



## Hydrolysis of solid ammonia borane

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### ABSTRACT

Ammonia borane  $\text{NH}_3\text{BH}_3$  is a promising hydrogen storage material by virtue of a theoretical gravimetric hydrogen storage capacity (GHSC) of 19.5 wt%. However, stored hydrogen has to be effectively released, one way of recovering this hydrogen being the metal-catalyzed hydrolysis. The present study focuses on  $\text{CoCl}_2$ -catalyzed hydrolysis of  $\text{NH}_3\text{BH}_3$  with the concern of improving the effective GHSC of the system  $\text{NH}_3\text{BH}_3\text{-H}_2\text{O}$ . For that,  $\text{NH}_3\text{BH}_3$  is stored as a solid and  $\text{H}_2\text{O}$  is provided in stoichiometric amount. By this way, an effective GHSC of 7.8 wt% has been reached at 25 °C. To our knowledge, it is the highest value ever reported. Besides, one of the highest hydrogen generation rates (HGRs,  $21 \text{ ml}(\text{H}_2) \text{ min}^{-1}$ ) has been found. In parallel, the increases of the water amount and temperature have been studied and the reaction kinetics has been determined. Finally, it has been observed that some  $\text{NH}_3$  release, what is detrimental for a fuel cell. To summarize, high performances in terms of GHSCs and HGRs can be reached with  $\text{NH}_3\text{BH}_3$  and since research devoted to this boron hydride is at the beginning we may be confident in making it viable in a near future.

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### 1. Introduction

In the R&D devoted to find effective hydrogen storage solutions, sodium borohydride ( $\text{NaBH}_4$ ) [1] changed from the status of the most promising complex hydride to that of an inefficient storage material in less than 10 years [2]. In 2007, the US DOE unambiguously recommended a no-go for  $\text{NaBH}_4$  for on-board vehicle hydrogen storage while suggesting developing ammonia borane ( $\text{NH}_3\text{BH}_3$ ) [3].

$\text{NaBH}_4$  stores 10.8 wt% of hydrogen, which can be released by hydrolysis, half of hydrogen being provided by water (Fig. 1). The GHSC of the system  $\text{NaBH}_4\text{-H}_2\text{O}$  is theoretically of 10.8 wt%. However, the stable form of the reaction by-product, sodium metaborate ( $\text{NaBO}_2$ ), is the hydrated one, i.e. either  $\text{NaBO}_2\cdot 2\text{H}_2\text{O}$  or  $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ , which requires an excess of water (value  $\alpha$  in Fig. 1) [4]. Accordingly, the effective GHSC decreases to either 7.3 or 5.5 wt%. Besides, the  $\text{NaBO}_2$  solubility (28 g/100 g( $\text{H}_2\text{O}$ )) limits the  $\text{NaBH}_4$  concentration (16 g/100 g( $\text{H}_2\text{O}$ )), decreasing further the GHSC to 2.9 wt%. As a solution to overcome such issue, it has been interestingly proposed to store  $\text{NaBH}_4$  as a solid and to provide the required amount of water only [5]. The maximum GHSC could then be 5.5–7.3 wt% or 21.1 wt% if liquid water (on-board stored)

or steam (from a fuel cell) is provided. Practically, effective GHSCs from 6.5 [6] to 9.0 wt% [5] were obtained. Today,  $\text{NaBH}_4$  is potentially intended to mobile, portable and niche applications which targets are much less severe than the automotive ones [7].

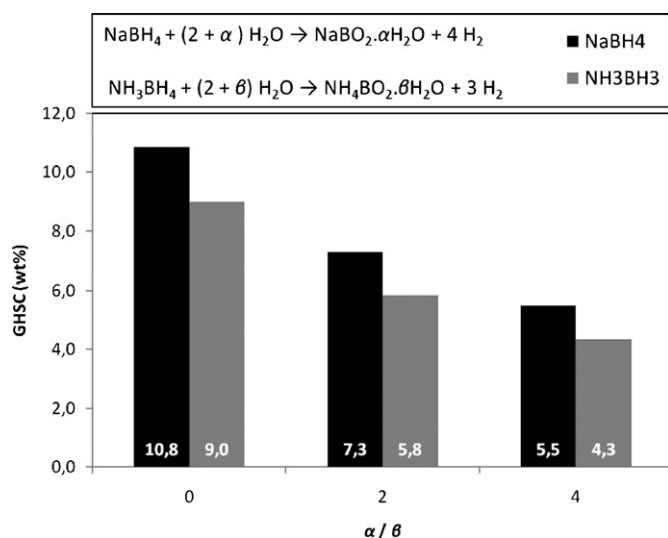
$\text{NH}_3\text{BH}_3$  is much more attractive than  $\text{NaBH}_4$  by virtue of its 19.5 wt% of stored hydrogen [8]. Nevertheless, the GHSC of the system  $\text{NH}_3\text{BH}_3\text{-H}_2\text{O}$  is only of 9.0 wt% when it is intended to be hydrolyzed in stoichiometric conditions. Further, the capacity decreases with the increase of the water excess  $\beta$  (Fig. 1), which represents the number of water molecules that are in excess while being not involved in the hydrolysis reaction. This is one of the  $\text{NH}_3\text{BH}_3$  issues. Another issue is the formation of  $\text{NH}_4^+$  [9]. Hence the highest  $\text{H}_2/\text{NH}_3\text{BH}_3$  mole ratio can only be 3. Up to now, the highest effective GHSC reported is inferior to 1 wt% [10] but it has to be recognized that the studies particularly focused on the catalytic materials intended to accelerate the  $\text{NH}_3\text{BH}_3$  hydrolysis. Accordingly, it seems that, like  $\text{NaBH}_4$ ,  $\text{NH}_3\text{BH}_3$  in aqueous solution can only be attractive for portable applications [2]. Actually, research on  $\text{NH}_3\text{BH}_3$  is at its beginning. And, the experience in  $\text{NaBH}_4$  hydrolysis could be decisive. Storing  $\text{NH}_3\text{BH}_3$  in its solid state and providing water in controlled amount have not been regarded so far. By this way, according to the hydration degree of the by-products, GHSCs of 4–6 wt% could be reached (Fig. 1). Another possibility is to provide steam, which is generated in a fuel cell. Water being not stored on-board, a theoretical GHSC of 19.5 wt% could be aimed at. In other words, there are still real improvement opportunities for the  $\text{NH}_3\text{BH}_3$  hydrolysis.

In our concern of improving the GHSC of boron hydrides intended to be hydrolyzed, we have studied the effective GHSCs of  $\text{NH}_3\text{BH}_3$  stored in solid state. Because  $\text{NH}_3\text{BH}_3$  difficultly self-

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**Fig. 1.** Hydrolysis of NaBH<sub>4</sub> and NH<sub>3</sub>BH<sub>3</sub>, with  $\alpha$  and  $\beta$  the water molecules in excess that are not involved in the hydrolysis of the hydride.

hydrolyzes, the hydrolysis was catalyzed by a simple material, i.e. cobalt chloride CoCl<sub>2</sub>, which often showed its higher capacity compared to more sophisticated cobalt catalysts [11,12]. Herein, it is reported for the first time hydrolysis of solid NH<sub>3</sub>BH<sub>3</sub>, catalyzed by CoCl<sub>2</sub>, water being provided in controlled amount. The main objective of the present study was to determine the effective GHSC of such storage system.

## 2. Experimental

Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, 97%, Sigma–Aldrich), cobalt chloride (CoCl<sub>2</sub>, anhydrous, 97%, Acros Organics) were used as received and were handled in an argon-filled glove box. Before hydrogen measurement test, pre-catalyzed sample of solid NH<sub>3</sub>BH<sub>3</sub> was prepared by mechanical mixing. In the argon-filled glove box, NH<sub>3</sub>BH<sub>3</sub> powder (90 wt%) and CoCl<sub>2</sub> as catalyst (10 wt%) were mechanically mixed together in a mortar for 30 min. A weight of 100 ± 1 mg of solid NH<sub>3</sub>BH<sub>3</sub>–CoCl<sub>2</sub> was then transferred into a glass tube (16 mm diameter), which was hermetically sealed with a silicon septum. The tube was under argon.

The hydrogen generation measurement was as follows. The tube containing the fresh solid NH<sub>3</sub>BH<sub>3</sub>–CoCl<sub>2</sub> was placed in a water bath thermostated at 25, 50 or 80 ± 1 °C. The tube exhaust was connected to a water-filled inverted burette (water colored in blue) via a cold trap maintained at a temperature lower than –140 °C. The H<sub>2</sub>O/NH<sub>3</sub>BH<sub>3</sub> mole ratio was varied. Table 1 shows the experimental conditions. No stirring was used for the kinetic experiments, except the stirring action of the evolved hydrogen. The room temperature was 20 ± 1 °C. To start hydrogen evolution, argon-purged distilled water was injected into the tube (using a titration apparatus). Hydrogen evolved immediately and displaced the liquid in the inverted burette. Water vapor was trapped in the cold trap.

The experiments were video-recorded by using a camera connected to a computer. Time was controlled using simultaneously the computer chronometer and a chronometer put near the burette (time evolution was also video-recorded). Hydrogen evolution was then analyzed using the software Matlab and the data were controlled visually. Hydrogen generation rate (HGR, ml(H<sub>2</sub>) min<sup>-1</sup> or l(H<sub>2</sub>) min<sup>-1</sup> g<sub>catalyst</sub><sup>-1</sup>; for the latter the whole mass of the catalyst is taken into account, not only the active metal) and total conversion (TC, %) were calculated. HGR was calculated over the linear part of the catalyzed hydrolysis. TC was calculated as the ratio between the volume of hydrogen generated and the maximum volume of hydrogen generable and, above all, it was based on the fact that only 3 mol(H<sub>2</sub>) per mol(NH<sub>3</sub>BH<sub>3</sub>) could be generated. The measurements were repeated as least two times in order to ensure the reproducibility of the results.

The by-products and the cobalt black precipitate, stem from the catalyzed hydrolysis of NH<sub>3</sub>BH<sub>3</sub>, were analyzed by X-ray diffraction (XRD, Bruker D5005 powder diffractometer, Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ )). For that, 270 mg of NH<sub>3</sub>BH<sub>3</sub> and 50 mg of CoCl<sub>2</sub> were mixed as described above and transferred in a tube. Water (1.58 ml,  $\beta$  equal to 8) was injected. Hydrolysis proceeded upon completion. Cobalt black precipitate was separated from the aqueous solution of NH<sub>3</sub>BH<sub>3</sub> by-products. Cobalt black precipitate was washed three times and dried under vacuum at room temperature. The by-products solution was dried under vacuum at room temperature.

## 3. Results and discussion

### 3.1. Influence of $\beta$

Before studying the solid NH<sub>3</sub>BH<sub>3</sub>–CoCl<sub>2</sub> systems, neat NH<sub>3</sub>BH<sub>3</sub> was considered in order to check its stability in the presence of water at 25 °C. The experimental conditions given in Table 1 were applied. Whatever the volume of water, no hydrogen evolution was observed over a period of 1 h. This time was chosen because it is four times longer than the time required for the slowest hydrolysis of NH<sub>3</sub>BH<sub>3</sub>–CoCl<sub>2</sub> at 25 °C (upon completion). The stability of NH<sub>3</sub>BH<sub>3</sub> was thus confirmed in agreement with previous observations [9,13]. Nevertheless this emphasized the need of catalyzing the hydrolysis reaction. Accordingly, a simple catalytic material, i.e. cobalt chloride CoCl<sub>2</sub>, was chosen because it has often showed its high performances [11,12].

The hydrolysis of CoCl<sub>2</sub>-catalyzed NH<sub>3</sub>BH<sub>3</sub> was first studied at 25 °C. Fig. 2 shows the hydrogen evolutions that were got for the various water amounts, i.e. for  $\beta$  from 0 to 8. The volume of generated hydrogen reaches TCs of 96–100%, which increase with the increase of  $\beta$ . This puts in evidence that only 3 mol(H<sub>2</sub>) is released. In other words, for  $\beta$  equal to 0, an effective GHSC of 7.8 wt% (inferior to 8.1 wt% in Table 1 because the TC of 96% has been taken into account) can be reached, suggesting that the whole water was used for hydrolyzing NH<sub>3</sub>BH<sub>3</sub>. The GHSC 7.8 wt% is among the highest values ever reported for boron hydrides and the highest one for NH<sub>3</sub>BH<sub>3</sub> [2]. It is even higher than the best result concern-

**Table 1**  
Experimental conditions of NH<sub>3</sub>BH<sub>3</sub>–CoCl<sub>2</sub> hydrolysis, with  $\beta$  as defined in Fig. 1.

Values of $\beta$	H <sub>2</sub> O/NH <sub>3</sub> BH <sub>3</sub> (mol/mol)	m(NH <sub>3</sub> BH <sub>3</sub> ) (mg)	V(H <sub>2</sub> O) (ml)	Th. GHSC <sup>a</sup> (wt%)	Eff. GHSC <sup>b</sup> (wt%)
0	2	100	0.10	9.0	8.1
2	4	100	0.21	5.8	5.2
4	6	100	0.32	4.3	3.9
6	8	100	0.42	3.4	3.1
8	10	100	0.53	2.9	2.6

<sup>a</sup> As theoretical GHSC, i.e. GHSC of neat NH<sub>3</sub>BH<sub>3</sub>.

<sup>b</sup> As effective GHSC, i.e. GHSC of NH<sub>3</sub>BH<sub>3</sub>–CoCl<sub>2</sub>, taking into account the CoCl<sub>2</sub> weight.

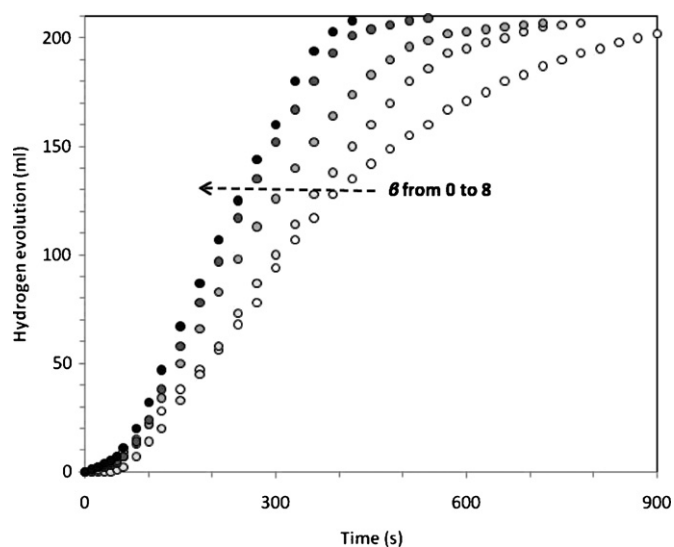


Fig. 2. Hydrogen evolution of  $\text{CoCl}_2$ -catalyzed  $\text{NH}_3\text{BH}_3$  at 25 °C: dependence on the water amount (i.e.  $\beta$ ).

ing the catalyzed thermal dehydrocoupling of  $\text{NH}_3\text{BH}_3$ . With an iridium pincer complex ( $(\text{POCOP})\text{Ir}(\text{H})_2$ ,  $\text{POCOP}$  as  $[\eta^3\text{-}1,3\text{-}(\text{OP-tert-Bu}_2)_2\text{C}_6\text{H}_3]$ ), 1 equiv.  $\text{H}_2$  was released in approximately 14 min at ambient temperature, in mild experimental conditions ( $\text{NH}_3\text{BH}_3$  was dissolved in THF at a concentration of 0.5 M and the Ir catalyst loading was of 0.5 mol%) [14]. In other words, 6.5 wt% of stored hydrogen was released within 14 min while in the present study 7.8 wt% was liberated within 15 min.

Fig. 2 shows that the variation of  $\beta$  has an effect on the hydrogen evolution profile, especially on the HGR. First of all, each profile is characterized by an induction time [13] (about 1 min), during which injected water dissolves both  $\text{NH}_3\text{BH}_3$  and  $\text{CoCl}_2$  while the first molecules of hydrogen evolve. This induction time is very short compared to those reported by Kalidindi et al. [12] for  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (60 min for diluted  $\text{NH}_3\text{BH}_3$  solutions). After the induction time, the proper catalyzed hydrolysis starts and is characterized by a constant HGR. Finally, the HGR decreases with the hydrolysis of the last  $\text{NH}_3\text{BH}_3$  molecules. Note that such profile was already reported [13] and is also typical of the hydrolysis of  $\text{NaBH}_4$  [11]. The three-step evolution was also observed by monitoring the variation of the temperature in the core of the  $\text{NH}_3\text{BH}_3\text{-CoCl}_2$  system (Fig. 3):

- First, the endothermic solubilization of  $\text{NH}_3\text{BH}_3$  and  $\text{CoCl}_2$  leads to a decrease of the temperature.
- Second, the temperature markedly increases up to about 30 °C because of the exothermic catalyzed hydrolysis.
- Third and finally, the temperature decreases to the set value of 25 °C by virtue of the water bath.

The HGRs were determined and are 21, 25, 30, 36 and 37  $\text{ml min}^{-1}$  for  $\beta$  equal to 0, 2, 4, 6 and 8, respectively. The HGR linearly increases up to  $\beta$  equal to 6 and is afterwards constant. Actually, water excesses permit solubilizing larger amounts of  $\text{NH}_3\text{BH}_3\text{-CoCl}_2$  and making species diffusion easier, and thus it favors higher kinetics.

### 3.2. Influence of temperature

Hydrolysis at various temperatures was studied. Fig. 4 shows the hydrogen evolutions obtained at 50 °C, which profiles are similar to those obtained at 25 °C but there are also 2 significant differences. First, the hydrogen generation is faster because of the higher temperature (HGRs of 115, 170, 185, 190 and 210  $\text{ml min}^{-1}$  for  $\beta$

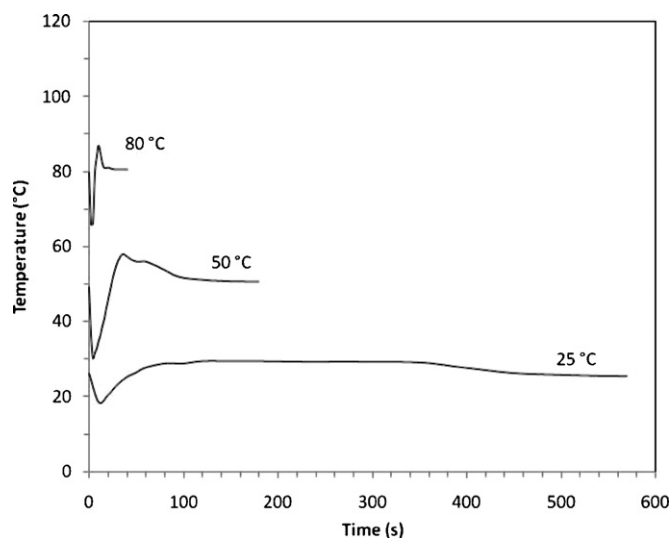


Fig. 3. Temperature evolution of  $\text{CoCl}_2$ -catalyzed  $\text{NH}_3\text{BH}_3$  at 25, 50 and 80 °C for  $\beta$  equal to 8 (the profiles for the other  $\beta$  values are similar; not given).

equal to 0, 2, 4, 6 and 8, respectively). Temperature has evidently an influence on the hydrolysis kinetics (i.e. better species diffusion, accelerated adsorption/desorption processes, and enhanced reactivity,) but it also benefits the solubilization of both  $\text{NH}_3\text{BH}_3$  and  $\text{CoCl}_2$ , making the induction time shorter (typically, less than 20 s). Second, the TC obtained with  $\beta$  equal to 0 is 74% while it is 96–98% for the other  $\beta$  values. Actually, the hydrolysis at 50 °C is accompanied by an increase of the temperature in the core of the  $\text{NH}_3\text{BH}_3\text{-CoCl}_2$  sample (Fig. 3) and some water is inevitably evaporated. Accordingly, when water is provided in stoichiometric amounts (i.e.  $\beta$  equal to 0), the TC is much lower than 100%. Fig. 5, which shows the hydrogen evolutions obtained at 80 °C, confirms these observations. The following data stands out: HGRs of 780, 970, 1250, 1330 and 1410  $\text{ml min}^{-1}$ , TCs of 46, 84, 93, 94 and 94%, for  $\beta$  equal to 0, 2, 4, 6 and 8, respectively. Because of the high temperature (Fig. 3), much water evaporated, leading to TCs lower than 100% for  $\beta$  equal to 0 and 2.

At 50 °C, the highest effective GHSC reached in our experimental conditions is 6.0 wt% (for  $\beta$  equal to 0; TC < 100% taken into account). At 80 °C, the highest effective GHSC reached is 4.4 wt% (for  $\beta$  equal to 2; TC < 100% taken into account). The tempera-

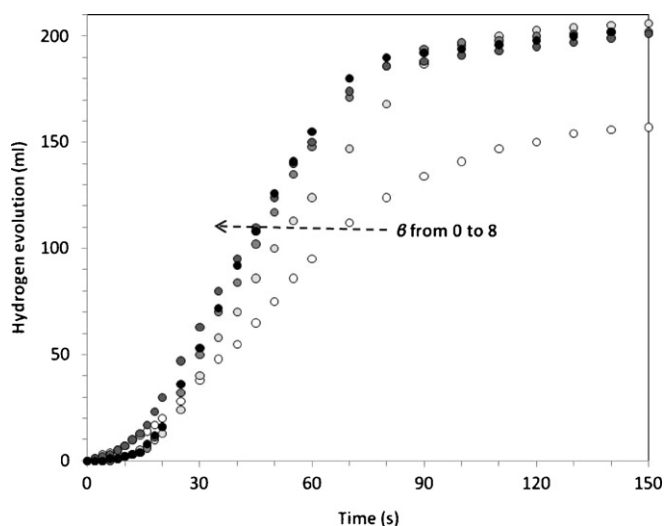


Fig. 4. Hydrogen evolution of  $\text{CoCl}_2$ -catalyzed  $\text{NH}_3\text{BH}_3$  at 50 °C: dependence on the water amount (i.e.  $\beta$ ).

ture increase has a detrimental effect on the GHSC of the system  $\text{NH}_3\text{BH}_3\text{-CoCl}_2$  because some water is evaporated, being not available for the hydrolysis anymore. Of course, if this water could be kept in the reaction chamber, the TC would be higher, and the temperature would positively influence the HGRs.

### 3.3. Kinetics

As showed in Figs. 2, 4 and 5, after the induction time, the volume of generated hydrogen increases linearly with time as the reaction proceeds. This implies zero-order kinetics. In other words, the hydrolysis reaction in our experimental conditions is independent on the  $\text{NH}_3\text{BH}_3$  concentration and this suggests that the hydrolysis generation rate is controlled within surface reaction [13,15].

From the results given in Figs. 2, 4 and 5, the apparent activation energy  $E_a$  over the temperature range 25–80 °C was calculated for each of the  $\beta$  values. Because the temperature in the core of the  $\text{NH}_3\text{BH}_3\text{-CoCl}_2$  samples increased during the hydrolysis (Fig. 3), this was taken into consideration and  $E_a$  was calculated for the temperatures 25–30, 50–58 and 80–87 °C.  $E_a$  is therefore given as an average value with an error. It has been calculated as being  $51.9 \pm 5.7$ ,  $52.7 \pm 5.5$ ,  $53.6 \pm 5.7$ ,  $51.8 \pm 5.6$  and  $52.3 \pm 5.7$   $\text{kJ mol}^{-1}$  for  $\beta$  equal to 0, 2, 4, 6 and 8, respectively. It seems that  $E_a$  is not dependent on the water content and may be given as being equal to  $53 \pm 6$   $\text{kJ mol}^{-1}$ . This  $E_a$  value is consistent with  $51.5$   $\text{kJ mol}^{-1}$  determined for 20 wt% NiAg supported over carbon (20 mg) in milder conditions (0–50 °C, 50 ml of 0.02 M  $\text{NH}_3\text{BH}_3$ ) [16]. For comparison, values of 21, 21, 23 and 62  $\text{kJ mol}^{-1}$  were reported for 2 wt%, Rh, Pt, Ru, 10 wt% Co supported over alumina [10,15], 76  $\text{kJ mol}^{-1}$  for 3 wt% Ru supported over carbon [17] and 67  $\text{kJ mol}^{-1}$  for zeolite framework stabilized Rh nanoclusters [13].

### 3.4. By-products analysis

The by-products stem from  $\text{NH}_3\text{BH}_3$  hydrolysis were identified by XRD (Fig. 6) as being ammonium borate hydrate  $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$  (ref. 00-031-0043) and ammonium chloride  $\text{NH}_4\text{Cl}$  (ref. 01-077-2352). The XRD database does not provide evidence of the formation of either  $\text{NH}_4\text{BO}_2$  or  $\text{NH}_4\text{BO}_2 \cdot 2\text{H}_2\text{O}$  (or even more hydrated). Interestingly, for  $\text{CoCl}_2$ -catalyzed hydrolysis of  $\text{NH}_3\text{BH}_3$ , Kalidindi et al. [12] observed the formation of  $\text{B}(\text{OH})_3$  by infrared spectroscopy. However, the by-products solution was dried by heating at 100 °C, what might change the by-products nature.

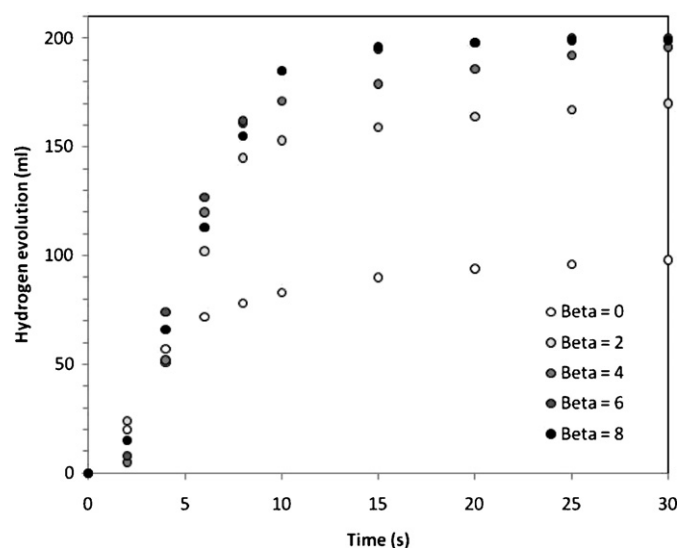


Fig. 5. Hydrogen evolution of  $\text{CoCl}_2$ -catalyzed  $\text{NH}_3\text{BH}_3$  at 80 °C: dependence on the water amount (i.e.  $\beta$ ).

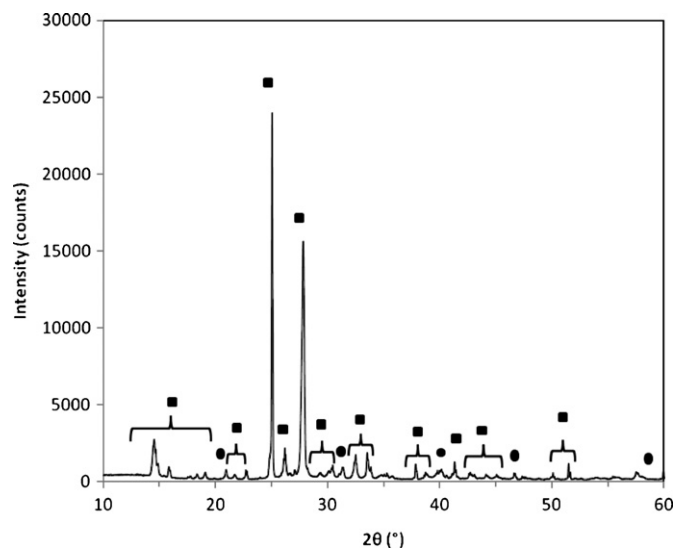


Fig. 6. XRD pattern of the by-products (square: ammonium chloride  $\text{NH}_4\text{Cl}$  ref. 01-077-2352; circle: ammonium borate hydrate  $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$  ref. 00-031-0043).

The nitrogen over boron ratio of 5 in  $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$  may suggest that some nitrogen compounds released in the hydrogen stream. Yao et al. [16] reported that the gaseous product liberated is exclusively  $\text{H}_2$ . This was put in evidence by aerating the gas product to a wet pH test paper that showed a pH value of 7. On the basis of that study, a trivial test was performed here. The hydrogen measurement system was slightly modified. The test was done as a typical hydrogen measurement but there were two main differences:

- First, the reaction tube exhaust was directly connected to a bottle filled with water (100 ml) at an initial pH of 7 and the hydrogen stream was made bubble in water. Evolved hydrogen was then evacuated in hood atmosphere.
- Second, the volume of hydrolysis water that was injected was in large excess (1 ml). At the end of the hydrolysis, the by-products solution was diluted with 9 ml of water, which was transferred in a beaker. The tube was besides washed three times with a total volume of 10 ml of water, also transferred in the beaker.

The pH of both aqueous solutions was then measured (called hereafter gas pH and by-products pH, respectively). Fig. 7 shows the gas and by-products pH values determined at 25, 50 and 80 °C. It is clearly observed a pH variation in both cases. On the one hand, the gas pH values increase from 7.5 to 9.9 with the temperature increase. This may be due to highly soluble  $\text{NH}_3$  (weak base,  $\text{NH}_4^+/\text{NH}_3$ ,  $\text{pK}_a$  of 9.2) in  $\text{H}_2$  stream, leading to the formation of  $\text{NH}_4^+$  and  $\text{OH}^-$  in water. On the other hand, the by-products pH values decrease from 9.3 to 8.8 with the temperature increase, supporting the pH 9.0 reported by Kalidindi et al. [12] for a  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  catalyzed hydrolysis. This may be due to either an increase of the by-products concentration because of water loss at higher temperatures or a higher  $\text{NH}_3$  release. This pH study is qualitative but it has the merit to show that some by-products release. These observations are rather in contradiction with Yao et al.'s [16]. Accordingly, it appears to be important to bring evidences of both nature and amount of released gaseous by-products since  $\text{NH}_3$  in the  $\text{H}_2$  stream is detrimental to a fuel cell. Further studies, especially focusing on the gas stream, are in progress.

Because  $\text{NH}_3\text{BH}_3$  is a reducing agent,  $\text{Co}^{2+}$  of  $\text{CoCl}_2$  reduces into cobalt black, which then precipitates. Cobalt black precipitate was

**Table 2**  
HGRs for several transition metal-based catalysts used in the hydrolysis of AB at 20–25 °C.

	GHSC <sup>a</sup> (wt%)	HGR (ml(H <sub>2</sub> ) min <sup>-1</sup> )	HGR (l(H <sub>2</sub> ) min <sup>-1</sup> g <sub>catalyst</sub> <sup>-1</sup> )	HGR <sup>b</sup> (l(H <sub>2</sub> ) min <sup>-1</sup> g <sub>M</sub> <sup>-1</sup> )	Reference
Fe <sub>0.5</sub> Ni <sub>0.5</sub>	0.1	61	5.5	5.5	[19]
CoCl <sub>2</sub>	7.8	21	2.1	2.1	Present work
CoCl <sub>2</sub> -6H <sub>2</sub> O	0.1	1	<0.1	<0.1	[12]
Co-γAl <sub>2</sub> O <sub>3</sub> (10 wt%)	0.2	3	0.1	1.0	[10]
NiCl <sub>2</sub> -6H <sub>2</sub> O	0.1	1	<0.1	<0.1	[12]
Ni-γAl <sub>2</sub> O <sub>3</sub> (10 wt%)	0.2	3	0.1	1.0	[10]
CuCl <sub>2</sub> -6H <sub>2</sub> O	0.1	3	<0.1	<0.1	[12]
Ru-γAl <sub>2</sub> O <sub>3</sub> (2 wt%)	0.2	78	0.3	15.0	[15]
Ru-C (3 wt%)	0.2	13	0.8	26.7	[17]
Rh-γAl <sub>2</sub> O <sub>3</sub> (2 wt%)	0.2	181	0.6	30.0	[15]
Rh-TiO <sub>2</sub> (1 wt%)	0.1	12	1.9	190.0	[18]
Rh-zeolite (1 wt%)	0.1	12	0.3	30.0	[13]
Pt-γAl <sub>2</sub> O <sub>3</sub> (2 wt%)	0.2	313	0.6	30.0	[15]
Pt-C (2 wt%)	0.2	156	0.2	10.0	[15]

<sup>a</sup> A GHSC of 0.1 wt% means either the value of 0.1 wt% or values <0.1 wt.

<sup>b</sup> For information, HGR given per gram of metal (M), which is the active phase of the supported catalysts.

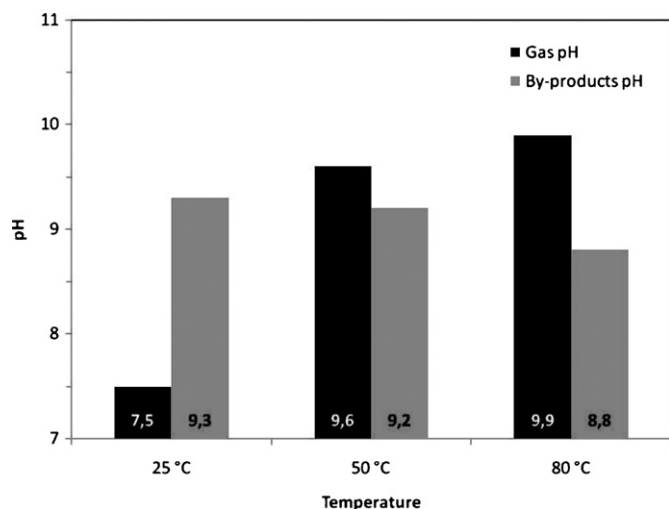


Fig. 7. Gas and by-products pH values.

thus recovered, washed three times, dried under vacuum and analyzed by XRD. Fig. 8 shows its XRD pattern. In agreement with Kalidindi et al.'s observations [12], cobalt black precipitate is amorphous.

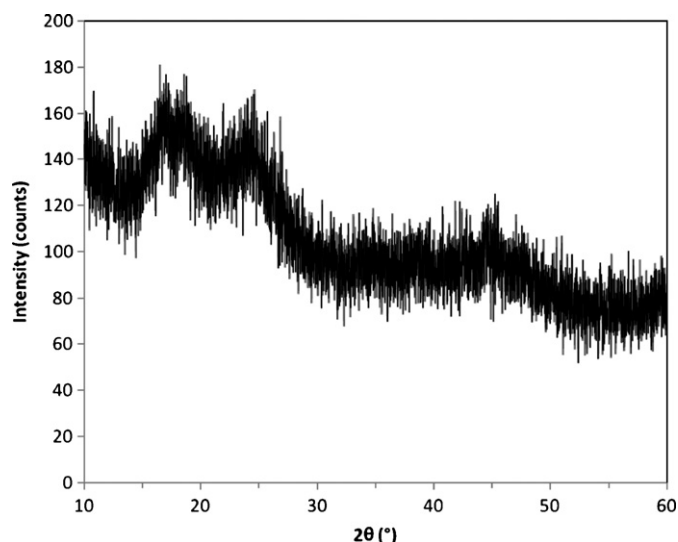


Fig. 8. XRD pattern of recovered Co after hydrolysis.

### 3.5. Application prospects

From a fuel cell application point of view, inlet H<sub>2</sub> flow and thus HGR are important features. Table 2 reports the HGR of CoCl<sub>2</sub> at 25 °C as well as those of various catalysts reported in the open literature [10,12,13,15,17–19]. Even if there are discrepancies in the experimental conditions, ours being much more severe, and even if the levels of catalysts are different, it may have interest to compare the catalysts reported in Table 2. Considering only the HGRs, CoCl<sub>2</sub> is among the best catalysts, second after the Fe<sub>0.5</sub>Ni<sub>0.5</sub> alloy. The latter showed its high HGR in much milder conditions (10 ml of NH<sub>3</sub>BH<sub>3</sub> at 0.16 M, ratio catalyst/NH<sub>3</sub>BH<sub>3</sub> equal to 0.12) and is a more sophisticated material. However, when both GHSC and HGR are considered, CoCl<sub>2</sub> in our experimental conditions is more efficient and attractive. Hence, the performances showed here are among the highest ones ever reported. Besides, as reported above, much higher HGRs can be obtained at higher temperatures and β values. It may be of interest to assess the power level that could be generated if the CoCl<sub>2</sub>-catalyzed NH<sub>3</sub>BH<sub>3</sub>-H<sub>2</sub>O storage system fed a fuel cell. It is assumed a standard polymer electrolyte membrane fuel cell operating at 0.7 V; generating 1 g(H<sub>2</sub>) min<sup>-1</sup> is equivalent to 1125 W (i.e. 26.8 A h × 60 min h<sup>-1</sup> × 0.7 V × 1 min<sup>-1</sup>); that is, 1 l(H<sub>2</sub>) min<sup>-1</sup> powers a 100 W fuel cell [20]. In our experimental conditions and for β equal to 0, 0.18 g(H<sub>2</sub>) min<sup>-1</sup> g<sub>catalyst</sub><sup>-1</sup> was generated at 20 °C, which is equivalent to a power level of 200 W g<sub>catalyst</sub><sup>-1</sup>. It is attractive for powering mobile, portable applications (1 W to few kW). These experimental values support previous conclusions with respect to the application potential of NH<sub>3</sub>BH<sub>3</sub> hydrolysis [2].

### 4. Conclusion

NH<sub>3</sub>BH<sub>3</sub> is a promising hydrogen storage material but hydrogen has to be recovered by e.g. hydrolysis. Catalyzed hydrolysis of NH<sub>3</sub>BH<sub>3</sub> is a quite novel research area and the storage system NH<sub>3</sub>BH<sub>3</sub>-H<sub>2</sub>O had not showed GHSCs higher than few tenths percents yet. For the first time, the present study reports that an effective GHSC of 7.8 wt% can be reached at 25 °C when NH<sub>3</sub>BH<sub>3</sub> is stored as a solid and water is provided in stoichiometric amount. Further, the HGR in such experimental conditions is 21 ml min<sup>-1</sup> or 2.1 l min<sup>-1</sup> g<sub>catalyst</sub><sup>-1</sup>. In parallel, it is showed that the water excess and the temperature increase have both detrimental effects on the effective GHSC. Nevertheless, both favor higher HGRs. For example, the highest HGR has been found at 80 °C for a H<sub>2</sub>O/NH<sub>3</sub>BH<sub>3</sub> ratio of 8. An apparent activation energy of 53 ± 6 kJ mol<sup>-1</sup> has been calculated. To summarize, the present paper shows that NH<sub>3</sub>BH<sub>3</sub> has really a high potential as hydrogen storage material for portable mobile and applications and suggests that its effective GHSC may be

further improved by using steam (e.g. stem from a fuel cell) instead of liquid water.

However, some issues have to be solved yet. For example, the present study shows that there may be some  $\text{NH}_3$  releases, what is detrimental for any fuel cell, the releases being intensified with the temperature increase. This is another issue adding further to those already identified: e.g. low effective GHSCs for automotive applications [2],  $\text{NH}_3\text{BH}_3$  reversibility/regeneration [8], by-products recycling [21], inefficiency of catalyst in terms of durability [2].

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