

Ammonia borane in chemical hydrogen storage – Ammonia release during hydrolysis of ammonia borane, an issue

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ABSTRACT

In hydrolysis of ammonia borane (NH_3BH_3), significant amounts of ammonia evolve. The liberation of this compound depends on parameters, such as temperature, amount of water, catalyst loading and catalyst nature. In the standard experimental conditions used here, which are much milder than operating conditions of implemented storage systems, a 4.5 vol% of NH_3 is measured in the stream of H_2 . This is clearly a significant drawback for ammonia borane in solid-state hydrogen storage because NH_3 is detrimental to low temperature fuel cell applications (specification of 1 ppm), as well as to user/environment (if over-exposure). Since NH_3 liberation in this reaction is unavoidable, the utilization of a trap is necessary. This is discussed herein.

1. INTRODUCTION

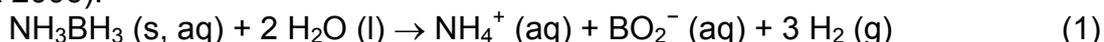
Chemical hydrogen storage via boron-based materials, such as sodium borohydride (NaBH_4 , and ammonia borane (NH_3BH_3), have in the past decade been presented as being an attractive and promising solution to store hydrogen safely and efficiently for fuel cell applications. For the moment, none of the compounds investigated has come up expectations (Eberle 2009). For instance, in the last 10 years, sodium borohydride, owing to its stability in anhydrous conditions and its theoretical gravimetric hydrogen density of 10.8 wt%, was introduced as being the storage solution for vehicular applications (Amendola 2000) but it has been shown that it does not have the effective capacity required (Demirci 2009a). In the meantime, ammonia borane emerged and seems to be a promising alternative (Gutowska 2005, Chandra 2006).

The strength of ammonia borane lies in its attractive qualities: it is relatively safe, has a high gravimetric hydrogen density and has the ability to dehydrogenate in mild conditions. Ammonia borane is known to be non-toxic, explosion-safe and stable. It stores 19.5 wt% of hydrogen, part of which is released either by thermolysis or hydrolysis (Staubitz 2010). The former process necessitates only ammonia borane,

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which therefore does not result in a decrease in the effective gravimetric hydrogen density. However, this process has three significant drawbacks: (i) high hydrogen release temperatures ($T > 100^{\circ}\text{C}$), (ii) sluggish hydrogen release kinetics, and (iii) emission of unwanted side-products (e.g. borazine $\text{B}_3\text{N}_3\text{H}_6$) (Wolf 2000, Benzoua 2010). In this context, hydrolysis of ammonia borane has proved to be a promising alternative (Chandra 2006). However, both processes are not yet sufficiently understood for technological implementation (Demirci 2009b).

In the presence of an acid- or metal-based homo- or hetero-geneous catalyst (Metin 2010), the system $\text{NH}_3\text{BH}_3\text{-H}_2\text{O}$ is able to release hydrogen in ambient conditions (Chandra 2006):



Though the gravimetric hydrogen density of the system $\text{NH}_3\text{BH}_3\text{-H}_2\text{O}$ is lower than that of ammonia borane (i.e. 9.0 vs. 19.5 wt%), the reaction shown by Eq. (1) is attractive due to the fact that hydrogen evolves in ambient conditions with satisfactory kinetics and that the hydrogen would be pure. The highest effective gravimetric hydrogen density has been reported as 7.8 wt%, with the hydrogen generation rate being $2.1 \text{ L min}^{-1} \text{ g}^{-1}(\text{catalyst})$ at 25°C (Demirci 2010). Besides this, much higher hydrogen generation rates are obtained with various metal catalysts (Chandra 2006, Metin 2010, Graham 2010). Unfortunately, the hydrogen released is not pure. The characteristic pungent odor of NH_3 (average odor threshold of 35 mg m^{-3} or $\sim 50 \text{ ppm}$) can be smelt in the hydrogen stream for reactions performed in our experimental conditions (Demirci 2010, Hannauer 2011). The stream is in fact polluted with undesired NH_3 , known to be detrimental to fuel cells, i.e. hydrolysis of ammonia borane, for the moment, fails to overcome the third drawback indicated above (Sanyal 2010). This is the topic of the present work.

Herein, we report results of a systematic study aiming at quantifying the amount of NH_3 released under various experimental conditions (i.e. temperature, water content, catalyst nature and proportion) and in the absence of an NH_3 trap. The conditions were changed in order to be closer to operating conditions necessary for the highest effective storage capacity and tunable hydrogen release kinetics. Besides this, simple traps were considered to test their efficiency in trapping the evolved NH_3 .

2. EXPERIMENTAL

The ammonia borane complex (97%, Acros Organics) is used as received. It is stored and handled in an argon-filled glove box in which both moisture and oxygen are maintained at $< 0.1 \text{ ppm}$. Argon-saturated Millipore milli-q water with a resistivity $> 18 \text{ M}\Omega \text{ cm}$ is also used. The other chemicals are given hereafter.

Quantification of the NH_3 released is done as follows. In the glove box, ammonia borane (90 mg) and a magnetic stirring bar are introduced into the reactor (glass tube of 27.5 mL and $\varnothing 16 \text{ mm}$) sealed with a silicon septum and protected with Parafilm M. The reactor is then placed in a water bath thermostated at the desired temperature and is connected to a 1-L Tedlar bag (Restek) to collect the generated hydrogen (about 210 mL in our conditions). In the case of experiments testing the effect of a NH_3 trap, a 100-

mL flask (bubbler-type) is placed between the reactor and the bag. To start hydrolysis, an aqueous solution of catalyst precursor, *i.e.* the catalyst is generated *in situ* by reduction with ammonia borane, is injected into the reactor (using a titration apparatus with a precision of 10^{-2}). In the experimental conditions used in previous studies (*i.e.*, excess of water and highly reactive metal catalyst) (Demirci 2010, Hannauer 2011), conversions of 100% (3 mol(H₂) per mol(NH₃BH₃)) are reached. Table 1 gives an overview of the experiments carried out, with details of temperature, amount of water, catalyst nature and quantity. The catalyst precursors used are as follows: cobalt chloride (CoCl₂, 97%, Acros Organics), nickel chloride hexahydrate (NiCl₂·6H₂O, 98%, Sigma-Aldrich), ruthenium chloride (45-55% Ru, anhydrous, Sigma-Aldrich), and hexachloroplatinic acid hydrate (H₂PtCl₆·6H₂O, 40% Pt, Sigma-Aldrich). Table 2 gives the details about the experiments using an NH₃ trap. Upon completion of hydrolysis, an argon flow (50 mL min⁻¹) purges the whole system, from the reactor to the collecting bag, and fills the bag up to 1 L. Finally, the bag tap is closed.

Table 1. Experiments performed to assess the NH₃ amounts in the hydrogen stream (in bold: the experimental parameter was changed; no trap is used here).

m(AB) mg	M.C.P. ^a	m(M) ^a mg	[M] ^a wt%	V(H ₂ O) mL	n _{H₂O} /n _{AB} mol/mol	T °C	V(H ₂) ^b mL	V(bag) ^c mL
90	CoCl ₂	10.0	10	2.10	40	14	210	1000
90	CoCl ₂	10.0	10	2.10	40	20	210	1000
90	CoCl ₂	10.0	10	2.10	40	40	210	1000
90	CoCl ₂	10.0	10	2.10	40	60	210	1000
90	CoCl ₂	10.0	10	2.10	40	80	210	1000
90	CoCl ₂	10.0	10	0.52	10	20	210	1000
90	CoCl ₂	10.0	10	1.05	20	20	210	1000
90	CoCl ₂	10.0	10	2.10	40	20	210	1000
90	CoCl ₂	10.0	10	4.20	80	20	210	1000
90	CoCl ₂	10.0	10	8.40	160	20	210	1000
90	CoCl ₂	3.7	5	2.10	40	20	210	1000
90	CoCl ₂	6.8	7	2.10	40	20	210	1000
90	CoCl ₂	7.8	8	2.10	40	20	210	1000
90	CoCl ₂	10.0	10	2.10	40	20	210	1000
90	CoCl ₂	12.3	12	2.10	40	20	210	1000
90	CoCl₂	10.0	10	2.10	40	20	210	1000
90	NiCl₂	10.0	10	2.10	40	20	210	1000
90	RuCl₃	10.0	10	2.10	40	20	210	1000
90	H₂PtCl₆	10.0	10	2.10	40	20	210	1000

^a M.C.P. as metal catalyst precursor, m(M) as the metal mass, and [M] as the metal proportion in AB-M. ^b V(H₂) as volume of pure hydrogen expected from hydrolyzed AB at 20°C. ^c V(bag) as the volume of the Tedlar bag after hydrolysis and filling with argon at 20°C.

The gases collected in the Tedlar bag are passed through Draeger-Tubes® with the help of a pump provided by the manufacturer (Draeger accuro®). The Draeger-Tubes® consist of graduated (calibrated) glass vials filled with a specific chemical reagent that reacts to NH₃, thus enabling the quantification of this compound. The gas detection is done by color change. The fresh reagent is yellow and turns violet after NH₃ passes through the tube. The accuracy of the Draeger-Tubes® has been confirmed (Luo 2007). Typically, we proceed as follows. The collected gases, consisting of H₂ (210 mL), NH₃ and Ar, are pumped through a Draeger-Tube®, knowing that 100 mL to 1 L of gas can be pumped. The NH₃ concentration can then be obtained by the length of the color change and read from the graduation. Under our conditions, we use the Draeger-Tubes® with the references 0.25/a, 5/a and 0.5%/a that enable us to measure NH₃ concentrations over the range 0.25-3 ppm for tests in the presence of an NH₃ trap, 5-70 ppm for tests in the presence of an NH₃ trap, and 0.5-10 vol%. In terms of reproducibility, the experiments were performed twice; then all of the 1-L bags were analyzed several times, and we found that the results fall within a range ±10%, especially for very low concentrations, whereas the error is less for higher concentrations.

Table 2. Details of the experiments using a trap; the other parameters were as follows: m(NH₃BH₃) = 90 mg, m(Co) = 10 mg, V(H₂O) = 2.1 mL, T = 20 °C, and V(bag) = 1 L.

Trap nature	V(flask) ^a	V(trap) ^a	DV ^a	Initial observations	Post-reaction observations
H ₂ O at pH 7	100	100	< 10	None	None
H ₂ O at pH 1	100	100	< 10	None	None
H ₂ O at pH 12	100	100	< 10	None	None
Al ³⁺ aq. sol. ^b	100	100	< 10	Translucent	Translucent
Fe ³⁺ aq. sol. ^b	100	100	< 10	Red	Red
Co ²⁺ aq. sol. ^b	100	100	< 10	Pink	Pink
Ni ²⁺ aq. sol. ^b	100	100	< 10	Light green	Light green
Cu ²⁺ aq. sol. ^b	100	100	< 10	Sky blue	Slight turbidity and precipitation of a blue solid after 2 h
Ag ⁺ aq. sol. ^b	100	100	< 10	Translucent	Light brown and precipitation of a brown solid after 2 h
SGB (sol.) ^c	100	100	< 10	Blue particles	None
P ₂ O ₅ (sol.) ^c	100	100	< 10	White dense powder	None

^a V(flask) - the recommended volume of the flask containing the trap; V(trap) - the volume of the material used as trap; DV - dead volume, *i.e.* the volume of the flask remaining unfilled. ^b Aqueous solutions of aluminum chloride hexahydrate (AlCl₃·6H₂O, > 99%, Sigma-Aldrich), iron (III) acetylacetonate (Fe(C₃H₇O₂)₃, > 97%, Sigma-Aldrich), cobalt chloride (CoCl₂, 97%, Acros Organics), nickel chloride hexahydrate (NiCl₂·6H₂O, > 98%, Sigma-Aldrich), copper sulfate pentahydrate (CuSO₄·5H₂O, > 98%,

Sigma-Aldrich) and silver nitrate (AgNO_3 , > 99%, Sigma-Aldrich). ° SGB as blue silica gel (solid, Roth Carl); P_2O_5 (Acros Organics).

3. RESULTS AND DISCUSSION

Ammonia is generally determined by acid/base titration of water (used as the trap) or by weighing a CuSO_4 solution, through both of which NH_3 has passed. In the studies dedicated to hydrolysis of ammonia borane, the presence of NH_3 in the hydrogen stream has rarely been reported. Other researchers found that NH_3 was always detected but in specific constant conditions (Kalidindi 2009, Brockman 2010). Ramachandran and Gagare's work (2007) is the only one assessing the effect on NH_3 release of a few experimental parameters. For hydrolyses in the presence of the catalyst precursor RuCl_3 , the RuCl_3 content (0.06-0.2 mol%), ammonia borane concentration (6-25 wt%), and addition time of the catalytic solution (15-45 min) were changed (25°C). On the one hand, it was found that 1-7% of NH_3 was liberated, depending on these parameters. On the other hand, for 6 wt% ammonia borane (mol ratio $\text{H}_2\text{O}/\text{NH}_3\text{BH}_3$ of ~27) and 0.06 mol% RuCl_3 under slow addition mode (15 min), no liberation of NH_3 was found by titration. However, the authors have not discarded the possibility of evolved NH_3 but in undetectable amounts. In addition, as shown through a more systematic approach, like the one we propose here, we also consider that very low amounts of NH_3 should have been released.

In this study, we chose to work with CoCl_2 because it is an efficient catalyst precursor consisting of nanoparticles formed *in situ* (Akdin 2009). Furthermore, we have shown that the as-formed catalyst is efficient in the hydrolysis of ammonia borane (Demirci 2010, Hannauer 2011). Above all, it is a well-documented material. The standard experimental conditions have been set as follows: no NH_3 trap, reaction temperature of 20°C, room/bag temperature of $20 \pm 1^\circ\text{C}$ (24 mol L^{-1}), 90 mg of ammonia borane to generate 210 mL of hydrogen, 2.1 mL of water to have a $\text{H}_2\text{O}/\text{NH}_3\text{BH}_3$ mol ratio of ca. 40, and 10 wt% Co. In these conditions, we found an NH_3 content of 4.5 vol% in the gas stream, *i.e.* about 10 mL NH_3 for 210 mL H_2 . This value is consistent with those reported by Ramachandran and Gagare (2007). However, such an amount is unacceptable for fuel cell applications, given that the specification for hydrogen from the storage system to the fuel cell inlet has been set at 1 ppm NH_3 . On the other hand, NH_3 is caustic, corrosive, toxic and very hazardous to aquatic organisms. For example, exposure at 25 ppm is acceptable for 8 h but an increase up to 35 ppm limits it to 15 min. These constraints have motivated the present systematic study of NH_3 liberation in hydrolysis of AB, where the reaction temperature, Co content and $\text{H}_2\text{O}/\text{NH}_3\text{BH}_3$ mol ratio were changed.

We first considered the effect of temperature, going from 14 to 80°C. Figure 1 shows the results and as can be seen, a higher temperature results in the liberation of more NH_3 . Over the range 14-40°C, the NH_3 content increases slightly from 4.3 to 5.6 vol%. However, a further temperature increase, up to 80°C, leads to an exponential-like rise in the NH_3 content, reaching a value of 15 vol%. This value corresponds to about 50% of the NH_3 from 90 mg of ammonia borane. At 80 °C, the hydrolysis is in fact violent: the hydrogen bubbles vigorously. Such conditions are favorable for water loss, and thus for a subsequent increase in concentration in the reaction slurry, and thus for

more NH_3 liberation. Given that the operating temperature of a fuel cell is around 80°C , one can easily imagine that such an NH_3 release is not conceivable for an industrial application.

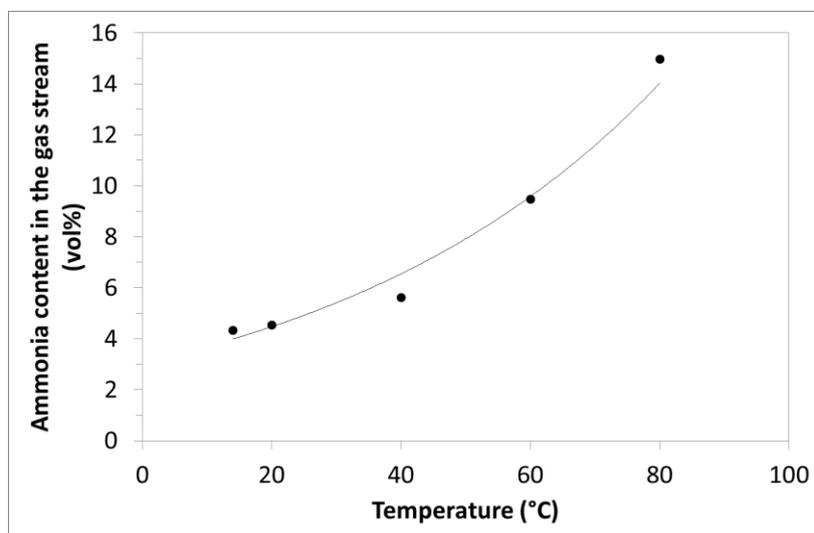


Fig. 1. Content of NH_3 (vol%) as a function of temperature.

Since NH_3 is highly soluble in water (862 vol/vol at 1.013 bar and 0°C), the effect of the quantity of water was studied for $\text{H}_2\text{O}/\text{NH}_3\text{BH}_3$ mol ratios from 10 to 160 (0.35 to $5.62 \text{ mol NH}_3\text{BH}_3 \text{ L}^{-1}$). The results are shown in Figure 2. We can see from this figure that the greater the amount of water, the less NH_3 is liberated. For example, with 4 times the quantity of water (mol ratios of 40 and 160) the NH_3 content in the gas stream decreases from 4.5 to 2.6 vol%. The trend observed is consistent with NH_3 solubility. More water appears to be preferable in terms of obtaining a decrease in the extent of NH_3 liberation. However, this is detrimental to the effective gravimetric hydrogen density of the system $\text{NH}_3\text{BH}_3\text{-H}_2\text{O}$. For example, an ammonia borane solution at 0.35 mol L^{-1} (an $\text{H}_2\text{O}/\text{NH}_3\text{BH}_3$ mol ratio of 10) can only release 1.9 wt% of hydrogen, which is far from the specifications in terms of effective capacities. These experiments also suggest that water could be envisaged as an NH_3 trap, which is reported hereafter.

Hydrolysis of ammonia borane being a purely catalytic reaction, the reaction order vs. the concentration of active Co sites is generally found to be in the range 0.5-1.0 (Jiang 2011). We thus studied the effect of Co content on NH_3 liberation (Figure 3). As can be seen from the figure, the Co content was varied from 5 to 12 wt% so that it approximately corresponded to the experimental conditions generally considered with the prospect of technological applications. We observed that the more Co there was, *i.e.* the faster the hydrolysis (Ramachandran 2007, Jiang 2011), the more NH_3 evolved. In addition, other metal catalyst precursors, like RuCl_3 , NiCl_2 and H_2PtCl_6 were tested. The results showed that the order was $\text{Ru} > \text{Co} > \text{Pt} > \text{Ni}$ in terms of reactivity, in our experimental conditions. In the gas stream, the NH_3 content decreased, consistent with

this same order (Figure 3). As for the effect of increasing temperature, very reactive catalysts lead to a vigorous release of hydrogen and, subsequently, large quantities of NH_3 are liberated, which is unfortunately not mitigated by the excess water.

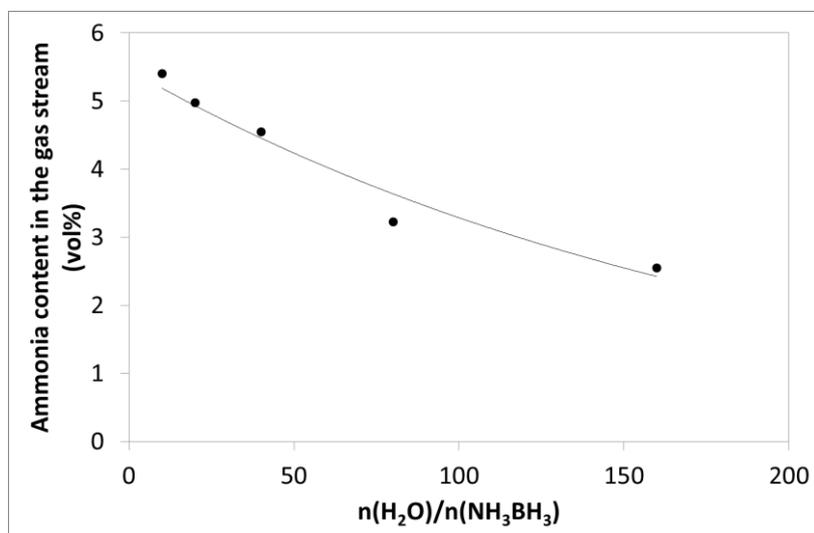


Fig. 2. Content of NH_3 (vol%) as a function of volume of water used as hydrolytic agent in ammonia borane hydrolysis.

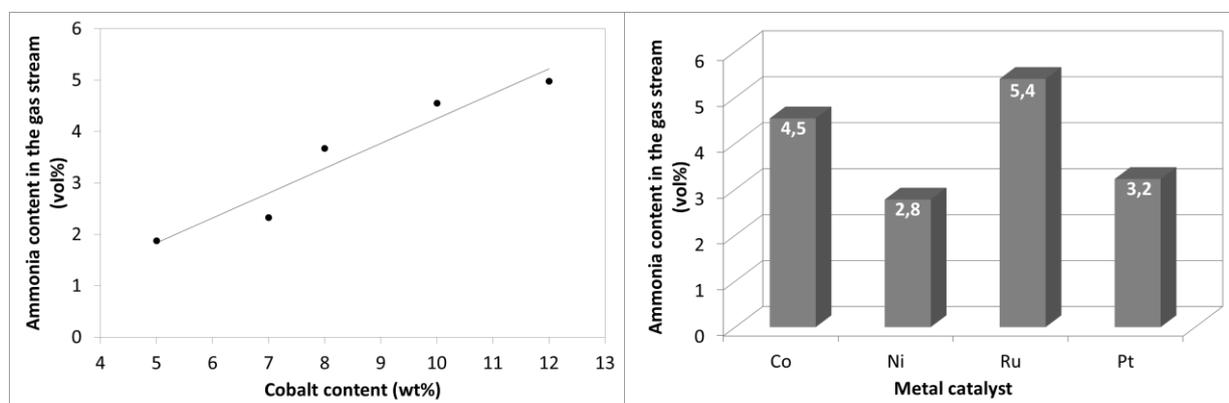


Fig. 3. Content of NH_3 (vol%) as a function of (a) the Co content and (b) the nature of the metal catalyst.

To sum up the aforementioned results, it is clear that NH_3 liberation during ammonia borane hydrolysis is unavoidable in harsh conditions, *i.e.* close to the operating ones (meaning temperatures up to 80°C and very low amounts of water) to have the highest effective storage capacity and acceptable catalytic activity to tune hydrogen generation rate. This thus means that the use of an NH_3 trap is necessary. A preliminary study is

reported hereafter, where our standard test, including a trap placed between the reaction and the gas collecting bag, was repeated several times.

Various traps were tested (Table 2 and Figure 4). From the results, we can say that water can act as an efficient trap of the highly soluble NH_3 . In its presence (100 mL, pH of 7), the NH_3 content dropped sharply to ca. 10 ppm; a solution of 86 L NH_3 (at 0°C) could therefore be expected. The effect of water pH (*i.e.* 1 and 12) was also studied and found to be positive; the NH_3 content was measured at ca. 2 ppm in both cases. Other simple solutions were also tested. For example, we have used aqueous solutions of metals that are known to form complexes in the presence of NH_3 . Content of NH_3 from a few to a few tens of ppm were measured: 0.6-1.2 ppm for Fe, Co, Ni; 8.3-10.7 ppm for Cu and Ag; and, 47.6 ppm for Al. Note that, in one experiment, we used two materials generally used as water trap (*i.e.* blue silica gel and P_2O_5) and the NH_3 content was found to be 2-3 ppm. This result shows that most of the NH_3 liberated can be efficiently trapped in various media. However, the solutions considered here cannot be envisaged with the prospects of industrial applications because they make the storage system heavy while also decreasing the hydrogen storage capacity. In other words, the possibility of implementing ammonia borane hydrolysis strongly depends on the efficiency in trapping NH_3 that inevitably forms in harsh conditions (*i.e.* low water content, highly reactive catalysts and temperatures up to 80°C).

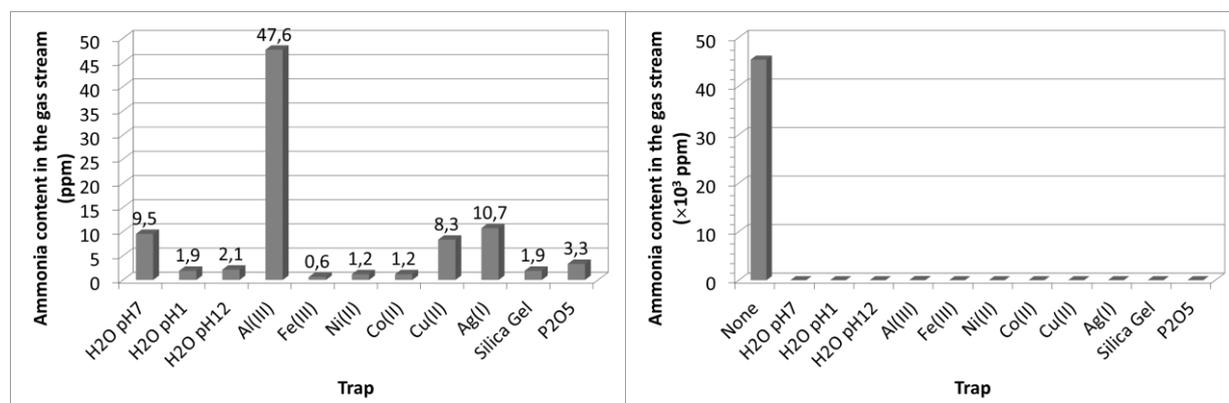


Fig. 4. Content of NH_3 (vol%) in the presence of a trap: (a) data only for the tests with a trap are shown; (b) the standard test without trap is added.

4. CONCLUSIONS

Hydrolysis of ammonia borane is a promising approach to safely store hydrogen and to easily release hydrogen in ambient conditions in the presence of a suitable catalyst. However, it suffers from a significant drawback: while hydrogen is formed, some NH_3 , from ammonia borane, is liberated. The NH_3 content in the gas stream can reach values up to 15 vol% at 80°C in our experimental conditions. It has been highlighted that for operating conditions that should be harsh in terms of ammonia borane

concentration, temperature and catalyst reactivity in the case of technological applications the NH_3 liberation will be significant, and thus be detrimental to fuel cell applications, and moreover, harmful to user and the environment. Traps, a simple concept, can be envisaged to trap evolving NH_3 . For example, it has been shown that water (at various pH) or aqueous solutions of metal cations very efficiently trap NH_3 : the content dropping to a few to tens of ppm.

The liberation of ammonia during the hydrolysis of ammonia borane appears to be unavoidable for pure $\text{NH}_3\text{BH}_3\text{-H}_2\text{O}$. One concept, NH_3 decomposition, is unconceivable as the reaction requires too high temperature, higher than the operating conditions of low temperature fuel cells. However, in the future to address the issue of NH_3 liberation, efficient and light traps (e.g. polymer or ceramic membranes) should be considered. To our knowledge, there has been no such work in the area of ammonia borane hydrolysis. There is thus still an unexplored aspect of this topic.

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