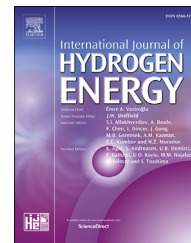


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Base-metal catalysts based on porous layered double hydroxides for alkaline-free sodium borohydride hydrolysis

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ARTICLE INFO

Article history:

Received 19 April 2017

Received in revised form

24 May 2017

Accepted 1 June 2017

Available online 27 June 2017

Keywords:

H₂ generation

Catalyzed borohydride hydrolysis

Supported base-metal catalysts

Inverse opal

Porous LDH

ABSTRACT

Catalyzed hydrolysis of sodium borohydride (SBH) has demonstrated promise for generation of a pure hydrogen stream for use with fuel cells. In designing an improved continuous hydrogen generator that uses the substantial heat released in the hydrolysis reaction to more effectively separate the sodium borate by-product, we sought a robust base-metal catalyst that could tolerate the exothermic reaction under flow conditions. Working under base-free conditions in ethanol solvent we identified reduced nickel and iron-containing particles supported on layered double hydroxides (LDHs) as robust catalysts. Catalytic activity was enhanced further using high surface area hierarchical supports prepared using the ‘inverse opal’ method. In particular, macroporous Ni–Mg–Al and Fe–Mg–Al LDHs produced 0.4 and 1.0 mol of hydrogen per minute per mole of active metal of the supported catalyst in aqueous ethanol solvent.

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Introduction

Polymer electrolyte membrane (PEM) fuel cells have emerged as one of the most efficient energy generators but their success in the portable power generation market depends on a convenient source of pure hydrogen fuel [1]. Hydrogen is an environmentally benign and gravimetrically energy-rich fuel that produces only water vapor effluent when combined with air in a PEM fuel cell [2]. The low volumetric energy density of

hydrogen, however, requires expensive compression that also hampers its practical applications [3,4]. An alternative approach involves storage of hydrogen in so-called ‘chemical hydrides’ that offer thermal stability, high density and ease of high purity hydrogen release [5]. Although azacycloalkanes could serve as liquid fuels capable of reversible hydrogen storage [6–10], the high temperatures (ca. 200 °C), long recharging times and precious metal catalysts required have limited their utility. In contrast, alkali metal borohydrides, MBH₄, where M is Li [11], Na [12–16], or K [17] have been well

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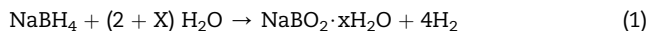
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<http://dx.doi.org/10.1016/j.ijhydene.2017.06.007>

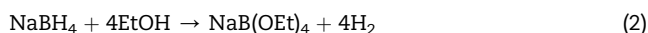
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studied as irreversible hydrogen sources (Eq. (1)) and metal-catalyzed hydrolysis of sodium borohydride has been demonstrated for transportation applications [18].



As the least expensive metal borohydride, sodium borohydride (SBH) is a stable solid at room temperature that is slowly hydrolyzed by moisture to produce minimal amounts of pure hydrogen [19]. As such, a catalyst is needed to increase the rate of reaction. Early investigations on SBH hydrolysis date back to 1953 [20] utilizing cobalt(II) chloride as a catalyst precursor that generates cobalt borides under the reaction conditions [21]. Consequently, there have been a plethora of studies using both precious- and base-metal heterogeneous catalysts [12,14,16,22–25]. Following the work by Schlesinger et al. [20], special attention has been dedicated to development of low-cost, highly active Co–B catalysts [26]. Copper supported nanostructured Co–B catalysts with high durability (80% of the original activity after 5 cycles) were reported to release $\sim 8 \text{ L}(\text{H}_2) \text{ min}^{-1} \text{ g}^{-1}$ [27]. Other supports such as reduced graphene oxide [28], acidic montmorillonite [29], metal-organic frameworks [30], TiO_2 [31], $\gamma\text{-Al}_2\text{O}_3$ [32] and polymeric microgels [33] along with several additives including Mo [34,35], Ce [31], Ni [12] and P [36] have been investigated to enhance the activity of the Co–B catalysts mainly using alkaline aqueous NaBH_4 solutions.

The US DOE made a “no-go” recommendation in 2007 for SBH hydrolysis for transportation purposes [18] due to the need for added base and excess water to solubilize the borate by-product and the large heat of reaction which makes the fuel regeneration energy intensive. However, the amount of hydrogen that can be released from catalytic SBH/ H_2O systems under ambient conditions exceeds that of most chemical hydrogen storage materials, making it an attractive candidate for portable power applications. In a recent review Demirci rightly notes that base-metal catalysts already achieve sufficient activity and that current research should be focused on catalyst lifetime, reaction engineering and scale-up and borate separation/recycling [25]. Reactions of base-stabilized aqueous SBH solutions, for example, afford a sticky, hydrated sodium borate product that coats the catalyst in batch reactions and leads to plugging in flow applications. One proposed solution to this problem involves conducting the hydrolysis reaction in an alcohol solvent [31,37–40]. In one example, high conversion of SBH was obtained at low temperatures (27–35 °C) in pure ethanol using acetic acid as a catalyst (Eq. (2)) [41].



More suitable hydrolysis conditions are proposed when an alcohol, particularly methanol or ethanol, is mixed with water [31]: 1) Alcoholysis of SBH proceeds with higher rate than the aqueous systems, even under uncatalyzed conditions. 2) Alcohol containing systems have lower freezing points than pure water which makes these systems more practical for subzero environments. 3) The borate by-products ($\text{NaB}(\text{OCH}_3)_4$ and $\text{NaB}(\text{OCH}_2\text{CH}_3)_4$), are completely soluble in the methanol

or ethanol solvent eliminating the plugging problems. 4) These borate by-products are readily hydrolyzed to methanol or ethanol, increasing the gravimetric energy density of the system.

To take advantage of these potential benefits we designed a continuous hydrogen generator that conducts the hydrolysis of SBH in aqueous ethanol solution without added base (Fig. 1). The ethanol solvent (1) is pumped through a cartridge of solid SBH (2) and water (3) is injected just prior to the solution's entry into the solid catalyst cartridge (4). As the generated hydrogen (5) is fed to the fuel cell, the spent fuel solution is pumped to the outer jacket (6) where the heat produced by the SBH hydrolysis reaction then distills the ethanol which is condensed back to the solvent reservoir (1), allowing the solid sodium borate product to build up in the detachable spent fuel cartridge (6). The hydrolysis of NaBH_4 is highly exothermic (-210 kJ/mol H_2 based on Eq. (1)) especially when excess water is used to generate hydrated sodium borate by-product, $\text{NaBO}_2 \cdot x\text{H}_2\text{O}$ [34,39]. Efficient capture of the released heat by the reactor's jacket should then provide enough energy to distill ethanol back to the reservoir (cf. for ethanol at RT: $C_{p,\text{liquid}} = 112 \text{ J/molK}$ and $\Delta_{\text{vap}}H = 38 \text{ kJ/mol}$ [42]). In contrast to its methanolysis reaction [37,38], the reactivity of SBH with ethanol or water is sluggish at room temperature thus limiting the hydrolysis reaction to the catalyst bed to ensure efficient reuse of the reaction heat. Moreover, ethanol is non-toxic and an 80% aqueous solution does not freeze until -59°C . Optimal operation of this generator will depend on the solvent flow rate, SBH particle size, and, most importantly, the activity and lifetime of the supported catalyst.

Herein, various base metal catalysts were investigated including layered double hydroxide matrices. To avoid particle attrition and catalyst bed plugging, we also prepared alternative porous layered double hydroxides and compared their performance.

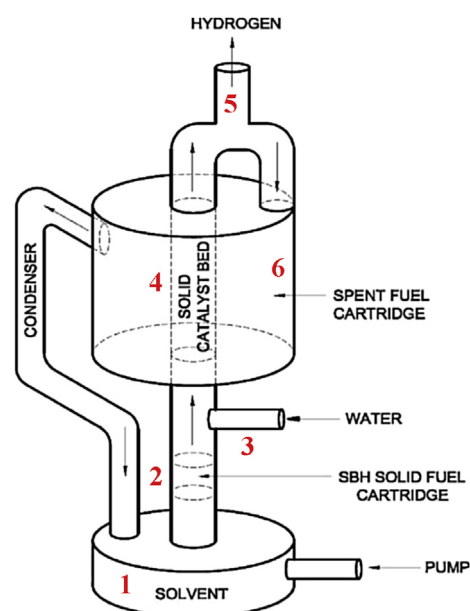


Fig. 1 – Prototype single-pass continuous reactor for hydrolysis of SBH.

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