High volume hydrogen production from the hydrolysis of sodium borohydride using a cobalt catalyst supported on a honeycomb matrix

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HIGHLIGHTS

- A Co_xB catalyst supported on Cordierite Honeycomb was synthesized.
- Apparatus for the H_2 generation from the Sodium Borohydride hydrolysis was showed.
- The catalyst was able to evolved up to 35 L min^{-1} g$_{Co}^{-1}$ at 5 bar pressure.
- The apparatus was able to feed a 2 kW scale PEMFC stack in principle.

ARTICLE INFO

ABSTRACT

Hydrogen storage and distribution will be two very important aspects of any renewable energy infrastructure that uses hydrogen as energy vector. The chemical storage of hydrogen in compounds like sodium borohydride ($NaBH_4$) could play an important role in overcoming current difficulties associated with these aspects. Sodium borohydride is a very attractive material due to its high hydrogen content. In this paper, we describe a reactor where a stable cobalt based catalyst supported on a commercial Cordierite Honeycomb Monolith (CHM) is employed for the hydrolysis of alkaline stabilized $NaBH_4$ (SBH) aqueous solutions. The apparatus is able to operate at up to 5 bar and 130 °C, providing a hydrogen generation rate of up to 32 L min^{-1}.

1. Introduction

The storage and distribution of hydrogen is one of the most important aspects of a hydrogen based economy [1,2]. The volume required to store 4 kg of hydrogen gas in compressed cylinders at 200 bar is about 225 L. The production and storage of liquefied H_2 is costly, as it requires high-energy input and sophisticated equipment. Alternatively, the use of sodium borohydride ($NaBH_4$, SBH) as

a potential hydrogen storage material has attracted significant interest from the late 1990s by virtue of its high Gravimetric Hydrogen Storage Capacity (GHSC) [1,3]. Hydrogen gas can be released from SBH by hydrolysis in the presence of water forming sodium metaborate ($NaBO_2$) and heat (Eq. (1))

$$NaBH_4 + (2 + x)H_2O \rightarrow NaBO_2 \cdot x\,H_2O + 4H_2 + \sim 300\ kJ/mol$$

(1)
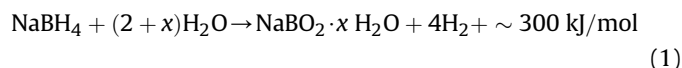
The value of GHSC depends upon the hydration state of the $NaBO_2$ by-product (GHSC = 10.8% with $x = 0$; GHSC = 7.3% with $x = 2$ and GHSC = 5.5% with $x = 4$). The most common hydration state of sodium metaborate is two [4]. For practical application of the $NaBH_4$–H_2O system for hydrogen generation in a controlled

manner, one has to take into account also the stability of $NaBH_4$ solutions given the thermodynamic spontaneity of reaction (1). For this reason alkali metal hydroxides, generally sodium or potassium hydroxides (NaOH or KOH) are used to stabilize $NaBH_4$ in aqueous solutions.

Reaction (1) is a spontaneous and exothermic process that can be accelerated by means of suitable catalysts, generally based on finely dispersed transition metals deposited on metal oxides or carbon supports. Catalysts employed include noble metal salts (Pt, Rh, Ir, Ru) [1,5,6], non-noble metal salts (Mn, Fe, Co, Ni, Cu) [7–9], and metal borides such as cobalt-boride (CoB), cobalt–cobalt boride (Co–CoB) and nickel–cobalt boride (Ni–CoB) which combine excellent catalytic activity with low cost [4,10–14]. The main drawback of the use of such cobalt based catalysts consists in the dramatic loss of activity after only a few operative cycles [10,12,13]. This decrease in activity is believed to be due to the formation of a hydrated salt of sodium metaborate which precipitates and blocks catalytic sites. The solubility of sodium metaborate (28 g in 100 g of H_2O at 25 °C) is lower than that of $NaBH_4$ (55 g in 100 g of H_2O). In order to avoid this deactivation process an initial $NaBH_4$ concentration lower than 16 g in 100 g of water is generally used [10,15]. A number of studies have been published dealing with both the catalytic activity and long-term stability of $Co_2–B$ catalysts doped with either Cr or W [1,4,5,7,13,16,17]. Cobalt oxides have also been extensively studied [14,18,19], using various catalyst supports, like nickel foam [20–22], carbon [23–25], polymers [26–34], soils [35] and minerals [36–38].

Several types of reactors, both static and dynamic have been designed to exploit the SBH reaction. In static devices, the catalyst either a powder, in pellet form or supported on an inert porous material such as honeycomb monoliths, is introduced into a vessel containing the $NaBH_4$ solution [6,39–43]. Static systems exhibit generally low efficiency due to various phenomena including: (a) the difficulty of catalyst separation from the exhaust solution; (b) catalyst leaching from the support, (c) the de-activation of the catalyst due to the precipitation of sodium metaborate and (d) mass transport problems. Dynamic systems are based on the flow of a $NaBH_4$–NaOH solution inside a tubular reactor containing an appropriate catalyst [44]. In a recent example Amendola et al., describe the use of a peristaltic pump that forces the $NaBH_4$ solution to pass through a reactor containing a Ru-based catalyst supported on ion-exchange resins. The reactor is part of the Millennium Cell and Horizon Fuel Cell technology applied to Hydropak generators with a nominal maximum power output of 50 W [45–49]. Kim et al. have reported a system using a Co-based catalyst supported on nickel foam, which feeds H_2 to a 400 W PEM Fuel Cell (Proton Exchange Membrane Fuel Cell) [40]. In another example Arzac et al. used a similar Co catalyst to develop a device which produces and feeds H_2 into a 60 W fuel cell stack [42]. Kojima et al. developed a 10 kW system using 240 g of a $Pt–LiCoO_2$ catalyst confined in a honeycomb monolith. This system was able to produce H_2 with a maximum flow of 120 L min^{-1} at about 110 °C [41].

The state of the art in this field is rather varied with a number of different devices and catalysts described in the literature. It is, however, equally apparent that such devices do not fully satisfy market requirements, regarding various factors that include: (a) low H_2 production capacity, (b) low catalyst stability, (c) the need for frequent catalyst replacement, (d) high catalyst cost, (e) the inability to interrupt hydrogen evolution on demand and (f) the need to use concentrated $NaBH_4$ solutions (more than 15 wt%). Here we describe the design and construction of a SBH reactor that utilizes a cobalt boride (Co_xB) catalyst supported on a commercial Cordierite Honeycomb Monolith (CHM). At ambient pressure, the system produces 7.5 L min^{-1} g_{Co}^{-1} of hydrogen at 70 °C. At 134 °C and

5 bar outlet pressure hydrogen production of up to 32 L min^{-1} g_{Co}^{-1} was obtained. The stability of the catalyst system studied under working conditions showed no significant decrease over up to 10 repeat cycles.

2. Experimental

2.1. General

The Cordierite Honeycomb Monolith (CHM) was purchased from Corning (Celcor® 600/4) and was used as is. All chemicals were purchased from Sigma Aldrich (ACS reagent grade purity) and used without any further purification.

2.2. Synthesis of Co_xB/CHM

The CHM was first cut to size with a base of 20 mm × 22 mm (about 400 cells) and 89 mm tall. The Co_xB/CHM catalyst was prepared as follows. (1) The CHM was dipped in a 0.5 M $Co(CH_3COO)_2\cdot4H_2O$ aqueous solution for 30 min, to absorb the cobalt salt precursor, and then drained; 2) dried at 120 °C for 30 min and heated at 400 °C for 40 min to decompose all the acetate to cobalt oxide, as reported by Grimes and Fitch [50]; and 3) cooled in air and weighed to calculate the metal loading of Co_3O_4/CHM. Each deposition cycle only deposits a small amount of metal oxide so it was repeated until the desired metal loading was reached (1.174 g or Co, 8.27 wt.%). The metal content was confirmed with ICP-OES analysis of a small portion of the catalyst. During preparation the colour of the CHM changed from light yellow to dark brown, the colour of cobalt oxide (see Supporting information, Fig. S1). Finally, the Co_3O_4/CHM was dipped in a 13 wt.% SBH aqueous solution for 20 min at room temperature to obtain the active catalyst. The colour of the CHM became immediately black.

2.3. Physical characterization

The samples were characterized by X-ray Powder Diffraction (XRPD), using a PAN analytical X'PERT PRO diffractometer, and by Scanning Electron Microscopy (SEM), acquired by a FEI ESEM Quanta 200 instrument. The XRPD measurements were conducted on a milled fraction of each sample employing CuKα radiation (λ = 1.54187 Å) and a parabolic MPD-mirror. The traces were acquired at room temperature in the 2θ range from 5.0 to 80.0°, using a continuous scan mode with an acquisition step size of 0.0263° and a counting time of 49.5 s. The SEM analysis was conducted on a single wall of the lamellar structure cut from the body of the catalyst.

2.4. Catalytic activity

The catalytic activity was evaluated using a stainless steel reactor, shown schematically in Fig. 1. The reactor was made of a cylindrical stainless steel chamber (diameter 77 mm and height about 40 cm) closed at the bottom with a disk, equipped with a tap to enable removal of the solution from the reactor. On the top, there is a removable head piece, with a stainless steel rod whose vertical movement is controlled by a stepper motor. At the tip of the rod, there is a perforated plastic cylinder as catalyst holder. The head system allows the control of hydrogen evolution thanks to control of the immersion of catalyst in the SBH solution. In the present study, the catalyst was completely immersed into the solution during all experiments. During the experiments conducted at atmosphere pressure, the generated hydrogen passed through a special channel in the head piece connected to a vapour trap and a flow meter, while an adjustable check valve was inserted between