

Hydrogen Generation from Sodium Borohydride Catalyzed by Cobalt(II) Acetate

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Sodium borohydride as a hydrogen storage material for portable application has attracted much attention. A newly designed reactor with a toroidal tube distributor has been developed to generate hydrogen from sodium borohydride accelerated by cobalt(II) salts. The effects of the cobalt solution flow rate, the cobalt(II) acetate concentration, as well as the reaction temperature on hydrogen generation are discussed. The newly designed reactor successfully reduced the hydrogen generation startup time and improved the water distribution. The results indicate that the startup time is decreased with an increase in (1) the concentration of the cobalt(II) acetate solution, (2) the reactor temperature and (3) the cobalt salt solution flow rate. The hydrogen yield increases with increase in cobalt(II) acetate concentration and reached a maximum at 1 wt %; further increases in the catalyst loading results in a decrease of the hydrogen yield. Furthermore, the hydrogen yields > 99 % is achieved using the novel reactor.

Keywords: Hydrogen generator, Hydrogen generation, Cobalt catalyst, Sodium borohydride.

INTRODUCTION

Hydrogen as an alternative to fossil fuels is one clean fuel for proton exchange membrane fuel cell (PEMFC) and some niche devices. The development of hydrogen energy can increase the diversity of growing energy needs and construct the low carbon economy society¹. Hydrogen can be stored using several methods including high pressure cryogenics and chemical compounds. Sodium borohydride (NaBH₄) as a promising hydrogen storage material has an ideal gravimetric hydrogen storage capacity of 10.7 wt %. Generating hydrogen from NaBH₄ solution has many advantages *i.e.*, NaBH₄ solutions are non-flammable and rate of H₂ generation is easily controlled in low temperature. The maximum concentration of sodium borohydride in water is 34.4 wt % at 25 °C. 1 L solution of 30 % NaBH₄ contains 67 g hydrogen^{2,3}. If using sodium borohydride in solid state, there will be no solubility limitation⁴. And it may also decrease excess water utilization to increase the hydrogen capacity of the hydrogen generation system. Furthermore the generated hydrogen usually contains certain of vapor that is benefit for proton exchange membrane fuel cells (PEMFCs). So, it can be directly provided to PEMFCs which were called "energy exchange machine".

Design of the reactor is critical to hydrogen generation from NaBH₄. Four points need to be considered including

(1) portability of device, (2) controllability of the hydrogen flow rate, (3) heat released and (4) combined with fuel cells.

Murugesan and Subramanian⁵ studied flow through type and diffusion through type hydrogen generators. The maximum hydrogen yield of 97 % is reached when 3 N HCl was used as catalyst. Gislou *et al.*⁶ designed, built and tested different reactor layouts and geometries for hydrogen production from NaBH₄. The reactor is capable of producing hydrogen flow rate in the 5-30 L/h range for several hours. Amendola *et al.*^{7,8} have proposed a safe, simple, compact process for generating pure hydrogen gas on demand from base stabilized, aqueous solutions of sodium borohydride by using a ruthenium catalyst. Gervasio *et al.*⁹ designed and tested a new generator by controlling the providing rate of NaBH₄ solution to the hydrogen generation. Pozio *et al.*¹⁰ had designed a device to generate 50 mL/min of hydrogen at atmospheric pressure. They made the solution of NaBH₄ enter the reactor from the bottom. After reacted over, the byproduct solution had been gone out from the reactor and then had been recycled to the tank. Wang¹³ designed a generator using a recycle method. It consists of a condensation chamber and an evaporation chamber. The former was out of the generator, while the later was in the generator. Heat was transferred out of the generator through changing vapor-liquid phase of water. Combining hydrogen generation system with fuel cells is one important issue to

investigate. Galli *et al.*¹¹ mentioned that a portable energy generator is able to produce on-demand hydrogen to be supplied to a small solid polymer fuel cell in their work. The compact hydrogen generator is designed around a tubular catalytic reactor, whose catalytic powder is held in place by magnetic field. The gas is generated by the exothermic hydrolysis reaction of an aqueous sodium borohydride solution in contact with no-noble catalyst particles inside the reactor. When hydrogen demand stops, the reactor is emptied and the hydrolysis reaction ceases.

However, the previous work⁶⁻¹³ had already made a great of work on the improvement of the experimental apparatus serving as the hydrogen production of sodium borohydride hydrolysis. But some problems are still existing and need to be solved to meet the requirements of reactor design mentioned above. For example, most of the previous work utilized the aqueous sodium borohydride as the reactant resulting in decreasing the portability of device. Thus, this work shows a reasonable solution to improve the portability of device by utilizing the solid sodium borohydride powder reacting with liquid water under catalysts producing hydrogen; meanwhile, a toroidal tube distributor is brought to the reactor and used to improve the water distribution and reduce the startup time of hydrogen production.

EXPERIMENTAL

Sodium borohydride (NaBH_4 , reagent grade = 98 %, AR) was used in solid forms as received. Cobalt chloride (CoCl_2 , reagent grade = 98 %, AR) and cobalt acetate [$\text{Co}(\text{CH}_3\text{COO})_2$, reagent grade = 98 %, AR] were tested as catalysts for this hydrolysis reaction. Pure water (18.25 $\text{M}\Omega \text{ cm}$ @ 25 °C) was obtained from EPED's water purification system (GREEN-10T).

Fig. 1 shows the schematic representation of the hydrogen generator used in this study. The hydrogen generator consists of a hydrogen generation chamber, a buffer chamber and a water distributor, which improves the water distribution. The hydrogen generator is purged by 99.999 % N_2 gas at flow rate of 600 mL/min before the reaction. Hydrogen immediately produces when catalyst solution contacts with NaBH_4 powders. Generated hydrogen flows into the buffer chamber and releases from the reactor through the outlet. The gas is then filtered to remove residual solution drops.

Detection method: The flow rate of dry hydrogen (Q) was measured by the gas flow meter. The hydrogen yield (%) is measured by eqn. 1. Hydrogen flow rate can be controlled by regulating the feed water flow rate. Typically a total weight about 2 g powders of NaBH_4 were placed in the hydrogen generation chamber.

Hydrogen yield % = $Q \times t \times (\text{Theoretical hydrogen volume})^{-1}$ (1)
here, t is reaction time to reach the maximum volume.

RESULTS AND DISCUSSION

Selection of metal catalyst: Hydrolysis of NaBH_4 can be catalyzed by a large number of salts, such as metal chlorides or metal acetates. Metal salts have different influences on half-life of NaBH_4 and the hydrogen generation characters. Schlesinger and Finbolt¹² investigated the effects of several chloride salts on half-life of NaBH_4 hydrolysis. They found

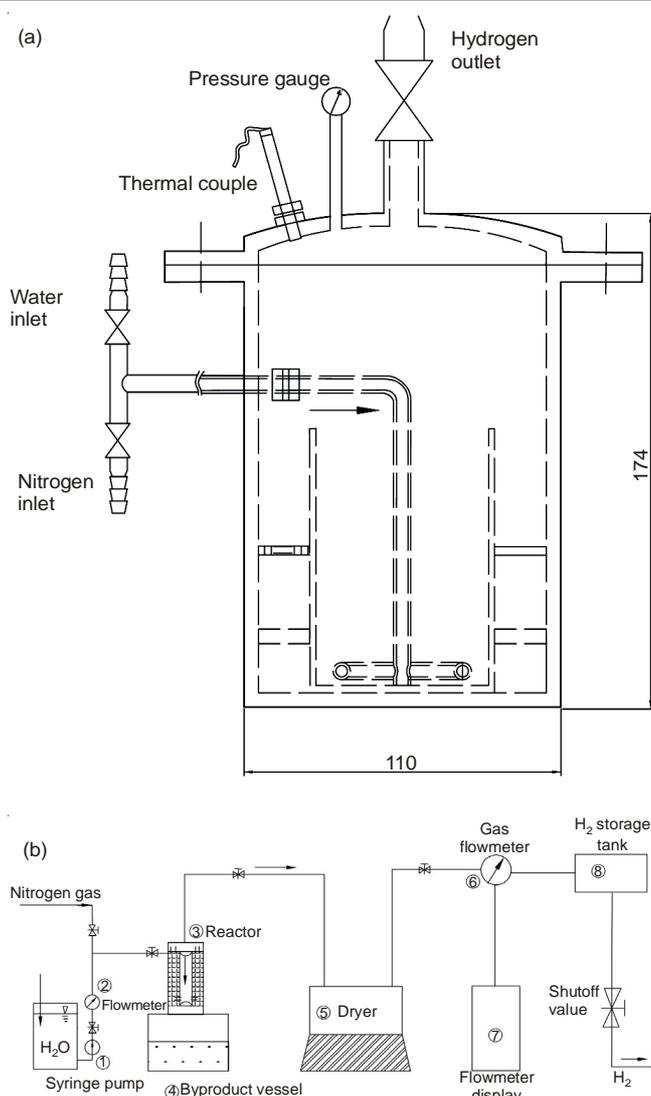


Fig. 1. Overview of hydrogen generator (a) and schematic representation of the reactor test (b)

that nickel, cobalt and iron salts were quite effective. Table-1 shows the half-life information of the studied catalysts. Half-life means the catalytic activity of catalysts. Shorter half-life means faster hydrolysis rate and higher catalytic activity and *vice versa*. The catalytic activity of cobalt chloride is two and four times higher than nickel chloride and iron chloride. Therefore, cobalt salt was selected as catalyst in present experiments.

TABLE-1
INFLUENCE OF HALF-LIFE OF SODIUM BOROHYDRIDE HYDROLYSIS BY USING DIFFERENT METAL-BASED CATALYSTS

Metal	Catalytic compound	$T_{1/2}$ (min)
Cobalt	CoCl_2	9
Nickel	NiCl_2	18
Iron	FeCl_2	38
Osmium	OsO_4	19
Iridium	IrCl_4	28

Fig. 2 shows the hydrogen generation from NaBH_4 using cobalt chloride and cobalt acetate as catalyst. Two cobalt catalysts both reached same hydrogen yield of 99 % at the

end of reaction. The results indicated that the anion ions (Cl^- and CH_3COO^-) have no significantly effect on the catalytic activity for hydrogen production from NaBH_4 . Similar results have also been reported by Schlesinger and Finbolt¹². Cobalt(II) chloride as a simple, efficient catalytic which generated almost 100 % of stored hydrogen with an HGR of $86.3 \text{ L min}^{-1} \text{ g}^{-1}$ (Co) was reported by Demirci *et al.*¹⁴. Therefore, cobalt acetate was used as catalyst in the flowing experiment.

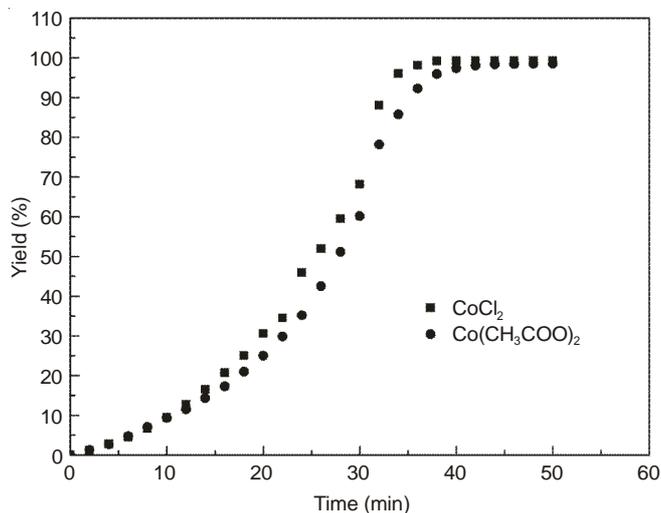


Fig. 2. Hydrogen generation characteristics of CoCl_2 and $\text{Co}(\text{CH}_3\text{COO})_2$ solutions. The experiments were performed at a cobalt solution flow rate of 0.27 mL/min with 2.0 g of sodium borohydride. T reaction temperature was kept at 26°C

Effect of catalyst concentration on hydrogen generation:

Fig. 3a shows the effect of cobalt acetate concentration on the hydrogen generation. The hydrogen generation volume increases with increase in cobalt(II) acetate concentration and reached a maximum at 1 wt %; further increases in the catalyst loading results in a decrease of the hydrogen volume. Fig. 3b shows the hydrogen yield from hydrolysis reaction of NaBH_4 . The hydrogen yield reached 99.3 % using 1 wt % of cobalt acetate solution. For low catalyst concentration (0.5 wt %), the number of available catalytic sites is low and was able to produce small amount of hydrogen. In case of excess of catalyst ($> 1 \text{ wt } \%$), significant amount of hydrogen were generated which prohibits the contact between catalysts and reactants. Therefore, an optimal value with proper reaction rate was found to be 1 wt % in this study. The reaction temperature increased slowly, however, the value of maximum temperature nearly kept same for all conditions (Fig. 4).

Effect of solution flow rate on hydrogen generation:

Fig. 5a,b illustrates the hydrogen generated volume at different solution flow rates. It was found that the hydrogen generated volume increased with increasing the solution flow rates. However, the final hydrogen yields of $> 98 \%$ were achieved for all flow rates. It is suggested that we can increase the solution flow rate to decrease the startup time of generator. Fig. 5c presents the reaction temperature as a function of solution flow rate ranging from $0.1\text{-}0.5 \text{ mL/min}$. As the solution flow rate increased, the reaction temperature raised sharply due to the severe hydrolysis reaction. The maximum temperature also increased as a result of high flow rate.

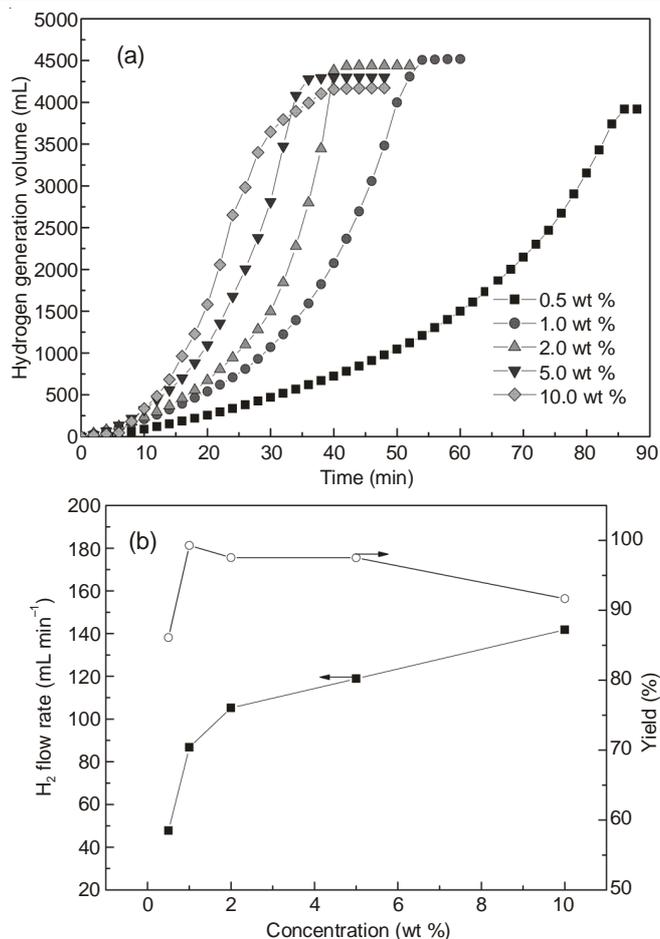


Fig. 3. (a) Hydrogen generation volume at different concentration of catalytic solution; (b) Yield and hydrogen flow rate at different concentration of catalytic solution (2.0 g NaBH_4 , solution flow rate of 0.3 mL min^{-1} at 26°C)

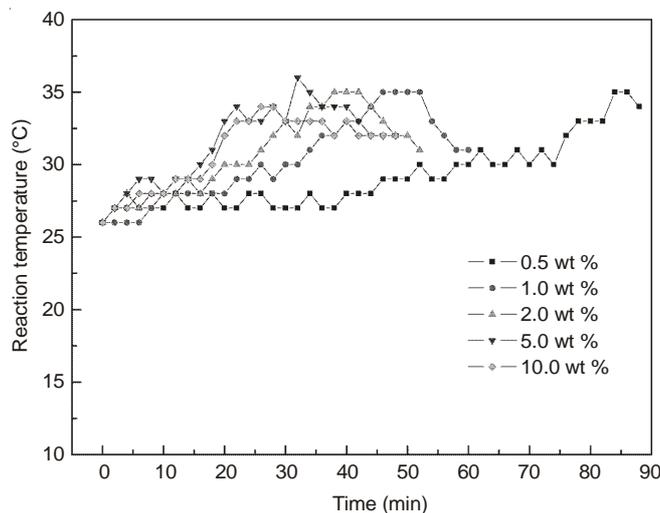


Fig. 4. Reaction temperature at different concentration of catalytic solution as a function of time (2.0 g NaBH_4 , solution flow rate of 0.3 mL min^{-1} , initial $T = 26^\circ\text{C}$)

Effect of reaction temperature on hydrogen generation:

Fig. 6a. b shows the effect of initial temperature on hydrogen generated volume and yield. The initial temperatures strongly affected the reaction rate of the NaBH_4 hydrolysis. However, similar total hydrogen volume and final yield were reached for all initial temperatures.

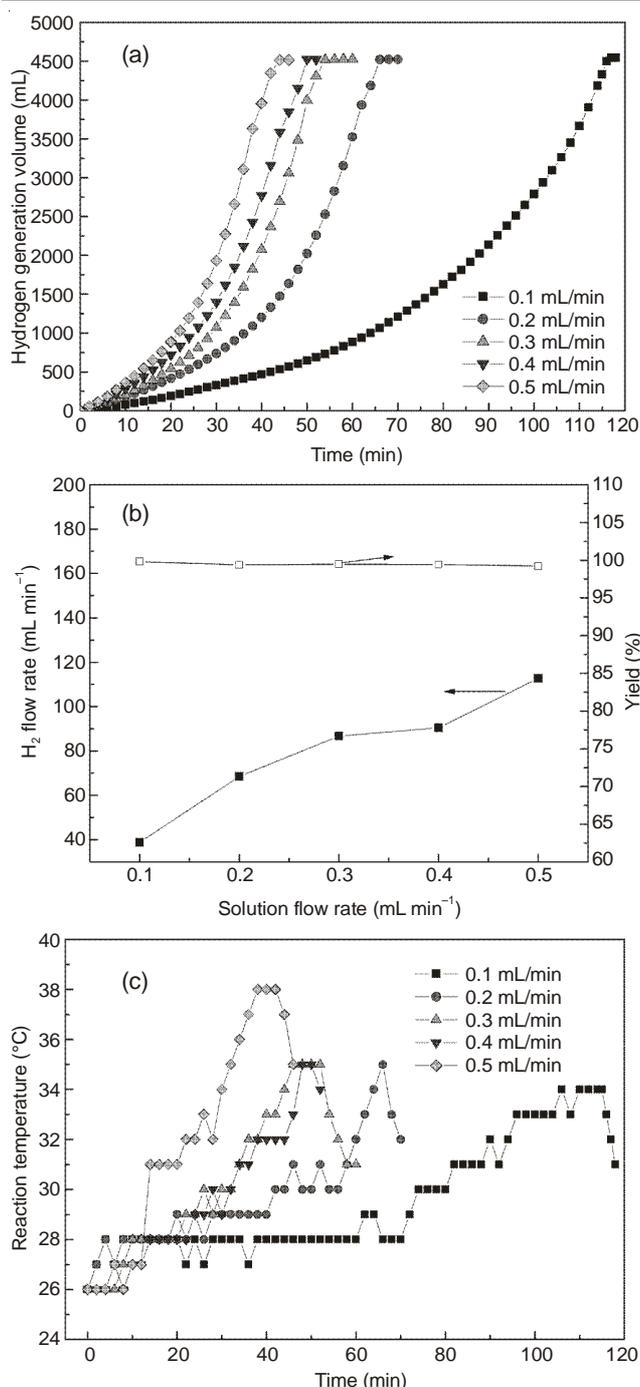


Fig. 5. (a) Hydrogen generation volume at different flow rates of catalytic solution; (b) Yield and H₂ flow rate; (c) reaction temperature at different flow rates of solution (2.0 g NaBH₄, 1 wt % solution flow rate of 0.1-0.5 mL)

Conclusion

Cobalt acetate and cobalt chloride were used as catalysts in this study. Both catalysts showed high catalytic activity for the hydrogen generation from hydrolysis of NaBH₄. The newly designed reactor with a toroidal tube distributor successful reduced the hydrogen generation startup time. The hydrogen yield is nearly 100 % at selected working conditions and the optimum catalyst concentration is 1 wt %. Our hydrogen generation system is promising and can be used to supply hydrogen for fuel cells.

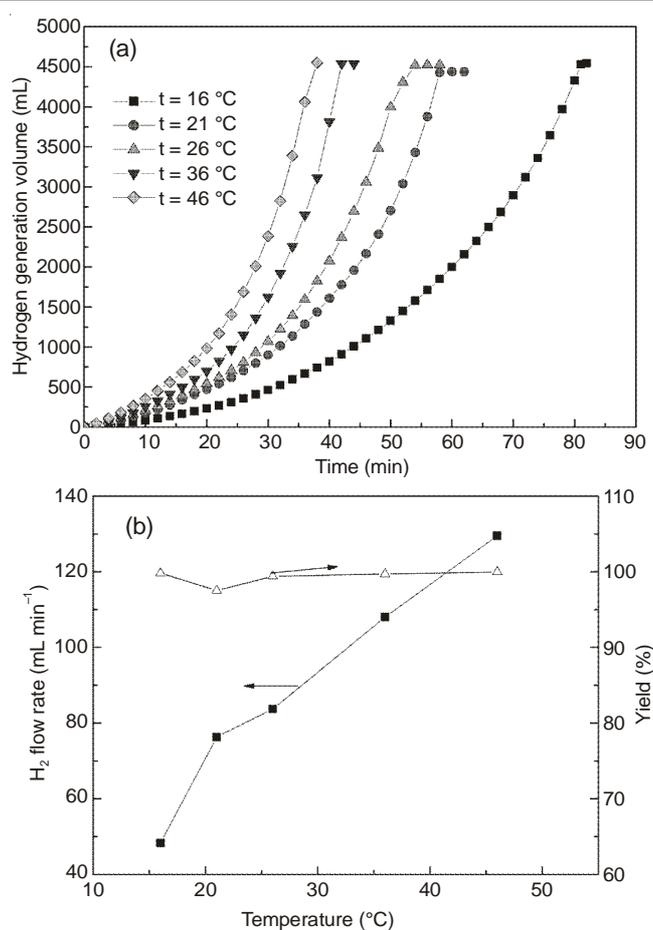


Fig. 6. (a) Hydrogen generation volume at different initial temperatures; (b) Yield and H₂ flow rate (2.0 g NaBH₄, 1 wt % solution flow rate of 0.3 mL/min, at 16-46 °C)

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