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

Andrea Marchionni a, *, Manuela Bevilacqua a, Jonathan Filippi a, Maria G. Foliero a, b, Massimo Innocenti a, c, Alessandro Lavacchi a, Hamish A. Miller a, Maria V. Pagliaro a, c, Francesco Vizza a, **

a Consiglio Nazionale delle Ricerche — Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Via Madonna del Piano 10, Sesto Fiorentino, 50019, Italy
b Università di Siena, Dipartimento di Biotecnologie, Chimica e Farmacia, Via Aldo Moro 2, Siena, 53100, Italy
c Università di Firenze, Dipartimento di Chimica, Via della Lastruccia 3, Sesto Fiorentino, 50019, Italy

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A B S T R A C T

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 (NaBH₄) 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 NaBH₄ (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.

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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 H₂ is costly, as it requires high-energy input and sophisticated equipment. Alternatively, the use of sodium borohydride (NaBH₄, 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 (NaBO₂) and heat (Eq. (1))

\[ \text{NaBH}_4 + (2 + x)\text{H}_2\text{O} \rightarrow \text{NaBO}_2 \cdot x\text{H}_2\text{O} + 4\text{H}_2 + \sim 300 \text{kJ/mol} \]  

(1)

The value of GHSC depends upon the hydration state of the NaBO₂ 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 NaBH₄–H₂O system for hydrogen generation in a controlled...
manner, one has to take into account also the stability of NaBH₄ 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 NaBH₄ 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 borohydride which precipitates and blocks catalytic sites. The solubility of sodium borohydride (28 g in 100 g of H₂O at 25 °C) is lower than that of NaBH₄ (55 g in 100 g of H₂O). In order to avoid this deactivation process an initial NaBH₄ concentration lower than 1 g in 100 g of water is generally used [10,15]. A number of studies have been published using along with both the catalytic activity and long-term stability of Co₂–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 NaBH₄ 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 borohydride and (d) mass transport problems. Dynamic systems are based on the flow of a NaBH₄–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 NaBH₄ 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 H₂ 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 H₂ into a 60 W fuel cell stack [42]. Kojima et al. developed a 10 kW system using 240 g of a Pt–LiCoO₂ catalyst confined in a honeycomb monolith. This system was able to produce H₂ 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 H₂ 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 NaBH₄ solutions (more than 15 wt%). Here we describe the design and construction of a SBH reactor that utilizes a cobalt boride (Co₈B) catalyst supported on a commercial Cordierite Honeycomb Monolith (CHM). At ambient pressure, the system produces 7.5 L min⁻¹ g⁻¹ of hydrogen at 70 °C. At 134 °C and 5 bar outlet pressure hydrogen production of up to 32 L min⁻¹ g⁻¹ was observed. 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 Co₈B/CHM

The CHM was first cut to size with a base of 20 mm × 22 mm (about 400 cells) and 89 mm tall. The Co₈B/CHM catalyst was prepared as follows. (1) The CHM was dipped in a 0.5 M Co(CH₃COO)₂·4H₂O 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 Co₈Oₓ/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 Co₈O₄/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 XPERT 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 20 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 movement is controlled by a stepper motor. A. Marchionni et al. / Journal of Power Sources 299 (2015) 391–397
the trap and the flow meter instrument during the high pressure experiments. Inside the reactor, a copper coil was used to control the initial temperature of the solution with circulating warm water (50 °C). The seal of the reactor was tested prior to any experiments using H₂ up to a pressure of 10 bar.

A 3.44 M (ca. 13 wt.%) NaBH₄ solution stabilized with 0.5 M (ca. 2 wt.%) of NaOH was used in all experiments. The actual volume of the solution was about 1.2 L. The hydrogen generation flow was recorded by a Bronkhorst® EL-FLOW® mass flow meter model F-101E-AGD-22-V with maximum flow rate of 10 NL min⁻¹ and with a Bronkhorst® EL-FLOW® mass flow meter model F-101E-AGD-22-V with a 200 NL min⁻¹ scale to comparison. The generated gas was dried with a two step filter (molecular sieves and a liquid nitrogen trap) before the flow meter. The temperature of the solution was measured with a PIXSYS 171-23ABC-T module connected to a PC. Each experiment was stopped when hydrogen flow ceased. Between two subsequent experiments, the catalyst was washed with deionised water and dried in air.

3. Results and discussion

3.1. Physical characterization

The XRPD patterns of the CHM support, catalyst precursor Co₃O₄/CHM after calcination at 400 °C and catalytic phase are shown in Fig. 2. The CHM support shows typical Bragg reflections of Cordierite with chemical formula M₆Si₄Fe₂O₈Al₄Si₅O₁₈ [50], at 10.40°, 18.00°, 18.95°, 21.61°, 26.37°, 28.35°, 29.42°, 33.88°, 38.74° and 54.36° (trace a).

The catalyst precursor also shows the spinel Co₃O₄ (Fd-3m) signals at 31.26° (022), 36.84° (113), 44.80° (004), 59.35° (115) and 65.22° (044) (trace b) [51,52]. Debye–Scherrer analysis [53] indicates an average Co₃O₄ crystallite size of 18.5 nm.

After treatment with SBH (trace c) signals for NaB(OH)₄(H₂O)₂, a
sodium metaborate hydrate phase, are visible at 16.51°, 18.64°, 23.83°, 25.74°, 31.32°, 32.38° and 38.00° [54]. No presence of CoB [55,56] or any other Co species was detected even after washing sample c with water (trace d). To understand the reasons for this behaviour, we synthesized CoB in powder form not supported on cordierite (see Supporting Information). The XRPD pattern of this material did not show any clearly identified peak for any Co species, suggesting that the CoB was in an amorphous phase not detectable by XRPD. For comparison, we analysed also the same CoB powder after a heating treatment at 300°C (to favour sintering) and a commercial (Sigma Aldrich) cobalt boride. Both materials showed peaks (see Fig. S4) with low intensity (large signal to noise ratio). These results support evidence of the presence of an amorphous phase of cobalt boride on the cordierite support.

Scanning electron microscope (SEM) images of the CHM support (Fig. 3A) show the macro channels of the honeycomb structure at low magnification and pores, cavities and surface roughness at high magnification (insert). Energy-dispersive X-ray spectroscopy (EDX) analysis (Fig. S2A–C) confirm the main components of CHM: Mg, Al, and Si. An image of the Co3O4/CHM pre-catalyst (Fig. 3B) shows particle aggregates on the surface support ranging from a few μm to 50 μm. The EDX analysis conducted on these particles confirms the presence of Co and O of Co3O4 in addition to those of CHM (Fig. S2D–F). The morphology of the catalyst obtained from Co3O4/CHM by treatment with SBH (Fig. 3C), changes significantly with respect to Co3O4/CHM. In fact, it becomes difficult to see the macro channels of the honeycomb structure of CHM support. Large (100–200 μm) and amorphous particles cover completely the surface. At higher magnification, a layer composed by needles is visible. EDX analysis identified it as sodium borate, in agreement with the pattern c of XRD graph (Fig. S2G–I).

After a washing treatment with deionized water, the sodium metaborate in the form of needles disappears from the surface, leaving an amorphous layer. The EDX analysis (Fig. S2J–L) showed a drastic decrease of the metaborate salt (sodium signal), while the signal of boron remains as well as both the signals of Co and support (Mg, Al, Si). This evidence supports the hypothesis of the existence of an amorphous phase of CoB, anchored on the support, still covered by some residue of sodium metaborate which has not been completely eliminated by washing with water [52].

To complete the understanding of this morphology behaviour, was also analysed a sample after ten catalytic cycles and the images are reported in Fig. S2M–O. The surface appears very similar to the sample after the first catalytic cycle, meaning that no significant change in morphology occurs over repeated cycling.

3.2. Hydrogen generation

The hydrolysis of NaBH4 was carried out in the stainless steel reactor shown in Fig. 1, the structure of which is described in detail in the experimental section. The main features of the reactor consist of: i) a removable head that allows a vertical movement of a stainless steel rod, on whose tip is installed the catalyst holder, controlled by a stepper motor; and ii) a copper coil with circulating warm water to control the initial temperature of the solution.

The hydrogen generation rate (HGR) can be varied by controlling the immersion of the catalyst in the SBH aqueous solution. In the experiments described here, the catalyst was completely immersed. The solution (1.2 L of a 3.44 M NaBH4 aqueous solution stabilized with NaOH 0.5 M) contained in the reactor was gently stirred.
warmed by means of the internal coil to promote the initial stage of the catalytic process [12,15,26].

The pre-catalyst in the form Co3O4/CHM, was used in the first cycle of SBH hydrolysis. In this way the catalyst CoxB was generated in situ. In Fig. 4 are reported the profiles performed at ambient pressure of the HGR (lines), reported as L min\(^{-1}\) g\(^{-1}\)C0\(_2\), showing the total outflow of hydrogen produced during the first, second and tenth cycle (for comparison, Fig. S6 in the Supporting Information reports the total volume of evolved hydrogen). In all cycles, the HGR showed a bell-like profile. In agreement with the literature data [4,12], the first phase (induction period) where almost no hydrogen evolution is observed lasts approx. 12 min and is due to the formation of active a CoxB phase from the Co3O4; the second phase shows a fast growth of HGR, due to the catalytic activity of the CoxB phase, which reaches a maximum and, finally, during a third period a decrease of HGR is observed due to the depletion of the SBH in the solution. It has also been proposed that in this third phase, the alkaline pH due to the formation of sodium borate, can also lead to the oxidization of the catalyst CoxB to hydrated cobalt hydroxide species [10,18,56,57]. This would justify why the induction period remains in the following cycles.

After each cycle, the reactor was emptied and refilled with a fresh solution of SBH. No leaching of cobalt or solid material from the support into the exhaust solution was observed and this was confirmed by ICP-OES analysis of solutions.

The maximum HGR value of 7.2 L min\(^{-1}\) g\(^{-1}\)C0\(_2\) was reached during the first cycle (Fig. 4), while the second cycle showed a max value of 5.45 L min\(^{-1}\) g\(^{-1}\)C0\(_2\), with a decrease of hydrogen evolution of 25%. In the following ten cycles the activity was stable, with a max HGR of about 5.5 L min\(^{-1}\) g\(^{-1}\)C0\(_2\). This behaviour is in line with the literature data, in particular as observed by Demirci, Miele and co-workers that explained the decrease in HGR is due to hydrated sodium metaborate (NaBO\(_2\)·H\(_2\)O) precipitation on the catalyst surface [58]. Also SEM analysis results reported in Fig. S2M–O show a very similar surface morphology between the samples after the first and the tenth cycle.

The efficiency of hydrogen generation with respect to the theoretical total volume was between 95 and 98% for all cycles. The temperature within the reactor during the first cycle, reached a maximum of ca. 70 °C during the period of maximum hydrogen production (Fig. 4, squares) cooling to 50 °C at the end of the reaction. The increase in temperature is due to the high reaction rate that releases about 3.3 kJ of heat per L of hydrogen produced. A similar trend was observed in the other reaction cycles.

To better understand the role of the CHM support in the catalytic reaction, we studied also the behaviour of a homemade CoxB powder catalyst (for more details see the Supporting Information). The performance was very good with a maximum HGR of 7.4 L min\(^{-1}\) g\(^{-1}\)C0\(_2\), and conversion efficiency of 97% which is very close to the values obtained for the CoxB/CHM catalyst (see Fig. S5). So we can conclude that the CHM support does not participate in the catalytic reaction, its role being to increase mechanical resistance and adhesion of the catalyst layer. Indeed, when the catalyst was soaked in the SBH solution the evolved hydrogen passed through the internal channels without breaking any of the superficial layers (see Fig. S5). The absence of active phase leaching permits the design and development of real practical devices for the hydrogen generation from SBH hydrolysis. Moreover, the CHM support has a large surface area (34.5 cm\(^2\) cm\(^{-1}\)) allowing large dispersion of CoxB particles.

We also carried out a set of hydrogen evolution experiments at 5 bar outlet pressure, by inserting a check valve in the line between the vapour trap and the flow meter instrument (Fig. 1 and S3) that allows the passage of hydrogen at pressures above 5 bar. In Fig. 6 are reported the HGR and the temperature profiles of the first, second and tenth cycle conducted 5 bar. Also in this case, the HGR showed a bell-like shape but with a narrower profile with respect to the experiments conducted at ambient pressure. The first cycle reached a maximum production of 32.5 L min\(^{-1}\) g\(^{-1}\)C0\(_2\) while the temperature increased to 134 °C with an efficiency of hydrogen generation of 94%. The second cycle showed a decrease of ca. 25% of the hydrogen flow, while subsequent cycles showed no significant changes in hydrogen productivity. In the exhaust solutions after each test, no residues attributable to leaching of the catalyst were observed.

Here we have exploited the high activity of CoxB for the hydrolysis of SBH by incorporating the active phase of the catalyst in a high surface area monolith, which combines a high catalyst surface area with improved stability due to strong catalyst—support interactions. During the first cycle of batch experiments, a drop in hydrogen production rate is observed, associated with a complex modification of the catalytic system where cobalt oxides are transformed into CoxB with co-precipitation of sodium metaborate, while the performance remains stable during further cycles. Theoretically, the generated hydrogen at the ambient pressure experiments would be able to feed a 500 W PEMFC (Proton

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Fig. 4. HGR profiles of the first, second and tenth cycle. The temperature profile (squares) of the first cycle is also shown.

Fig. 5. Proposed diagram of operation of the CoxB/CHM catalyst. The catalyst surface in each channel on contact with SBH produce hydrogen gas and sodium borate.
Exchange Membrane Fuel Cell), while the HGR observed during the pressurized experiments at 5 bar would be able to feed a 2 kW size PEMFC stack.

4. Conclusions

In summary, we describe a reactor within which a cobalt-based catalyst supported on a commercial Cordierite Honeycomb Monolith (CHM), is used for the hydrolysis of alkaline stabilized Sodium Borohydride (SBH) aqueous solutions. The apparatus was able to operate at high temperature (>130 °C) and high pressure (5 bar).

The maximum HGR was 7.2 L min⁻¹ g⁻¹ at ambient pressure and 32.5 L min⁻¹ g⁻¹ at 5 bar. The combination of this reactor with a suitable PEMFC stack to form a standalone power unit will form the basis of our future development of this technology.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.09.006.

References


XRPD data were extracted from PDF-2 containing ICDD (International Centre for Diffraction Data) experimental powder data collection: http://www.icdd.com.


