Hydrogen Storage and Production at Low Temperatures from Borohydrides

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ABSTRACT

Chemical hydrides, particularly borohydrides, are currently being developed as hydrogen production and storage options. It is thought that their high volumetric and gravimetric efficiency enable them to compete with available storage options such as compression and liquefaction, for selected applications. In this work, a low temperature hydrogen producing process is studied using sodium borohydride as a hydrogen producing agent using own developed nickel-based catalysts. The hydrogen generation kinetics was studied at various temperatures with the catalyst found to be efficient in the hydrolysis of sodium borohydride with an activation energy associated to the process of ~67 KJmol⁻¹. The quantity of hydrogen generated is 100% stoichiometric. The catalyst is re-usable. The hydrogen generating rate increase linearly with the concentration of sodium hydroxide used as stabilizer. Even in highly concentrated solutions of the stabilizer, self-hydrolysis still occurred at moderate temperatures.

KEYWORDS: Sodium borohydride, Chemical hydride, Fuel cell, Hydrogen storage

Introduction

Sustainable hydrogen production and the development for storage materials is considered a serious drawback to commercial applications and to the full implementation of a hydrogen economy. Energy densities, cost, safety and ease of manufacture, are amongst the factors to be taken into account for the evaluation of storage systems; currently none satisfy all the needed requirements to gain wide-scale acceptance.

Available hydrogen storage options include the use of heavy pressurized tanks with efforts continuing to improve volumetric efficiency. Hydrogen can also be stored as a liquid in cryogenic tanks providing the highest storage density per unit volume in practical systems, nonetheless liquid hydrogen has a very low temperature of liquefaction (-253°C), which requires energy consumption; evaporative losses occur at a significant rate requiring a high degree of thermal insulation, which in turn adds to weight and cost of storage tanks. Hydrogen can also be stored as a solid in metal hydrides. Heat is required to release hydrogen. Metal hydride systems are compact with about a third of the volume of a pressurized hydrogen gas tank, say at 5000 psi. They are, however, very heavy: a metal hydride system holding 5 kg of hydrogen would weight up to 300 kg.

Chemical hydrides, particularly borohydrides, are currently being developed as hydrogen producing and storage options [1-11], since they exhibit high intrinsic energy densities, see table 1. Cost effective recycling methods are needed for improvement of this storage option, for use in selected fuel cell applications.

Figure 1 compares the advantages of high volumetric and gravimetric efficiencies of chemical hydrides with other available storage options. Cost issue targets are also stated in the figure. Furthermore, advantages includes the fact that hydrogen can be stored at ambient conditions in a water-based liquid fuel, which does not require conditions such as high pressure storage or low temperature.
Table 1. Chemical Hydrides: gravimetric and energetic density per unit mass.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>wt % H₂</th>
<th>kWh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH + H₂O → LiOH + H₂</td>
<td>7.7</td>
<td>1.46</td>
</tr>
<tr>
<td>NaH + H₂O → NaOH + H₂</td>
<td>4.8</td>
<td>0.91</td>
</tr>
<tr>
<td>CaH₂ + 2H₂O → Ca(OH)₂ + 2H₂</td>
<td>5.2</td>
<td>0.99</td>
</tr>
<tr>
<td>LiAlH₄ + 4H₂O → LiOH + Al(OH)₃ + 4H₂</td>
<td>7.3</td>
<td>1.38</td>
</tr>
<tr>
<td>LiBH₄ + 4H₂O → LiOH + H₃BO₃ + 4H₂</td>
<td>8.6</td>
<td>1.63</td>
</tr>
<tr>
<td>NaAlH₄ + 4H₂O → NaOH + Al(OH)₃ + 4H₂</td>
<td>6.4</td>
<td>1.21</td>
</tr>
<tr>
<td>NaBH₄ + 2H₂O → NaBO₂ + 4H₂</td>
<td>7.3</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Fig. 1. Volumetric and gravimetric efficiencies for some storage options including chemical hydrides. Cost per kWh is also shown together with targets for 2010 and 2015.
When using sodium borohydride, hydrogen can be produced by hydrolysis using an appropriate catalyst. In the literature there are a few reports on suitable catalysts, even though none have been forward as commercially viable. Most of the works report experiments performed in reaction vessels at ambient pressure. Ruthenium supported on anion exchange resin [3,4], a series of metal catalyst coated on metal oxides [5] and nickel-based catalyst and supports [6,8,10,11], are within the most frequently reported.

The choice of a chemical hydride in this work, as a hydrogen-producing agent, is sodium borohydride. Hydrogen is produced by a hydrolysis process using an own developed nickel-based catalyst that can be reuse with excellent reproducibility.

**Experimental**

Typical experiments involved 0.1 to 0.2 g of catalyst for a 10 wt % sodium borohydride (from Rohm and Haas) stabilised solution, typically 3 wt % NaOH. Concentrations up to 20% NaOH were also used.

A nickel-based catalyst in the form of a finely divided powder was prepared from nickel salts in a reducing environment.

A study of the hydrolysis reaction was first conducted in order to determine reaction rates in different conditions. The produced hydrogen volumes were measured as a function of time at controlled temperature, till complete exhaustion of the reactant.

An scanning electron microscope image (SEM) of the produced catalyst powder is shown in figure 2, exhibiting the structure of the catalyst at a nanoscale.

![Fig. 2.- SEM typical view of synthesized nickel-based catalyst used in this work.](image)

**Results and Discussion**

**Storage capacity**

Figure 3 shows the amount of hydrogen that can be generated as a function of the concentration of sodium borohydride for a 3 % NaOH solution (up to 7.7 wt % in a 35 wt % solution). The volumetric storage density for the same system, is also shown (up to 921 standard litters for a 35 wt % sodium borohydride solution).
Fig. 3.- Volumetric and gravimetric storage densities for sodium borohydride solutions of various concentrations.

Self-hydrolysis, stability and half life time

Self-hydrolysis of sodium borohydrides in water occurs, the process rate increases with increasing solution temperature. The kinetics of hydrogen production from a 10% wt sodium borohydride solution was studied at controlled temperatures varying from 27º to 90 ºC. Figure 4 shows the volume of produced hydrogen as a function of time.

Fig. 4.- Self-hydrolysis of sodium borohydride in water (10wt%) as a function of temperature.

Solutions are not stable unless maintained at sufficiently high pH, even though there is a temperature dependence of the hydrogen generation rate that is evident in solutions as concentrated as 20 wt % NaOH. Solution half-life (the time for one-half of a sodium borohydride solution to decompose) depends on pH and solution temperature [12], see fig 5.
Catalysed Hydrolysis

In order to produce hydrogen in a controlled manner from sodium borohydride, both alkalinization of the solution and the use of a catalyst are necessary to stabilise the solution and produce significant amounts of hydrogen, respectively. Figure 6 shows the volume of hydrogen produced in a solution of 10% sodium borohydride stabilised in 3 % NaOH. The variation in the temperature of the solution during the course of the reaction is also shown in the figure. The reaction is exothermic and requires no heat input. All hydrogen present in the reactant was exhausted at variable reaction rate and temperature, in relatively short times.

Fig.5.- Self-hydrolysis in water: Half-life (min) for a sodium borohydride solution as a function of pH at 25°C according to [12].

Fig.6.- Production of hydrogen (ml) as a function of time from a 10 % wt sodium borohydride solutions stabilized in 3 % wt NaOH in contact with a nickel-based catalyst. The increase in temperature of the solution due to the proceeding of the reaction was registered simultaneously.
Every molecule of borohydride produces 8 atoms of hydrogen - all hydrogen atoms present in the borohydride are converted to hydrogen gas with water participating also as a reactant:

\[
\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{NaBO}_2 \cdot 2\text{H}_2\text{O} \quad (-218 \text{KJmol}^{-1})
\]  

(1)

The hydrogen generation kinetics was studied at ambient pressure and at controlled temperature within an interval from 25°C to 90°C in the presence of various Ni-based catalyst. The quantity of hydrogen generated is stoichiometrically 100%, for all studied temperatures, always exhibiting a linear relationship between the produced volume and time. An activation energy of ~ 67 KJmol\(^{-1}\) was estimated from a linear Arrhenius type plot. More favourable activation energies were obtained when modified catalyst were used, see figure 7a). Catalyst were re-used with excellent reproducibility.

Increase in NaOH concentration also increased the generation rate of hydrogen, see figure 7b), contrasting with results obtained in Ru based catalyst [4].

The use of higher concentrations of sodium borohydrides brought about the question of water management in the catalysed system with decreasing rates in the hydrogen production.

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![Graph showing catalyst improvement and hydrogen generation rate vs NaOH concentration.](image_url)

**Fig.7.** Catalyst improvement shown as hydrogen volume generation rate per gram of catalyst at a controlled temperature of 45°C (a); the effect of the concentration of NaOH as stabilizer in the generation rate of hydrogen at 45°C for the nickel-based catalyst referred to as Catalyst100.
**Concluding Remarks**

Sodium borohydride is a reducing agent capable of reducing protonic hydrogen from water whilst simultaneously being oxidising to produce hydrogen gas. The use of sodium borohydrides as hydrogen producing and storage agents brings the following advantages:

- borohydride dissolved in water is non-flammable,
- the reaction is exothermic and does not need energy input,
- high purity hydrogen can be produced at low temperatures with high volumetric and gravimetric storage efficiencies,
- reaction products are non-toxic and recyclable.

In this work, a cheap, non-noble nickel based non-commercial catalyst is proven to be efficient in the hydrolysis of sodium borohydride with an activation energy associated to the process of ~67 KJmol⁻¹. The quantity of hydrogen generated is 100 % stoichiometric. The catalyst is re-usable.

The hydrogen generating rate increase linearly with the concentration of sodium hydroxide used as stabilizer.

Even in highly concentrated solutions of the stabilizer self-hydrolysis still occurs at moderate temperatures.

Research in progress includes electrochemical characterization of the catalyst and the use of stabilized sodium borohydrides for fuelling of fuel cells using on-demand and pressurized reactors.

**References**


