Catalytic hydrolysis of sodium borohydride by a novel nickel–cobalt–boride catalyst

J.C. Ingersoll [a,*], N. Mani [a], J.C. Thenmozhiyal [b], A. Muthaiah [c]

[a] *Aatral Energy Research Organization, 42/9, Avvai Nagar, Kannagi Street, Choolaimedu, Chennai 600 094, India*
[b] *Albany Molecular Research Inc., Singapore Research Centre, 61 Science Park Road, #05-01 The Galen,*
Singapore Science Park III, Singapore 117525, Singapore
[c] *Röhm America L.L.C, 2 Turner Place Piscataway, NJ 08855-0365, USA*

Abstract

With the aim of designing an efficient hydrogen generator for portable fuel cell applications nickel–cobalt–boride (Ni–Co–B) catalysts were prepared by a chemical reduction method and their catalytic hydrolysis reaction with alkaline $NaBH_4$ solution was studied. The performance of the catalysts prepared from $NaBH_4$ solution with NaOH, and without NaOH show different hydrogen generation kinetics. The rate of hydrogen generation was measured using Ni–Co–B catalyst as a function of the concentrations of NaOH and $NaBH_4$, as well as the reaction temperature, in the hydrolysis of alkaline $NaBH_4$ solution. The hydrogen generation rate increases for lower NaOH concentrations in the alkaline $NaBH_4$ solution and decreases after reaching a maximum at 15 wt.% of NaOH. The hydrogen generation rate is found to be constant with respect to the concentration of $NaBH_4$ in the alkaline $NaBH_4$ solution. The activation energy for hydrogen generation is found to be 62 kJ mol^{-1}, which is comparable with that of hydrogen generation by a ruthenium catalyst.

1. Introduction

With the ever-growing demand for environment friendly and efficient energy sources for transportation and personal electronic applications, fuel cells are attracting current global attention. The proton-exchange membrane fuel cell (PEMFC) has been widely studied in recent years [1–6] as an energy source with high specific energy. The performance of PEMFCs is sensitive to the concentration of carbon monoxide in hydrogen [2–6] when the latter is produced from the steam reforming of natural gas. Even a few parts per million of carbon monoxide can cause poisoning of the electro catalyst in a PEMFC. Therefore, there is a crucial need to develop a method for the generation of pure hydrogen in portable PEMFCs.

Hydrogen storage capability in terms of specific energy density is still less than that required for various applications. Chemical hydrides are promising hydrogen storage systems [7].

Among them, sodium borohydride ($NaBH_4$) is a stable, non-flammable, easy-to-handle and non-toxic chemical hydride that is capable of storing 10.8 wt.% of hydrogen [8]. It is also an efficient hydrogen storage system that could produce double the amount of its stored hydrogen through hydrolysis with water. At room temperature, however, only a small percentage of the theoretically calculated amount of hydrogen is released by hydrolysis of aqueous $NaBH_4$ solution [9]. The efficiency of hydrogen release can be significantly enhanced by using suitable catalysts. When catalysts are added, the release of hydrogen is rapid via the following reaction [10]:

$$NaBH_4 + 2H_2O \xrightarrow{\text{Cat}} NaBO_2 + 4H_2 \uparrow,$$
$$\Delta H = -217\,\text{kJ mol}^{-1} \quad (1)$$
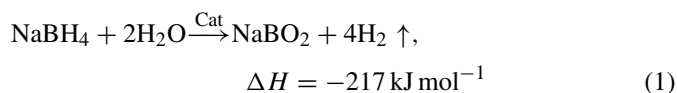
It is an exothermic reaction and can be initiated quickly even at $0\,^\circ\text{C}$. The by-product sodium metaborate ($NaBO_2$) does no harm to the environment, and can be recycled as the starting material for synthesizing $NaBH_4$ [8].

The rate at which $NaBH_4$ solution undergoes self-hydrolysis in water in the absence of catalyst depends on the pH and tem-

* Corresponding author. Tel.: +91 44 23610737; fax: +91 44 23610737.
E-mail address: ingersolljc@yahoo.com (J.C. Ingersoll).

perature. Kreevoy and Jacobson [11] reported that this rate can be empirically represented by

$$\log t_{1/2} = \mathrm{pH} - (0.034T - 1.92) \qquad (2)$$

where $t_{1/2}$ is the half-life (the time taken for one-half) of the NaBH$_4$ solution to decompose in minutes, at a particular pH and temperature T (expressed in Kelvin). For example, at pH 14 and 25 °C, NaBH$_4$ solution has a half-life of 430 days. In the presence of selected catalysts, however, the hydrolysis rate (and hence, H$_2$ generation rate) markedly increases, even in high pH values at 25 °C.

It is clear from Eq. (2) that a high pH would help in stabilizing the solution against self-hydrolysis and that a high NaBH$_4$ concentration would provide more hydrogen density [8]. Hence, there is an essential need to discover an efficient catalyst for the hydrolysis of alkaline NaBH$_4$ solution at high pH values and high NaBH$_4$ concentrations. Certain conventionally known catalysts are colloidal platinum, activated carbon, fluorinated Mg-based hydride [12] or ruthenium supported on an anion exchange resin [8,13], Pt–LiCoO$_2$ [14], PtRu (atomic ratio, 48:51)/LiCoO$_2$ [15], acids, transition metals, metal chlorides and borides of cobalt and nickel [16–19]. Among them, ruthenium has good performance, but their inadequacy and relatively high cost make it imperative to explore a cost-effective and high-performing catalyst [20]. Moreover, hydrogen generation rates decrease with increase in NaOH concentration when using a ruthenium catalyst [8,13]. Cobalt and nickel borides are considered as good choices of catalysts for the hydrolysis of the NaBH$_4$ due to their good catalytic activity and cost-effectiveness. At high pH values, alkaline NaBH$_4$ solution has been reported to show a faster hydrolysis rate in the presence of cobalt boride as well as nickel boride [18,21]. On the other hand, these compounds exhibit a slower rate of hydroly-sis at high NaBH$_4$ concentration, which restricts their usage as catalysts in high-power portable applications where higher concentrations of NaBH$_4$ are required to provide more hydrogen density. In the present work, an alloy of nickel and cobalt (termed Ni–Co–B) is used for the hydrolysis of NaBH$_4$ to circumvent the disadvantages of ruthenium, cobalt boride and nickel boride catalysts.

2. Experiment

The Ni–Co–B alloy was synthesized by a chemical reduction method using NaBH$_4$ and metal chlorides. A 100 ml of an aqueous solution of the two metal chlorides (MCl$_2$·6H$_2$O, M = Ni and Co; purity 99.95%, Aldrich) was prepared in a 1:1 molar ratio and 100 ml of aqueous NaBH$_4$ (purity 99%, Aldrich) solution (1.2 M) was added dropwise to this solution using a peristaltic pump (Model: Ranin rabbit plus, made in France) for 2 h at room temperature. The molar ratio of metallic salt to borohydride was 1:5 to enable completion of the reduction reaction. The reaction was carried out in an argon atmosphere to avoid oxidation. The black metal–boron reaction product was washed with deionized water and acetone thoroughly to remove unwanted Cl$^-$ and Na$^+$ ions that were formed during the reaction. The samples were vacuum dried for 48 h and dried further at 150 °C for 2 h, to eliminate completely the remaining water molecules, and then annealed at 575 °C for 3 h under an argon atmosphere.

In order to compare the catalytic activity of Ni–Co–B alloy prepared under different pH values in alkaline NaBH$_4$ solution, the alloy was made with (1 wt.%) and without NaOH. The nomenclature of the catalysts with respect to the method of preparation is given in Table 1. The crystallinity of the powder samples was studied by means of powder X-ray diffraction (Cu Kα radiation, JEOL). Scanning electron microscopy and energy dispersive X-ray analysis (Cambridge Instruments) were performed to investigate the surface morphology and elemental composition of each sample.

The hydrolysis reactions were conducted over the temperature range 8–28 °C in the tiny batch reactor shown in Fig. 1. Initially, the reactor vessel was evacuated and flushed with high-purity argon (99.95%) to prevent oxidation. The alkaline NaBH$_4$ solution was added to 0.1 g of catalyst in the reactor. The quantity of hydrogen evolved was measured by the water-displacement method. The reactor was partially immersed in a water bath in which water was circulated using a small motor to maintain the temperature.

Table 1
Nomenclature and hydrogen generation rate of Ni–Co–B catalysts

Sample name	Preparation condition	Rate of hydrogen generation (15 wt.% NaOH, 0.16 g NaBH$_4$ at 28 °C) (ml min^{-1} g^{-1} catalyst)	
		Fuel supplied for 15 min using peristaltic pump	Fuel supplied suddenly using syringe
Ni–Co–B-1	As prepared (with aqueous NaBH$_4$ solution)	168	1788
Ni–Co–B-2	Annealed at 575 °C (with aqueous NaBH$_4$ solution)	270	2608
Ni–Co–B-3	As prepared (with alkaline NaBH$_4$ solution: 1 wt.% NaOH)	150	699
Ni–Co–B-4	Annealed at 575 °C (with alkaline NaBH$_4$ solution: 1 wt.% NaOH)	216	1375

Fig. 1. (a) Experimental set-up. (b) Reactor: (1) argon inlet for flushing; (2) hydrogen outlet; (3) temperature sensor; (4) NaBH$_4$ solution inlet.

3. Results and discussion

3.1. Powder X-ray diffraction

The powder X-ray diffraction studies were performed on 'as prepared' and 'annealed' Ni–Co–B alloys; the diffraction patterns are shown in Fig. 2. The 'as prepared' samples (Ni–Co–B-1 and Ni–Co–B-3) exhibit an amorphous nature. The presence of sharp peaks for the 'annealed' samples (Ni–Co–B-2 and Ni–Co–B-4) indicate an increase in the crystallinity. These peaks
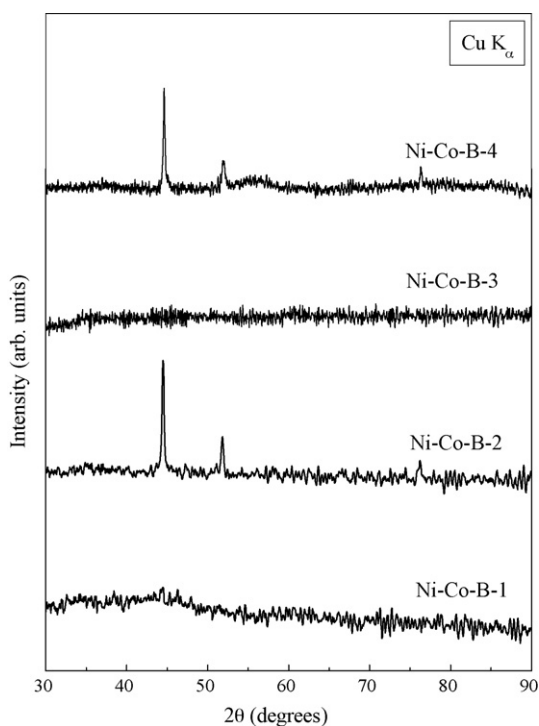
correspond to cubic Ni [JCPDS 87-0712], which signifies an increase in the crystallinity of Ni. An increase in the crystallinity of other phases, such as, cubic Co, Co–B and Ni–B could also be present in the same region of the X-ray diffraction pattern [JCPDS 01-1254, 65-2410, 17-0335, 39-1107] [18,19,22]. No difference is observed in the X-ray diffraction patterns of the Ni–Co–B alloys prepared with (Ni–Co–B-1 and Ni–Co–B-2) and without NaOH (Ni–Co–B-3 and Ni–Co–B-4), as inferred from Fig. 2.

3.2. Surface morphology

Scanning electron micrographs were recorded for 'as prepared' Ni–Co–B-1 alloy. As is evident from the image (Fig. 3), the particles are aggregated into a fine powder. This observation is consistent with the 'as prepared' X-ray diffraction patterns, which demonstrate short-range ordering. Jeong et al. [21] observed a plate-like structure in the case of the Co–B catalyst and found a range of particle sizes from several tens to hundreds of nanometers and a specific surface area of 77 m^2 g^{-1}.

Fig. 2. Powder XRD patterns of catalysts prepared in aqueous NaBH$_4$ solution (without NaOH): Ni–Co–B-1 (as prepared), Ni–Co–B-2 (annealed at 575 °C) and in alkaline NaBH$_4$ solution (1 wt.% NaOH): Ni–Co–B-3 (as prepared), Ni–Co–B-4 (annealed at 575 °C).
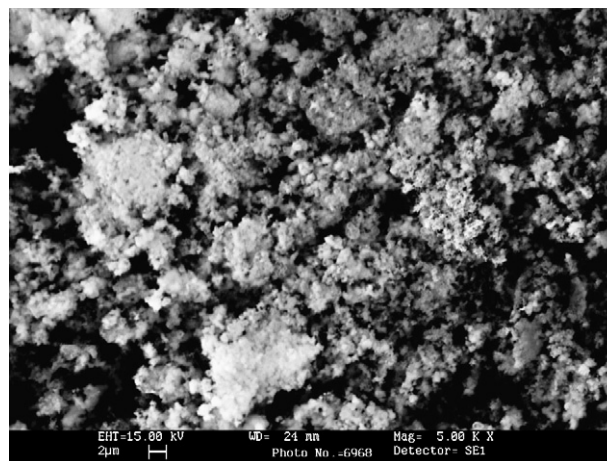

Fig. 3. Scanning electron micrograph of Ni–Co–B-1 catalyst.

Ma et al. [23] reported net-like morphology for a $Ni_{65}B_{35}$ alloy prepared at 268 K and found that the net was formed by many interconnected fine particles with sizes <10 nm. Their investigations on Ni–Co–B showed its morphology to be analogous to that of $Ni_{65}B_{35}$; the particle size was about 5 nm. Hence, the particle size of an Ni–Co–B alloy prepared via chemical reduction might also be in the order of nanometers.

From EDX studies, it is found that the chemical composition is almost the same in different zones and that the powders contain only the Co and Ni elements (note, the EDX spectrum cannot detect boron). The atomic percentage of the powder is calculated to be 49.29% for cobalt, and 50.71% for nickel, which confirms the 1:1 molar ratio of Ni^{2+} to Co^{2+}. Whereas the chemical composition of the Ni–Co–B compounds found from inductively coupled plasma is reported to be $Ni_{31}Co_{34}B_{35}$ [23], $Ni_{35.6}Co_{34.7}B_{29.7}$ and $Ni_{32.5}Co_{31.7}B_{35.8}$ [24].

3.3. Hydrogen generation

3.3.1. As-prepared and annealed samples

Catalytic reactions were carried out with 'as prepared' (Ni–Co–B-1, Ni–Co–B-3) and 'annealed' (Ni–Co–B-2, Ni–Co–B-4) samples. In these reactions, 5 ml of alkaline $NaBH_4$ solution (15 wt.% NaOH and 0.16 g of $NaBH_4$) was added to 0.1 g of the respective catalyst kept in the batch reactor as a sudden supply through a syringe at 28 °C. The total hydrogen yield obtained from this solution was >99% of the theoretically expected value based on Eq. (1). The rate of the hydrogen generation is found to be zero order (Fig. 4a), which is consistent with the finding of Amendola et al. [8]. It is observed that the hydrogen generation rate is faster in the case of the 'annealed' samples when compared with that of the 'as prepared' ones (Fig. 4a). This can be attributed to the increase in the crystallinity of phases, such as, cubic Ni, Co, Co–B, Ni–B and Ni–Co–B that may be present in the alloy [18,19]. However, the X-ray diffraction patterns clearly reveal an increase in the crystallinity of the cubic Ni after annealing. Liu et al. [25] reported the hydrogen generation rates of crystalline Ni and Raney Ni as 19.5 and 228.5 ml min^{-1} g^{-1} catalyst, respectively (Table 1). Interestingly in the present work, the hydrogen generation rate for Ni–Co–B-2 catalyst is found to be 2608 ml min^{-1} g^{-1} catalyst, which is 11 times faster than the reported [25] values with an initial $NaBH_4$ concentration of 0.16 g (Fig. 4a). This remarkable difference in the hydrogen generation rate between crystalline Ni and the present Ni–Co–B alloy indicates the increase in the crystallinity of other phases (Co, Co–B and Ni–B and Ni–Co–B) that may be present in the alloy due to annealing.

The reaction is found to be faster in the case of alloys (Ni–Co–B-1 and Ni–Co–B-2) prepared in aqueous $NaBH_4$ (without NaOH) solution when compared with that of the corresponding alloys (Ni–Co–B-3 and Ni–Co–B-4) prepared in alkaline $NaBH_4$ (1 wt.% NaOH) solution. In 1952, Paul et al. [26] reported that the catalytic activity of nickel boride was strongly dependent on the pH during its formation. They also found that metal borides prepared in alkaline solution exhibited lower activity than those prepared in acidic or neutral conditions. Further investigation in this regard would be useful to determine
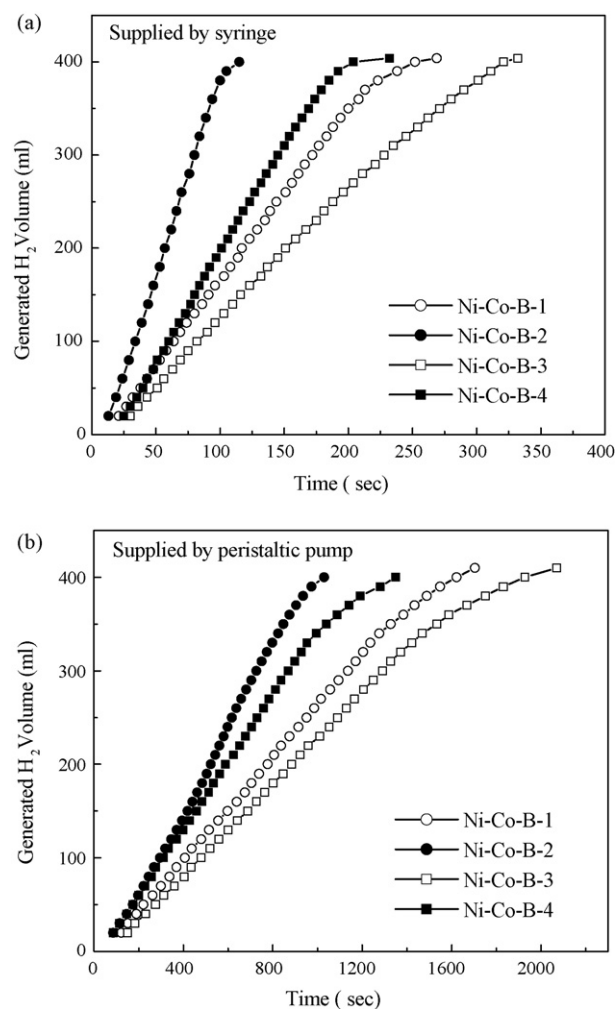

Fig. 4. Comparison of hydrogen generation kinetics of Ni–Co–B catalysts: 5 ml alkaline $NaBH_4$ solution (15 wt.% NaOH and 0.16 g of $NaBH_4$) added to 0.1 g of catalyst kept in batch reactor using (a) a syringe and (b) a peristaltic pump at 28 °C.

the differences in the composition or surface structure for metal borides prepared in various pH conditions and to relate them with catalytic activities.

Fig. 4b shows the catalytic reactions of 5 ml of alkaline $NaBH_4$ solution (15 wt.% NaOH and 0.16 g of $NaBH_4$) added gradually to 0.1 g of the respective catalyst kept in the reactor over a period of 15 min using a peristaltic pump at 28 °C. The rate of reaction is slower in the case of gradual supply of the fuel using a peristaltic pump, when compared with a sudden supply by means of a syringe (Table 1). This may be due to the uncontrolled generation of hydrogen immediately after the sudden supply. Hence, it is clear that the reaction rate can be altered by varying the rate of supply of the fuel at the lower $NaBH_4$ concentrations. The rate of reaction at higher $NaBH_4$ concentration (up to 1.5 g in 10 ml solution) is discussed in Section 3.3.3.

3.3.2. Effect of NaOH variation

Catalytic hydrolysis reactions of Ni–Co–B alloys with different NaOH concentrations of alkaline $NaBH_4$ solution were performed. The rate of hydrogen generation was studied by
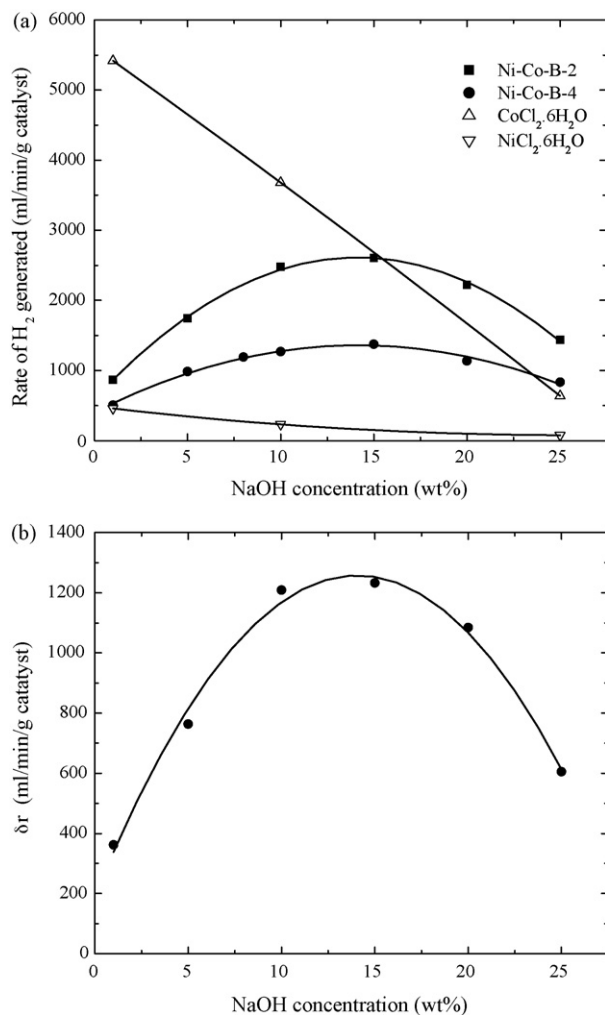
Fig. 5. Effect of NaOH concentration on (a) hydrogen generation rate with different catalysts and (b) difference in hydrogen generation rate, δr, between Ni–Co–B-2 and Ni–Co–B-4 catalysts (catalyst: 0.1 g, solution: 0.16 g $NaBH_4$ in 5 ml NaOH solution, temperature: 28 °C).

adding the alkaline $NaBH_4$ solution into the reactor containing 0.1 g of the catalyst using a syringe (sudden supply). Five millilitres of solution containing 0.16 g of $NaBH_4$ with different NaOH concentrations (1, 5, 8, 10, 15, 20 and 25 wt.% of NaOH) were supplied at 28 °C. Experiments were conducted on two catalysts, namely, Ni–Co–B-2 (prepared without NaOH) and Ni–Co–B-4 (prepared with 1 wt.% NaOH).

The rate of hydrogen generated versus the concentration of NaOH in wt.% is given in Fig. 5a. The rate of hydrogen generation increases with increase in NaOH concentration. It reaches a maximum value around a concentration of 15 wt.% of NaOH and subsequently decreases with further increase in NaOH concentration for both Ni–Co–B-2 and Ni–Co–B-4 alloys. This is the first report of a Ni–Co–B catalyst exhibiting such anomalous behaviour in the catalysis of $NaBH_4$ for hydrogen generation. Other catalysts for $NaBH_4$ either increase or decrease the rate of hydrogen generation with respect to the NaOH concentration [13,18,21]. It was reported that Ni–B and Co–B alloys exhibit faster rate of hydrolysis in alkaline $NaBH_4$ solution at higher

NaOH concentrations [18,21] and the reverse is the case with a Ru [13] catalyst.

Hydrolysis reactions have been carried out at different NaOH concentrations for the catalysts $CoCl_2·6H_2O$ and $NiCl_2·6H_2O$ in order to compare their catalytic performance with Ni–Co–B alloys. The rate of hydrogen generation rate exhibits a linear decrease with respect to the NaOH concentration (Fig. 5a) analogous to Ru catalyst. By contrast, Ni–Co–B alloy shows anomalous behaviour, as discussed above. This can be attributed to the fact that the reaction with nickel–cobalt based catalysts used in this work involves complicated surface reactions with the hydroxide ions. The accelerating effect of NaOH ensures a good efficiency for hydrogen generation during the reaction. It compensates for a possible negative effect caused by reduced activity of water and a lower solubility of the reaction product at higher hydroxide concentrations. Hence, the rate of hydrogen generation is not only dependent on the concentration of NaOH of the solution but also the nature of the catalyst.

The rate of hydrolysis is faster in the case of the alloy prepared using aqueous $NaBH_4$ solution (Ni–Co–B-2) when compared with that of the alkaline $NaBH_4$ (1 wt.% NaOH) solution (Ni–Co–B-4). This is clearly illustrated in Fig. 5b. The difference in the hydrogen generation rate (δr) between Ni–Co–B-2 and Ni–Co–B-4 catalysts is found to increase initially and reached a maximum at around 15 wt.% NaOH and decreases with the further increase in the NaOH concentration. This demonstrates the effect of NaOH during preparation of the catalyst.

A comparison of the hydrogen generation rate of Ni–Co–B with certain other catalysts is given in Table 2. Amendola et al. [13] reported that IRA-400 supported Ru catalyst produced a hydrogen generation rate of 1098 ml min^{-1} g^{-1} catalyst and Liu et al. [25] found that Ni_2B, Co_2B catalysts gave a hydrogen generation rate of 18.3 and 468.3 ml min^{-1} g^{-1} catalyst, respectively, at 10 wt.% of NaOH. Further, it was reported that rates of 954 and 2400 ml min^{-1} g catalyst were obtained at 1 and 5 wt.% NaOH for electrodeposited Co–P and PtRu–LiCoO$_2$ catalysts, respectively [27,15]. It is worthy to note that in the present work, for the Ni–Co–B catalyst, the hydrogen generation rate is remarkably high at 2608 ml min^{-1} g^{-1} catalyst when the NaOH concentration is 15 wt.%. It is known that the alkaline $NaBH_4$ solution is highly stable at high pH values (i.e., a high NaOH concentration at 15 wt.%). Hence, Ni–Co–B alloy will be a best performing catalyst in the hydrolysis of highly stable alkaline $NaBH_4$ solution at 15 wt.% of NaOH.

3.3.3. Effect of $NaBH_4$ variation

The catalytic properties of Ni–Co–B-2 (prepared without NaOH) alloy with different $NaBH_4$ concentrations were carried out as demonstrated in Fig. 6a. Ten milliliters of alkaline $NaBH_4$ solution (15 wt.% of NaOH) with different $NaBH_4$ contents (0.5, 0.75, 1.0 and 1.5 g) was supplied to 0.1 g of catalyst kept in the reactor using a syringe at 20 °C. Fifteen weight percentage of NaOH was chosen for the study as this concentration displayed the best performance of the catalyst. The hydrogen generation volume is observed to increase steadily at all $NaBH_4$ concentrations (0.5–1.5 g) as shown in Fig. 6a. Consequently,
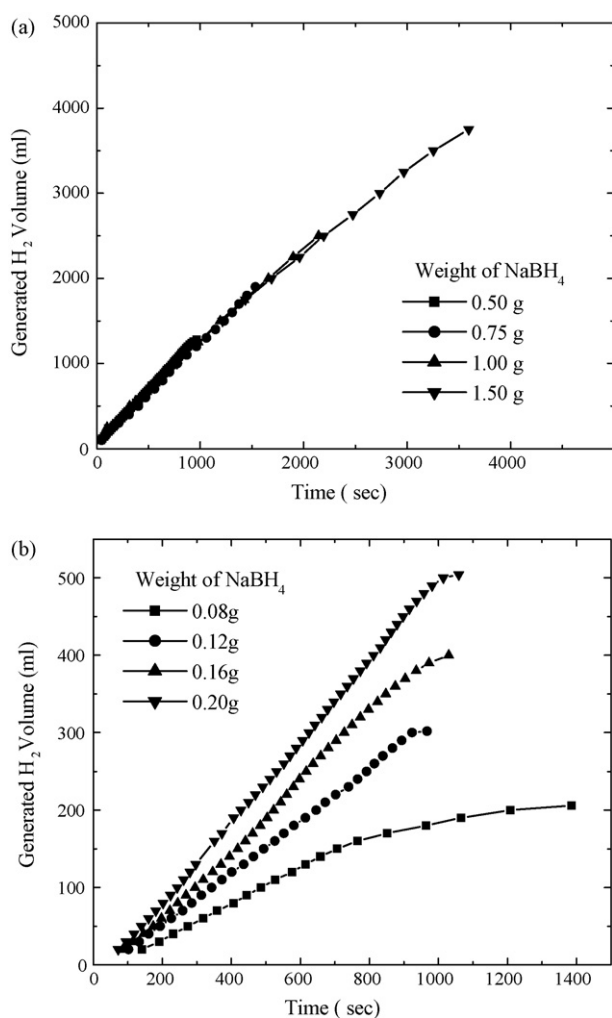
Fig. 6. Effect of NaBH$_4$ concentration on hydrogen generation kinetics measured for NaBH$_4$ + 15 wt.% NaOH solution supplied by: (a) a syringe at 20 °C (weight of NaBH$_4$ = 0.5, 0.75, 1.00, 1.50 g) and (b) a peristaltic pump at 28 °C (weight of NaBH$_4$ = 0.08, 0.12, 0.16, 0.20 g) using 0.1 g of Ni–Co–B-2 catalyst.

from NaBH$_4$ + NaOH solution decreased at higher NaBH$_4$ concentrations and attributed the results to an increase in solution viscosity affecting the generation rate.

The discrepancy in the hydrogen generation rate observed between Ni–B, Co–B and Ru catalysts from previous reports and Ni–Co–B-2 alloy in the present work with respect to the variation in the NaBH$_4$ concentration could be due to the difference in the way by which alkaline NaBH$_4$ solution was prepared for the investigation. In the previous reports [8,13,21,28] on the catalytic activity of Ni–B, Co–B and Ru catalysts, different concentrations of NaBH$_4$ solution were prepared as a weight percentage of NaBH$_4$, NaOH and H$_2$O so that the variation in the concentration of NaBH$_4$ would affect that of the other two components of the final solution, which in turn, would influence the pH of the solution. Moreover, the decrease in the hydrogen generation rate observed with high NaBH$_4$ concentrations could be attributed to the formation of the reaction side-product NaBO$_2$ leading to blockage of the catalytic sites during the reaction. In the present study, 10 ml of 15 wt.% of NaOH solution was taken first and then the desired amount of NaBH$_4$ was added to form the final solutions. Similar to the present observation, a constant hydrogen generation rate with respect to higher NaBH$_4$ concentrations was reported by Liu et al. [25] for Raney Ni–Co alloy.

Five milliliters of the alkaline NaBH$_4$ solution with different low NaBH$_4$ concentrations (0.08, 0.12, 0.16 and 0.2 g) at 15 wt.% NaOH was supplied to 0.1 g of catalyst kept in the reactor for 15 min using the peristaltic pump at 28 °C. Although the reaction displays zero-order kinetics, the hydrogen generation rate is increased up to 0.2 g of NaBH$_4$, as shown in Fig. 6b. Faster hydrogen generation rates at low NaBH$_4$ concentrations are possibly due to reduced solution viscosity, i.e., reduced mass transport, which allows more NaBH$_4$ and water to contact catalyst surfaces [13].

3.3.4. Effect of temperature variation

The hydrogen generation rate predominantly depends on the temperature. The NaBH$_4$ hydrolysis reaction is a rigorous exothermic reaction and generally, at high temperatures the reaction kinetics are faster. It is easier, however, to control the reaction temperature and foamy effervescence at lower rather than at higher temperatures. The hydrogen generation reaction

the rate of generation of hydrogen is almost constant for various NaBH$_4$ concentrations. Previous report showed that in the case of Ni–B [28] and Co–B [21] catalysts the rate of hydrolysis is slower at higher NaBH$_4$ concentration. Amendola et al. [8,13] reported that, for a Ru catalyst, the hydrogen generation rate

Table 2
Comparison of hydrogen generation performances of various catalysts

| Catalyst	Temperature (°C)	NaBH$_4$ concentration	Average H$_2$ generation rate (ml min^{-1} g^{-1} catalyst)	NaOH concentration (wt.%)	Reference
5 wt.% Ru on IRA-400	32.5	7.5 wt.%	606	1	[13]
Ni$_x$B	28	1.5 wt.%	233	4	[18]
Ni$_2$B	20	0.2 g in 20 ml of NaBH$_4$ solution	18.3	10	[25]
Co$_2$B	20	0.2 g in 20 ml of NaBH$_4$ solution	468.3	10	[25]
PtRu–LiCoO$_2$	25	5 wt.%	2400	5	[15]
Electrodeposited Co–P catalyst	30	10 wt.% NaBH$_4$	954	1	[27]
Ni–Co–B	28	2.7 wt.% or 0.16 g of 5 ml of NaBH$_4$ solution	2608	15	This paper
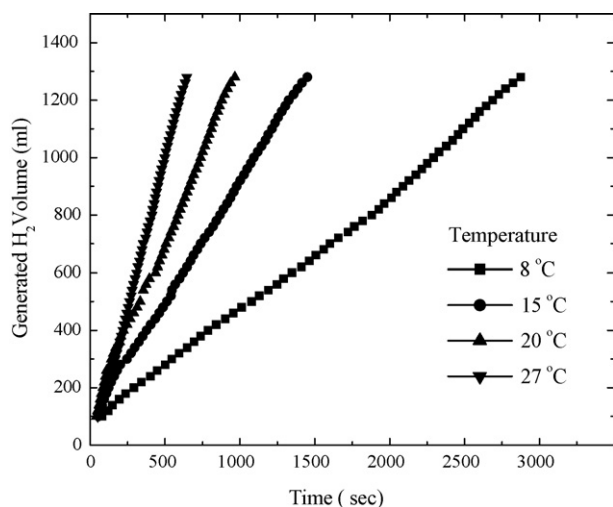
Fig. 7. Effect of temperature on hydrogen generation kinetics of Ni–Co–B-2 catalyst: 10 ml of alkaline NaBH$_4$ solution (15 wt.% NaOH and 0.5 g of NaBH$_4$) added via a syringe to 0.1 g of catalyst kept in batch reactor.

was studied by supplying 10 ml NaBH$_4$ solution containing 0.5 g NaBH$_4$ with 15 wt.% NaOH into the reactor containing 0.1 g of Ni–Co–B-2 catalyst using a syringe (sudden supply) at various temperatures in the range 8–27 °C (Fig. 7). The rate of reaction is faster at higher temperatures and demonstrates a linear relationship with reaction time. Further, when the NaBH$_4$ concentration is decreased, the reaction rate remains almost constant as the hydrolysis process proceeds at a given temperature. This indicates zero-order reaction kinetics for NaBH$_4$, as found for a Ru catalyst [8]. Thus, it is concluded that the hydrogen generation rate is controlled by a surface reaction [14].

The rate equation can be written as follows:

$$r = k_0 \, e^{-(E_a/RT)} \qquad (3)$$

where r is the reaction rate (mol min^{-1} g^{-1}), k_0 the reaction constant (mol min^{-1} g^{-1}), E_a the activation energy for the reaction, R the gas constant and T is the reaction temperature (K). An Arrhenius plot, in which log [hydrogen generation rate, r] is plotted against the reciprocal of absolute temperature ($1/T$), is shown in Fig. 8a. From the slope of the straight line, the activation energy is calculated to be 62 kJ mol^{-1} for the Ni–Co–B-2 catalyzed hydrolysis of sodium borohydride. This value compares favourably with an activation energy of 47 kJ mol^{-1} for a Ru catalyst that was determined by Amendola et al. [8] at 20 wt.% NaBH$_4$ and 10 wt.% NaOH concentrations, and with activation energies found by Kaufman and Sen [17] for the same hydrolysis but with different bulk metal catalysts, namely: 75 kJ mol^{-1} for cobalt, 71 kJ mol^{-1} for nickel, and 63 kJ mol^{-1} for Raney nickel.

The Eyring plot in Fig. 8b provides the activation enthalpy and activation entropy values of $\Delta H^{\neq} = 60$ kJ mol^{-1} and $\Delta S^{\neq} = -123$ J K^{-1} mol^{-1} for the Ni–Co–B-2 catalyzed hydrolysis of sodium borohydride solution. The small value of the activation enthalpy and the large negative value of the activation entropy indicate the negative free energy of activation and the spontaneity of the reaction. These thermodynamic parameters support an associative mechanism for the Ni–Co–B-2 hydrolysis
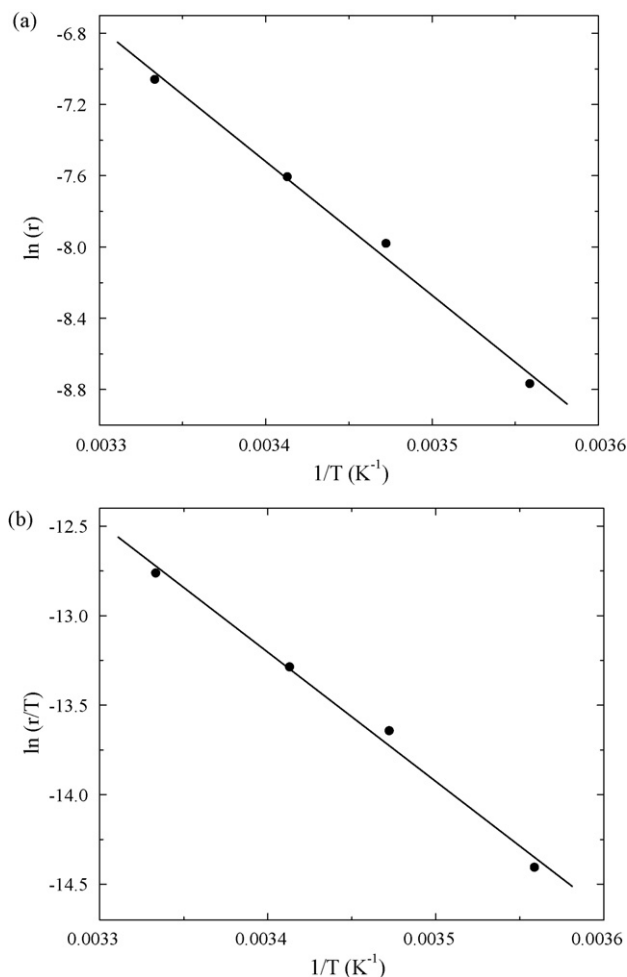

Fig. 8. (a) Arrhenius and (b) Eyring plots for the Ni–Co–B-2 catalyzed hydrolysis of 10 ml alkaline NaBH$_4$ solution (15 wt.% NaOH and 0.5 g of NaBH$_4$) added to 0.1 g of catalyst.

of sodium borohydride that consists of a short-lived intermediate BH$_5$ that decomposes into BH$_3$ and H$_2$. This conclusion is in line with the mechanism suggested for the hydrolysis of sodium borohydride given by Mesmer and Jolly [29].

4. Conclusions

The present investigation has unveiled three important observations in the catalytic hydrolysis of NaBH$_4$ with a novel, non-noble, catalyst Ni–Co–B that could positively contribute to an enhanced efficiency of hydrogen generation. First, the hydrogen generation rate of NaBH$_4$ with a Ni–Co–B-2 catalyst is found to be 2608 ml min^{-1} g^{-1} catalyst with a 15 wt.% NaOH (highly stable) solution at 28 °C. This value is remarkably high and 11 times faster than the reported rates with an initial NaBH$_4$ concentration of 0.16 g. Second, the rate of hydrogen generation in the catalysis of alkaline NaBH$_4$ solution is shown to increase with increase in NaOH concentration and displays a parabolic trend by reaching a maximum value around a concentration of 15 wt.% of NaOH and subsequently decreasing with further increase in NaOH concentration. This is the first report of such behaviour for the generation of hydrogen from

alkaline $NaBH_4$ solution with a non-noble catalyst. Third, the hydrogen generation rate is almost constant with respect to variation in the $NaBH_4$ concentration, which is a rare observation with a Ni–Co–B catalyst. The activation energy of the hydrolysis reaction with a Ni–Co–B-2 catalyst is $62\,kJ\,mol^{-1}$. Eyring plots over the temperature range 8–27 °C reveal an enthalpy of activation of $\Delta H^{\neq} = 60\,kJ\,mol^{-1}$ and an entropy of activation of $\Delta S^{\neq} = -123\,J\,K^{-1}\,mol^{-1}$ for the Ni–Co–B-2 catalyst, which indicate an intermediate, short-lived, transition state.

Catalysts prepared with and without NaOH yield different rates of hydrogen generation. The rate of hydrogen generation can be controlled by the rate of fuel supply. Thus, a cost-effective, non-noble, Ni–Co–B catalyst prepared by a very simple method has been found to be an effective catalyst for the hydrolysis of $NaBH_4$. It could be improved further by varying the concentrations of Ni and Co in Ni–Co–B alloy.

Acknowledgements

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