannot be applied. Within such storage methods and materials are encountered metal hydrides [1], on-board reforming of hydrocarbon into hydrogen [2], metal organic frameworks [3,4], organic hydrides [5] and chemical storage [6,7]. Chemical storage, particularly using liquid-phase hydrogen materials, is one of the safe alternatives to hydrogen storage. These materials have relatively high hydrogen content and more important have the potential to be used as hydrogen sources suitable for portable fuel cells. Among them boron based compounds, such as sodium borohydride [8–11], ammonia borane [12], and hydrazine borane [13], have been largely investigated over the past years. These materials have common advantages, they all have high hydrogen storage capacity, they are soluble in water, stable in air, and they can release hydrogen under mild operational conditions through hydrolysis. These features make them an attractive storage material to be conjugated with portable fuel cell systems. However, several problems still need to be

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overcome, such as, catalyst durability, cost, by-products recyclability, and the need to use water in excess during hydrolysis. The main drawback of sodium borohydride when compared with the other boron based compounds is to be instable in water, self-hydrolysis occurs in aqueous solution; to stabilise sodium borohydride in water a strong base is added to the solution. In spite of that, sodium borohydride is one of the most studied boron based compounds because of its relatively high reaction rate at low temperatures using non-noble based catalysts. On the other hand, ammonia borane and hydrazine borane still need further experimental and theoretical studies to solve several problems, such as, (i) ammonia borane hydrolysis only occurs at appreciable rate in the presence of a suitable catalyst at ambient temperature, (ii) B–O bonds formed during the hydrolysis of ammonia borane are very strong and difficult to beak and (iii) a more selective catalyst enabling to reach 100% selectivity to hydrogen needs to be found for the hydrazine borane hydrolysis. Therefore, this work is focussed on hydrogen storage through sodium borohydride.

The application of sodium borohydride as hydrogen storage material for on-board systems was discarded in 2007, when the U.S. Department of Energy gave a no-go decision for this technology. However, this conclusion was only based on specifications for on-board vehicular storage. For other uses, such as portable and niche applications, there are not any specific targets, and several authors believe in the potential of sodium borohydride for these particular applications [11,14,15].

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

$$NaBH_4 + (2 + x)H_2O \rightarrow NaBO_2 \cdot xH_2O + 4H_2 \quad (1)$$

where, x is the hydration factor.

New materials have been proposed including both noble and non-noble metal catalysts, and much effort has been made to understand and increase the reaction efficiency. From the results obtained by several research groups, catalysts based on noble metals (mainly Ru and Pt) are superior in terms of specific activity; however, non-noble catalysts have been developed in recent years with activities of a similar order of magnitude. A good example of these new materials is cobalt alloyed with boron. This material can be even more interesting when deposited on a support, as demonstrated by Dai et al. [16]. For more details several reviews, which were published over the last years, can be consulted [8,10,11,17].

In terms of storage system design much work have been developed since the system reported by Amendola et al., in 2000 [18]. In this system and in all the others based on it, sodium borohydride solution was pumped through a catalyst bed where the hydrolysis reaction occurred. With this kind of continuous flow system the best results were obtained by Gervasio et al., in 2005 [19]. They developed a small reactor to power a 10 W fuel cell and they used as catalyst Ru on Al_2O_3. With this architecture they were able to attained virtually 100% conversion of 30 wt% sodium borohydride. These outstanding results may have been due to the excess of Ru used in the micro reactor [9]. One of the main problems of these systems is the precipitation of $NaBO_2$ (one of the hydrolysis products) at high sodium borohydride concentrations. As this product precipitates it may block the flow channels, besides at ambient conditions precipitating in a hydrated form, which means that less water is available for the hydrolysis reaction. In 2006 Sang et al. [20] developed a mathematical model to predict the maximum concentration of $NaBH_4$ at different temperatures for $NaBO_2$ to be kept from precipitation. For instance, even at high temperatures $\approx$100 °C the maximum sodium borohydride concentration usable was around 25 wt%. Besides the continuous flow design other systems have been proposed over the last years. Aiello et al. [21] proposed a system where the hydrolysis of solid sodium borohydride was achieved using high temperature steam. They reached 100% yield without catalyst, however a 400% excess of steam at 110 °C was used. This excess of steam reduced significantly the gravimetric hydrogen storage capacity. In 2006 Prosini et al. [22] also proposed a system without the use of catalyst, where instead of steam they mixed concentrated HCl with solid $NaBH_4$ in order to drive the reaction. They achieved a hydrogen storage capacity of 4 wt% (reactants only). This system seemed to be a good alternative to catalytic hydrolysis; however the need to supply acid with each tank of sodium borohydride would increase the cost of fuel and additional safety measures needed to be taken when dealing with strong acids. More recently a new approach has been the focus of much attention; a small amount of catalyst precursor is added to the solid $NaBH_4$, the precursor is reduced to form the catalyst proper as water is added. The big advantage of this method is that sodium borohydride and its by-products do not have to be kept in solution, thus increasing the overall gravimetric hydrogen storage capacity. Three good examples of this system were published in 2009 by Liu et al. [23], Gilson et al. [24] and Akdim et al. [25].

In comparison with experimental testing, very little work has been done on reactor modelling. So far, only three models have been reported [26,28]. Zhang et al. [26] published the first work in this field in 2007. They developed a one dimensional (1D) numerical model for a 1 kWe system, which they had used previously for experimental testing. In this model they assumed homogeneous catalysis and to validate it they used the collected experimental data, mainly the temperature inside the reactor. The transport processes involving multicomponent and multi-phase were coupled with reaction kinetics, which was the subject of intensive study by the same research group. They used this model to predict reactor behaviour at different fuel concentrations, flow rates and reactor pressure; the obtained results compared reasonably well with the experimental data. By using only one dimension, the impact on performance by the geometric parameters of the reactor is not totally taken into account, besides the variation of the dependent variables being only assumed on the flow direction. Pinto et al. [27] developed a zero dimensional model to simulate a sodium borohydride-based hydrogen generator with a polymer electrolyte membrane fuel cell (PEMFC) stack system. In this model the sodium borohydride reactor was simply modelled with the kinetic equation, which was sufficient because in this case the