Novel fabrication of solid-state NaBH$_4$/Ru-based catalyst composites for hydrogen evolution using a high-energy ball-milling process

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ABSTRACT

Solid-state NaBH$_4$/Ru-based catalyst composites have been fabricated for hydrogen generation through a high-energy ball-milling process, providing uniform dispersion of resin-supported Ru^{3+} catalysts among pulverized NaBH$_4$ (SBH) particles, so as to increase the contacts of SBH with active catalytic sites. Consequently, the gravimetric hydrogen storage capacity as high as 7.3 wt% could be achieved by utilizing water as a limiting reagent to overcome the issue of deactivated catalysts whose active sites are often blocked by precipitates caused by limited NaBO$_2$ solubility occurring in conventional aqueous SBH systems for hydrogen productions. Products of hydrolyzed SBH that greatly influence the gravimetric H$_2$ storage capacity are found to be most likely NaBO$_2$·2H$_2$O and NaBO$_2$·4H$_2$O from SBH/H$_2$O reacting systems with initial weight ratios, SBH/H$_2$O = 1/2 and 1/10, respectively, according to the TGA and XRD analyses.

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1. Introduction

To overcome severe problems of global warming and climate change owing to the excess emission of carbon dioxide resulted from the combustion of fossil fuels, the development of clean and renewable energies is of urgent necessity. Among various potential candidates of green energies, hydrogen is likely one of the promising alternatives due to the fact that the environmentally benign product, water, was the main product generated through the reaction with oxygen via a device like proton exchange membrane fuel cells (PEMFCs) to emit the energy. In addition, almost 80% of the theoretical power efficiency can be obtained from PEMFCs, which are generally higher than that from conventional internal combustion engines using fossil fuels as the power source. So far, the most common industrial process to produce hydrogen is the steam reforming reaction of hydrocarbon compounds such as natural gas, methanol and ethanol [1–3]. However, the inevitable presence of impurities, such as carbon monoxide (CO), contained conjointly in produced hydrogen via the reforming process dramatically poison noble metal catalysts used in PEMFCs leading to deactivation of the fuel cells.

Recently, several alternative hydrogen storage technologies have been continuously investigated. These include high-pressure tanks, metal hydrides, liquefied hydrogen and chemical hydrides (e.g., KBH$_4$, NaBH$_4$, and LiH). Among various hydrogen storage methods mentioned above, chemical hydrides have appealed to most attention because of their higher purity of produced hydrogen, less energy-loss, more cost-effective and lower operation-pressure at ambient conditions. Among these chemical hydrides, sodium borohydride (SBH)—NaBH$_4$, is one of the promising H$_2$ storage materials, of which H$_2$ can be easily released through the hydrolysis reaction in the presence of proper catalysts [4] as shown in Eq. (1):

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} NaBO_2 + 4H_2 + 217 \ kJ \tag{1}$$
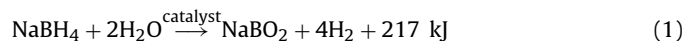
In addition, NaBH$_4$ can be stably stocked under alkaline environment [5]. Furthermore, a higher hydrogen content (i.e. 10.8 wt%) could be obtained theoretically, which could possibly meet the set 2010 goal of 6 wt% for on-board automotive hydrogen storage declared by the USA Department of Energy (US DOE) [6]. The reaction rate, namely the rate of hydrogen evolution via NaBH$_4$ hydrolysis, can be easily regulated through different ways such as addition of catalysts and introduction of water to the reacting systems. Various types of catalysts with enhanced performance on NaBH$_4$ hydrolysis reaction have been widely investigated in recent years; among which, supported precious metals such as ruthenium (Ru) and platinum (Pt) were found to be quite effective [7,8]. In our previous study, satisfactory performance from polymer supported

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Ru and Ru–Ni-based catalysts to hydrolyze alkaline $NaBH_4$ aqueous solution for hydrogen generation was achieved [9,10].

Although relentless efforts and numerous works have been conducted in developing suitable catalysts to promote the H_2 generation from aqueous $NaBH_4$ systems, still, existence of intrinsic defects, such as poor aqueous solubility of spent borohydride–metaborate, restricts the progress of practical applications of such aqueous $NaBH_4$ systems. For example, instead of that ideal condition presented by Eq. (1), various sodium metaborate hydrates, of which poorer aqueous solubility often resulted in solid precipitates on catalysts blocking active catalytic sites for subsequent hydrolysis of sodium borohydrides to produce hydrogen, were found as dominative hydrolyzed products of $NaBH_4$ as shown in Eq. (2) [11]:

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 \cdot xH_2O + 4H_2 \qquad (2)$$
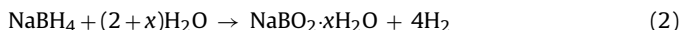
As a result, in an aqueous $NaBH_4$ system, the hydrogen storage capacity would generally decrease from theoretically predicted 10.8–7.5 wt% when the aqueous solubility of $NaBH_4$, i.e. 55 g of $NaBH_4$ per 100 g of H_2O or equivalently 35.48 wt% at 25 °C, was considered. Moreover, if taking the aqueous solubility of $NaBO_2$, i.e. 28 g of $NaBO_2$ per 100 g of H_2O at 25 °C, into account, $NaBO_2$ becomes as a limiting reagent in the hydrolysis reaction of $NaBH_4$ for hydrogen generation. Consequently, the initial $NaBH_4$ concentration in the hydrogen generation system should not exceed 16 g of $NaBH_4$ per 100 g of H_2O at 25 °C in order to maintain a liquid state during the whole course of hydrogen production. Otherwise, excess $NaBO_2$ would precipitate out on the catalyst surface and, hence, would seriously reduce the performance of hydrogen generation by deactivating the active sites of catalysts [11]. Accordingly, the hydrogen storage capacity in an aqueous $NaBH_4$ system would further be decreased down to 2.9 wt% or even lower if any hydrated $NaBO_2$ present.

In order to overcome the bottleneck in practical applications of aqueous $NaBH_4$ systems for supply of ultrapure hydrogen due to the presence of excess water and resulted formation of hydrated metaborates, a concept of utilizing water, instead of borohydrides, as a limiting agent in hydrogen production was recently proposed [12,13]. That is, hydrogen production from such a $NaBH_4$ hydrogen storage system mainly takes place in solid phase. Therefore, the gravimetric storage capacity of hydrogen in $NaBH_4/H_2O$ system could be effectively raised. Liu et al. [12] and Gislon et al. [13] pointed out that effective H_2 storage capacities as high as 6.7 and 6.5 wt%, respectively, was achieved, which also indicated that superior H_2 storage capacities from such a solid $NaBH_4$ hydrogen storage system could possibly reach the set 2010 target of US DOE at 6 wt% for on-board hydrogen storage system. Nonetheless, such a solid $NaBH_4$ system for hydrogen storage still has many factors worthy of being investigated and yet to be studied.

In the present study, solid-state $NaBH_4/Ru$-based catalyst composites were fabricated for hydrogen generation via a high-energy ball-milling process [14], providing excellent contact between active catalytic sites and shattered $NaBH_4$ particles as well as raising surface area of Ru-based catalysts. With controlled addition of water into the $NaBH_4/Ru$ composites, various hydrated hydrolyzed products, $NaBO_2 \cdot xH_2O$, could be generated, which might profoundly affect the performance of H_2 production. These metaborate hydrates harvested from $NaBH_4/H_2O$ reacting systems were accordingly characterized with thermogravimetric analysis (TGA) and X-ray diffraction (XRD). It was found that a higher gravimetric H_2 storage capacity near 7.3 wt% could be obtained and, thus, the set 2010 goal of 6 wt% by US DOE was realized.

2. Experimental

2.1. Materials

Analytical reagent grade sodium borohydride ($NaBH_4$, Alfa-Aesar, 98%) and ruthenium chloride ($RuCl_3$, Sigma–Aldrich) were used without further purification. A strongly acidic cation exchange resin, Amberlite IR-120 in hydrogen form (16–45 mesh size), used as catalyst support was purchased from Supelco Chemical Co. (Bellefonte, PA, USA). Properties of Amberlite IR-120 were given in detail in our previous work as well [9]. The active sites on the surface of Amberlite IR-120 resin are mainly the $-SO_3H$ functional group. Deionized water from a Millipore Milli-Q ultra-purification system with resistivity greater than 18.2 MΩ cm was utilized in sample synthesis.

2.2. Fabrication of Ru-based catalysts

Weighed Amberlite IR-120 resin beads were placed into Ru^{3+} solutions at appropriate concentrations to initiate the chelating reaction between resin and metal ions at ambient conditions with moderate stirring. Amberlite IR-120 resin beads chelated with Ru^{3+} ions (denoted as Ru^{3+}/IR-120 catalysts), on which the appearance turned from original orange into deep black, were taken out from Ru^{3+} solutions and carefully cleaned with deionized water to remove any unchelated Ru^{3+} ions on catalyst surface. Afterward, Ru^{3+}/IR-120 catalysts were dried in an oven to get rid of residual water on catalysts. Element distributions on the surface of as-fabricated Ru^{3+}/IR-120 catalysts were analyzed using the energy dispersive spectrophotometer (EDS, Oxford Inca 400) installed on a Jeol JSM-6700F scanning electron microscope (SEM).

2.3. Fabrication of solid-state $NaBH_4/Ru$-based catalyst composite

Appropriately weighed mixtures of Ru^{3+}/IR-120 catalysts and $NaBH_4$ were pulverized uniformly with a high-energy ball mill, i.e. a shaker mill (Model 8000M, SPEX CertiPrep, Metuchen, NJ, USA), noting that the $NaBH_4$ content was fixed at 1 g while the amounts of Ru^{3+}/IR-120 catalysts varied from 24 to 96 mg. After being ball milled, the mixtures of Ru^{3+}/IR-120 catalysts and $NaBH_4$ were made into tablets with a manual tabletting machine (Model #3912, Carver, Inc., Wabash, IN, USA).

2.4. Generation of hydrogen

Experimental schematic on hydrogen generation and analysis is displayed in Fig. 1. The aforementioned solid composite tablet of $NaBH_4/Ru$-based catalyst was placed in the three-necked round-bottom flask with a thermocouple, followed by quick injection of controlled amount of deionized water with a syringe to initiate the hydrolysis reaction of $NaBH_4$ to produce hydrogen. The evolved hydrogen passed through a condenser with cold water kept at 5 °C at inlet to capture any possible steam generated at elevated temperatures in the reacting system for hydrogen production. Besides, the generated hydrogen was further conducted through a bottle filled with silica gel particles to trap any residual moisture in the gas. Afterward, ultrapure hydrogen was conveyed through a mass flow meter (MFM) to monitor the instantaneous flow rate of hydrogen and, meanwhile, the total volume of hydrogen produced was measured with a wet gas meter (WGM) connected after that MFM. It is noted that both variations of temperature and instantaneous flow rate of hydrogen were also recorded.
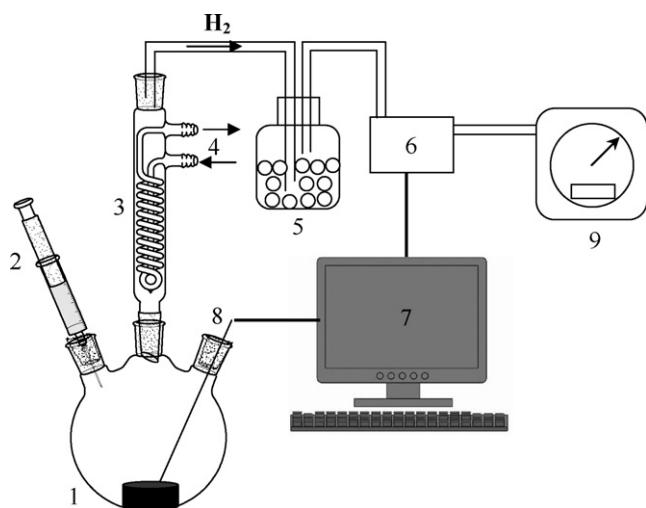
Fig. 1. Scheme of the experimental setup: 1, three-necked round-bottom flask; 2, syringe; 3, condenser; 4, cold water of 5 °C at inlet; 5, bottle filled with silica gel particles; 6, mass flow meter (MFM); 7, computer; 8, thermocouple; 9, wet gas meter (WGS).

2.5. Characterization of hydrolyzed products

The amount of water of crystallization existing in metaborates ($NaBO_2 \cdot xH_2O$), namely the main hydrolyzed products of $NaBH_4$, plays quite a significant role in view of the gravimetric H_2 storage capacity as displayed in Eq. (2). Thus, the hydrated $NaBO_2$ was investigated using thermogravimetric analysis (TGA) (Perkin Elmer TAC 7/DC), in which air was used as both purge gas and working gas at 50 mL min^{-1}. The temperature program was set up as follows: heating from 30 to 800 °C at a heating rate of 5 °C min^{-1} and eventually held at 800 °C for 1 min. It is noted that all samples were freeze-dried for 24 h to get rid of any possible residual moisture in the hydrolyzed products of sodium borohydrides prior to TGA. In addition, the characteristics of hydrated $NaBO_2$ were also analyzed using X-ray diffraction (XRD) (Rigaku RX III) over a range of diffraction angle (θ) from $2\theta = 10°$ to $2\theta = 80°$ with Cu Kα radiation (40 kV, 20 mA) filtered by a monochromater.

3. Results and discussion

The surface compositions of polymer support, Amberlite IR-120 resin beads, and as-prepared Ru^{3+}/IR-120 catalyst were examined with an EDS. Fig. 2 depicted the EDS analyses of (a) IR-120 resin beads, and (b) Ru^{3+}/IR-120 catalysts. It was found that carbon, oxygen and sulfur were main dominant elements on the surface of original IR-120 resin beads. Notably, platinum found should not be originated intrinsically, since the specimens must be deposited with a thin layer of platinum to increase their surface conductivities prior to SEM/EDS analysis. After Ru^{3+} was chelated onto the surface of IR-120 resin beads, the characteristic peak of Ru was detected at around 2.5 keV (Fig. 2(b)), which confirmed successful deposition of Ru on the Amberlite IR-120 resin beads. Excluding the peaks associated with Pt, the quantified surface compositions are tabulated in Table 1. As a result, ruthenium took up about 4.66 wt%, or equivalently 0.7 at% on the surface of Ru^{3+}/IR-120 catalysts.

As mentioned above, different amounts of water added to the reacting system of $NaBH_4$ would profoundly affect the resulted gravimetric hydrogen storage capacity. Effect of different water loading to the reacting system on the gravimetric hydrogen storage capacity and the conversion of sodium borohydride were investigated using 1 g of $NaBH_4$ added with 2 and 10 g of deionized water in the presence of 96 and 24 mg of Ru^{3+}/IR-120 catalysts, respectively.
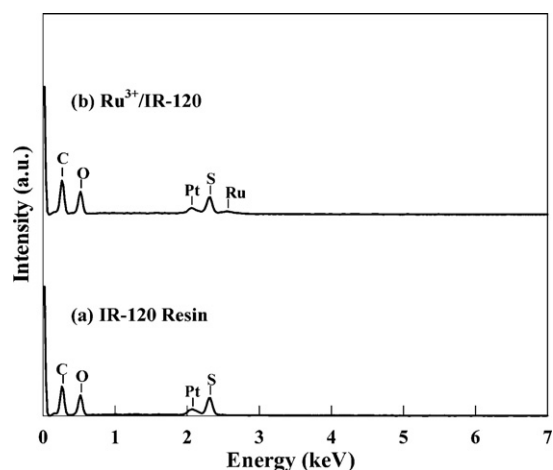
Fig. 2. EDS spectra of (a) IR-120 and (b) Ru^{3+}/IR-120.

The previous system was ensured that during hydrogen production course all reacting systems were in solid phase, whereas the latter was eventually as a liquid system.
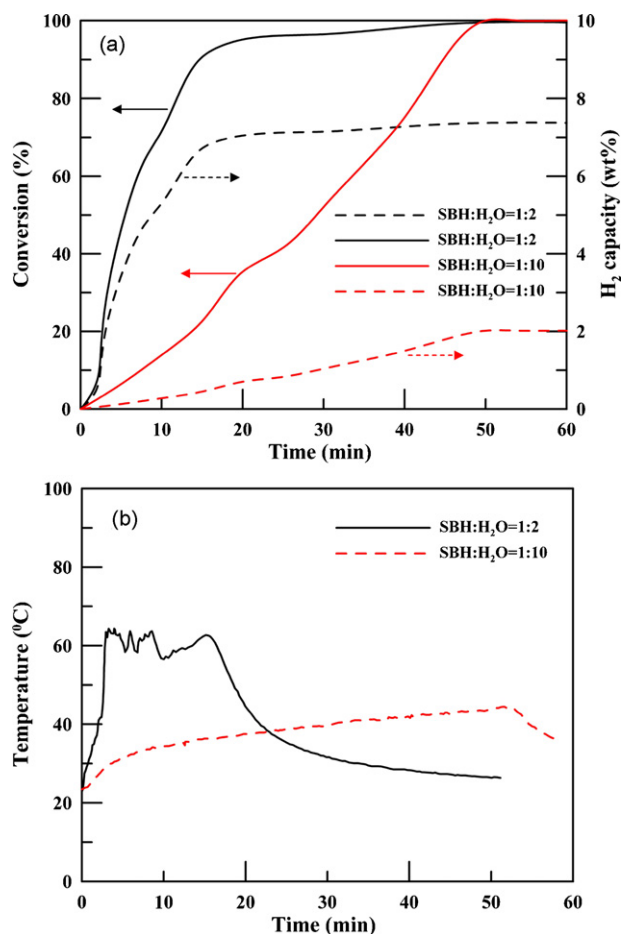
Fig. 3(a) shows the time-dependent H_2 conversion and gravimetric H_2 storage capacity of $NaBH_4$ with different amounts of water introduced to the reacting system. It is of note to mention that water was quickly injected into the reacting system of $NaBH_4$ using a syringe to initiate the hydrolysis reaction of $NaBH_4$ for hydrogen evolution. After 2 g of deionized water was introduced into the system, namely the system marked with a weight ratio of SBH/H_2O = 1/2, the hydrolysis reaction of $NaBH_4$ was immediately initiated. It was observed that pulverized $NaBH_4$ particles reacted so vigorously in the presence of uniformly dispersed Ru^{3+}/IR-120 catalysts and, accordingly, the conversion of borohydride into hydrogen increased significantly and reached a plateau near 90% at about 15 min from the onset of hydrolysis reaction. Noticeably, the slope of time-dependent hydrogen conversion curve is proportional to the production rate of hydrogen, namely the reaction rate of $NaBH_4$ hydrolysis. Eventually, the conversion of $NaBH_4$ to hydrogen reached 100%.

In contrast, with an excess addition of 10 g of water to the reacting system, which was denoted as SBH/H_2O = 1/10, the reacting system turned from initially solid-state to finally an aqueous one. Without agitation, the Ru^{3+}/IR-120 catalysts were settled down to the bottom of the flask containing the reactants and became non-uniformly dispersed within $NaBH_4$ suspension. Further, the reactant concentrations and catalyst loadings were less than those of SBH/H_2O = 1/2. As a result, the hydrolysis reaction of $NaBH_4$ was slower, which was observed on the gradual increase in hydrogen conversion (Fig. 3(a)).

The gravimetric hydrogen capacity of the $NaBH_4$/H_2O system was calculated as the weight percentage of released hydrogen to the total weights of the reacting system, including $NaBH_4$, water and catalyst. Although 100% of final conversion of hydrogen from hydrolysis of $NaBH_4$ could be reached in both systems with weight

Table 1
Surface compositions of Amberlite IR-120 resin and Ru^{3+}/IR-120 catalyst measured by EDS analysis.

| Elements	Amberlite IR-120 resin		Ru^{3+}/IR-120 catalyst	
	wt%	at%	wt%	at%
C	52.59	64.48	49.28	62.55
O	29.82	27.44	31.10	29.64
S	17.59	8.08	14.96	7.11
Ru	0	0	4.66	0.70

Fig. 3. (a) Time-dependent H_2 conversion and gravimetric H_2 capacity of $NaBH_4$ (SBH) with loading weight ratios of SBH/H_2O = 1/2 and 1/10; and (b) variation of reaction temperature during the hydrolysis reaction of $NaBH_4$ with SBH/H_2O = 1/2 and 1/10.

ratios of SBH/H_2O = 1/2 and 1/10, the gravimetric hydrogen storage capacity was completely different (Fig. 3). Clearly, with a system having a weight ratio of SBH/H_2O = 1/2, the gravimetric H_2 capacity could reach 7.3 wt%, which certainly exceeds 6 wt%, a goal by 2010 set for on-board automotive hydrogen storage by the US DOE [6], in contrast to 2.1 wt% obtained from that system with a weight ratio of SBH/H_2O = 1/10. This also reflects the superiority of a solid $NaBH_4$ system over an aqueous one, in terms of gravimetric hydrogen capacity of a $NaBH_4$/H_2O system. Excess addition of water really transformed the originally solid $NaBH_4$/H_2O system into an aqueous one, in which there exist disadvantages caused by the inferior aqueous solubility of $NaBO_2$ as aforementioned and the less gravimetric H_2 storage capacity. In addition, from the viewpoint of the temperature in the reacting system, a solid $NaBH_4$/H_2O system, e.g., that with SBH/H_2O = 1/2, is not any less favored, compared to that of an aqueous one.

Variations of temperatures in the $NaBH_4$/H_2O systems were monitored and shown in Fig. 3(b). As indicated earlier that the exothermic hydrolysis reaction of $NaBH_4$ could emit a heat of 217 kJ per mole of $NaBH_4$ involved for production of 4 moles of hydrogen (Eq. (1)), it would expect that heat generated and accumulated may significantly raise the temperature in the system and, thus, may lead to temperature runoff of the systems. Such an elevated temperature of the $NaBH_4$/H_2O system during the course of hydrogen production may limit its practical applications to portable microelectronics, such as cellular phones. During the course of hydrogen production from the system of SBH/H_2O = 1/2, the sys-
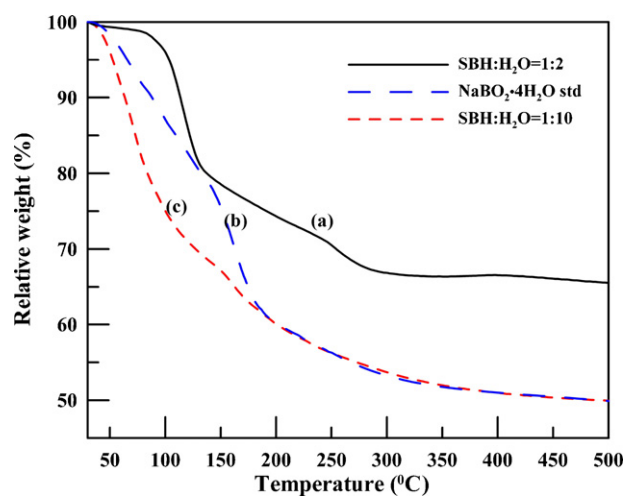

Fig. 4. TGA curves of (a) the hydrolyzed product from a reacting system with SBH/H_2O = 1/2; (b) pure $NaBO_2\cdot4H_2O$; and (c) the hydrolyzed product from a reacting system with SBH/H_2O = 1/10.

tem temperature quickly increased to a range in between 57 and 64 °C, compared to that gradually increasing temperature to 45 °C in that of SBH/H_2O = 1/10. After most $NaBH_4$ was converted to H_2 and metaborates, for example at about 15 min in the system of SBH/H_2O = 1/2, the reacting system was steadily cooled down (Fig. 3(b)) with almost no more heat generated in the reacting system.

To our scientific curiosity, whether the metaborates obtained from a solid $NaBH_4$/H_2O system or an aqueous one are the same? Effects of initial water loadings to the $NaBH_4$ reactant on the amount of water of crystallization in the main hydrolyzed product of $NaBH_4$, i.e. $NaBO_2\cdot xH_2O$, which would directly influence the gravimetric hydrogen storage capacity of the solid $NaBH_4$/H_2O system as shown in Eq. (2), was investigated using a TGA and an XRD, displayed in Figs. 4 and 5, respectively.

The TGA curve of the sodium metaborate hydrate harvested from the reacting system of SBH/H_2O = 1/2, i.e. curve (a) in Fig. 4 was similar to that previously reported for the standard $NaBO_2\cdot2H_2O$, on which the TGA curve could be divided into four regions [15]. In this study, a four-step dehydration of sodium metaborate hydrate
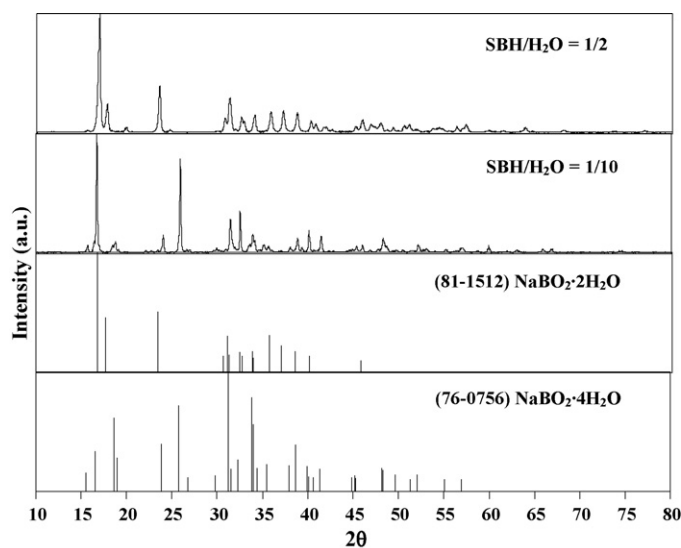
Fig. 5. XRD analyses of hydrolyzed products of reacting systems initially containing 1 g of $NaBH_4$ (SBH) and water in different weight ratios of SBH/H_2O.
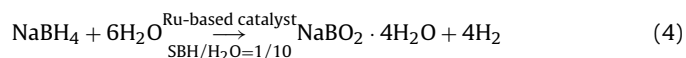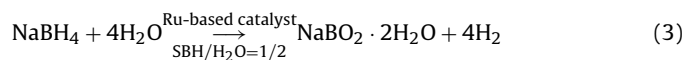
could also be observed. Initially, there was a steady plateau until the temperature was raised to about 100 °C, followed by a rapid dehydration resulting in weight loss of *ca.* 20% from 100 to 150 °C. In the second step, a further mass-loss of 9% was observed from 150 to 250 °C, and, subsequently, an additional mass-loss around 5% was found during 250 and 300 °C, which was referred as the third step. In the final step, less than 1% of mass-loss was noticed. These four steps accounted for a total mass-loss near 35% during dehydration course of the sodium metaborate hydrate collected from the $NaBH_4/H_2O$ system with a weight ratio of $SBH/H_2O = 1/2$. Furthermore, this 35% of thermogravimetric loss implied that, equivalently, two molecules of water of crystallization existed per molecule of the hydrolyzed product, i.e. $NaBO_2 \cdot 2H_2O$, from the $NaBH_4/H_2O$ system with a weight ratio of $SBH/H_2O = 1/2$.

Curve (c) in Fig. 4 represents the thermogravimetric loss of the sodium metaborate hydrates garnered from the $NaBH_4/H_2O$ system with a weight ratio of $SBH/H_2O = 1/10$. This obtained sodium metaborate hydrate, $NaBO_2 \cdot xH_2O$, started losing its crystallization-water at about 40 °C, which was also consistent with that in the literature [15]. By the end of the thermogravimetric analysis at 500 °C, a total weight loss of *ca.* 50% was attained. That is, the value of x in $NaBO_2 \cdot xH_2O$ was close to 4. Furthermore, the TGA curve almost coincides with that studied for the pure $NaBO_2 \cdot 4H_2O$ compound (curve (b) in Fig. 4) at a temperature hotter than 175 °C. Both would suggest that the hydrated hydrolyzed product from the $NaBH_4/H_2O$ system with a weight ratio of $SBH/H_2O = 1/10$ was mainly $NaBO_2 \cdot 4H_2O$.

In addition to TGA, the obtained hydrolyzed products, i.e. $NaBO_2 \cdot xH_2O$, from the reacting systems with weight ratios of $SBH/H_2O = 1/2$ and 1/10 were also further characterized using the XRD (Fig. 5). With aid of PCPDFWIN database, the XRD pattern of the hydrolyzed product from the reacting system with $SBH/H_2O = 1/10$ was in good agreement with that of $NaBO_2 \cdot 4H_2O$ from the database (76-0756), especially on characteristic diffraction at $2\theta = 15.49°$, $18.65°$, and $25.72°$, respectively. Likewise, the XRD pattern and even the relative XRD peak intensity of sodium metaborate hydrate collected from the $NaBH_4/H_2O$ system with a weight ratio of $SBH/H_2O = 1/2$ was quite consistent with that found in the database for $NaBO_2 \cdot 2H_2O$ (81-1512).

With evidence both from TGA and XRD analyses, $NaBO_2$ hydrates obtained from reaction of $NaBH_4$ in presence of Ru^{3+}/IR-120 catalysts with an initial loading of $SBH/H_2O = 1/2$ and 1/10 by weight were conjectured as $NaBO_2 \cdot 2H_2O$ and $NaBO_2 \cdot 4H_2O$, respectively. Consequently, the hydrolysis reaction of $NaBH_4$ with weight ratios of $SBH/H_2O = 1/2$ and 1/10 can be rewritten as follows:

$$NaBH_4 + 4H_2O \underset{SBH/H_2O=1/2}{\overset{Ru\text{-based catalyst}}{\longrightarrow}} NaBO_2 \cdot 2H_2O + 4H_2 \qquad (3)$$

$$NaBH_4 + 6H_2O \underset{SBH/H_2O=1/10}{\overset{Ru\text{-based catalyst}}{\longrightarrow}} NaBO_2 \cdot 4H_2O + 4H_2 \qquad (4)$$

From Eqs. (3) and (4), the theoretical maximum gravimetric hydrogen capacities of the $NaBH_4/H_2O$ could be estimated at 7.3 and 5.5 wt%, respectively, implying that the concept of considering H_2O as limiting reagent could efficiently raise the hydrogen storage capacity of chemical hydrides, which was also confirmed in the present study as shown in Fig. 3(a).

The formation of various $NaBO_2$ hydrates upon different temperature ranges can be illustrated from Fig. 6, firstly reported by Nies and Hulbert [16]. It is clear that, if water relative to $NaBO_2$ is abundant enough, the stable form of $NaBO_2$ hydrates from −5 to 53 °C is dominated by $NaBO_2 \cdot 4H_2O$, while $NaBO_2 \cdot 2H_2O$ mainly exists in between 53 and 105 °C. Certainly, this observation is quite consistent with our results found for the formation of sodium metaborate hydrates from hydrolysis of $NaBH_4$ in the work. For example, as aforementioned, the temperature of the $NaBH_4/H_2O$
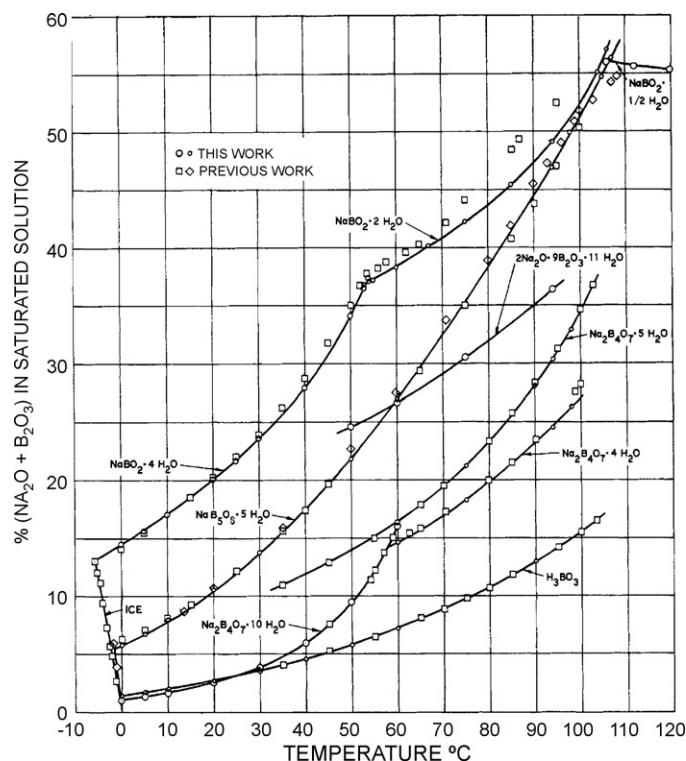

Fig. 6. Temperature-dependent aqueous solubilities of boric acid, borax, sodium pentaborate, and sodium metaborate, cited from Nies and Hulbert [16].

reacting system with initial weight ratio of $SBH/H_2O = 1/2$ reached the maximum near 64 °C during the whole course of hydrogen generation. Hence, $NaBO_2 \cdot 2H_2O$, rather than $NaBO_2 \cdot 4H_2O$, was the dominant hydrated product.

Alternatively, according to Eqs. (3) and (4), 1.904 and 2.857 g of water are required to convert stoichiometrically completely 1 g of $NaBH_4$ to $NaBO_2 \cdot 2H_2O$ (2.692 g) and $NaBO_2 \cdot 4H_2O$ (3.644 g), respectively. Hence, in this work, the system with $SBH/H_2O = 1/2$ will preferentially form more $NaBO_2 \cdot 2H_2O$ than $NaBO_2 \cdot 4H_2O$. On the contrary, if water is in excess, such as the system with $SBH/H_2O = 1/10$, $NaBO_2 \cdot 4H_2O$ will be dominant species as the hydrolyzed product of $NaBH_4$. Coincidentally, the temperature of this reacting system, shown in Fig. 3(b) was in the temperature range for existence of $NaBO_2 \cdot 4H_2O$. Utilizing water as a limiting reagent would help inhibit the formation of metaborates with more water of crystallization. Consequently, the theoretic value of gravimetric hydrogen storage capacity of $NaBH_4/H_2O$ could be greatly increased.

4. Conclusions

Solid-state $NaBH_4$/Ru-based catalyst composites were fabricated for hydrogen generation using a high-energy ball-milling process. No sophisticated procedures were required to prepare Ru^{3+}/IR-120 catalysts, Instead, the catalysts were simply fabricated from ion-exchange of Ru^{3+} ions with Amberlite IR-120 ion-exchange resin, which resulted in an averaged Ru loading of 0.7 at%, or equivalently 4.66 wt%, on the Ru^{3+}/IR-120 catalysts. Uniform dispersion of Ru^{3+}/IR-120 catalysts in pulverized $NaBH_4$ particles increased the reaction surface area and, thus, raised the rate of hydrogen evolution. Utilizing water as a limiting reagent in hydrolysis reaction of $NaBH_4$ can efficiently overpass the barrier arising from poorer aqueous solubilities of $NaBH_4$ and $NaBO_2$. Consequently, a gravimetric hydrogen storage capacity as high as 7.3 wt% could be achieved. Hydrated $NaBO_2$, namely the main hydrolyzed products, from $NaBH_4$ reacting systems with initial

weight ratios of SBH/H_2O = 1/2 and 1/10 were characterized to be likely $NaBO_2 \cdot 2H_2O$ and $NaBO_2 \cdot 4H_2O$, respectively, using TGA and XRD analyses. These results were consistent with those previously reported in the open literature from the similar solid SBH/H_2O systems in regard to different reaction temperatures. Certainly, it shows that addition of controlled amount of water could deter formation of sodium metaborates with more water of crystallization and, in return, could raise the gravimetric hydrogen storage capacity.

Acknowledgement

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