Closing the hydrogen cycle with the couple sodium borohydride-methanol, via the formation of sodium tetramethoxyborate and sodium metaborate

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Running title: **Closing the hydrogen cycle with sodium borohydride-methanol"**

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Abstract

Methanolysis of sodium borohydride ($NaBH_4$) is one of the methods efficient enough to release, on demand, the hydrogen stored in the hydride as well as in 4 equivalents of methanol (CH_3OH). It is generally reported that, in methanolysis, sodium tetramethoxyborate ($NaB(OCH_3)_4$) forms as single component of the spent fuel. It is however necessary to clearly investigate some critical aspects related to it. We first focused on the methanolysis reaction where $NaBH_4$ was reacted with 2, 4, 8, 16 or 32 equivalents of CH_3OH. With 2 equivalents of CH_3OH, the conversion of $NaBH_4$ is not complete. With 4 to 32 equivalents of CH_3OH, $NaBH_4$ is totally methanolized (conversion of 100%). The best conditions are those involving 4 equivalents of CH_3OH as they offer the highest effective gravimetric hydrogen storage capacity with 4.8 wt%, an attractive H_2 generation rate with 331 mL(H_2) min^{-1} – a performance achieved without any catalyst –, and the formation of $NaB(OCH_3)_4$ as single product as identified by XRD, FTIR and NMR. We then focused on the transformation of this product $NaB(OCH_3)_4$ into sodium metaborate ($NaBO_2$), via the formation of sodium tetrahydroxyborate ($NaB(OH)_4$). $NaB(OCH_3)_4$ is easily transformed in water, by hydrolysis, at 80 °C and for 90 min, into $NaB(OH)_4$ and 4 equivalents of CH_3OH. In doing so, the cycle with

CH_3OH is closed. Subsequently, $NaB(OH)_4$ is recovered and converted into $NaBO_2$ under heating at 500 °C. This reaction liberates 4 equivalents of H_2O, which allows to close the cycle with water. Based on these achievements, we have finally proposed a triangular recycling scheme aiming at closing the cycle with the protic reactants of the aforementioned reactions. This scheme may be used as base for implementing a closed cycle with the couple $NaBH_4$-CH_3OH.

Keywords

Methanolysis; Recycling; Sodium borohydride; Sodium metaborate; Sodium tetramethoxyborate; Spent fuel

1. Introduction

Hydrogen, owing to its clean nature and high energy density, is clearly one of the most attractive sustainable energy technologies [1]. Hydrogen has grown up very quickly. However, its deployment is confronted with a number of issues touching the whole chain of the so-called "hydrogen economy". One of the main roadblocks concerns its storage [2]. Various solutions (physical and chemical) have been explored within the past decades [3,4] and chemical hydrogen storage has shown to face a very positive outlook going forward [5–7].

As chemical hydrogen storage material, sodium borohydride ($NaBH_4$) has been widely investigated as it is considered as a reliable candidate for mobile applications [2], especially because it carries 10.8 wt% of (atomic) hydrogen (in hydridic form) and is able to readily release (molecular) hydrogen by reaction with water (by hydrolysis [8]) or methanol (by methanolysis [9]) at ambient conditions:

$$NaBH_{4\,(aq)} + 4H_2O_{\,(l)} \rightarrow NaB(OH)_{4\,(aq)} + 4H_{2\,(g)} \qquad (1)$$

$$NaBH_{4\,(aq)} + 4CH_3OH_{\,(l)} \rightarrow NaB(OCH_3)_{4\,(aq)} + 4H_{2\,(g)} \qquad (2)$$

The reaction, e.g. the hydrolysis one, is spontaneous ($\Delta H = -217$ kJ mol^{-1} at 25 °C) [10] and the solution is generally stabilized by increasing the pH beyond 11 (alkaline conditions) [11]. The use of a heterogeneous (metallic) catalyst is required to catalyze the release of hydrogen by hydrolysis [12]. The research field dedicated to $NaBH_4$ has mainly focused on finding the best catalyst whereas other crucial aspects (by-products, scaling up, among others) have been clearly under-investigated [13].

One of the main challenges with $NaBH_4$ is related to the by-product, i.e. sodium tetrahydroxyborate ($NaB(OH)_4$) in hydrolysis or sodium tetramethoxyborate ($NaB(OCH_3)_4$) in methanolysis. Recycling it to regenerate $NaBH_4$ is of importance for closing the hydrogen cycle and for the implementation of the technology. In the field of hydrolysis, a number of studies have focused on identification of the hydrolytic (intermediate and final) by-products [14–16] as well as on regeneration options [17–20], and it may be concluded that the challenge is enormous. Using methanol for dehydrogenating $NaBH_4$ has advantages over the use of water. One of them is related to the nature of the by-product. In methanolysis (Eq. 2), $NaB(OCH_3)_4$ forms [21]. Unlike $NaB(OH)_4$ [22], $NaB(OCH_3)_4$ does not have the propensity to readily polymerize into polyborates [23,24], avoiding then their precipitation that are known to cause blocking of pipes and catalyst poisoning [25]. Another attractive feature with $NaB(OCH_3)_4$ is that it is one of the intermediate products of the $NaB(OH)_4$ regeneration process developed by Kemmitt et al. [26]. According to this process, $NaB(OH)_4$ is first dehydrated into $NaBO_2$, then $NaBO_2$ is reacted with methanol to form $NaB(OCH_3)_4$, and finally $NaB(OCH_3)_4$ is reduced into $NaBH_4$ in the presence of sodium alanate $NaAlH_4$ in refluxing diglyme. Yet, in methanolysis, $NaB(OCH_3)_4$ forms directly (Eq. 2), which then allows getting a cheaper process (free of the two steps of dehydration and methoxylation). To our knowledge, the open literature dedicated to methanolysis of $NaBH_4$ mainly deals with reaction parameters [27–30], catalysts [27,31–33], and kinetics [23,29,30]. The catalysis topic has been disproportionately investigated with a large number of possible catalysts reported so far [34]. Examples of recent catalysts are as follows: supported cobalt [35–37] and nickel [38] and bimetallics [39,40], TiO_2 [41], metallurgic sludge [42], polymer-based systems (e.g. microgels) [43–46], treated microalgae [47,48] and other natural materials like spent coffee [49,50]. With respect to the by-products like $NaB(OCH_3)_4$, very few reports focused on their identification and their solid-state structure. Fernandes et al., who primarily investigated the effect of methanol on the kinetics of hydrolysis of $NaBH_4$ for methanol-water mixtures, showed that $NaB(OCH_3)_4$ is only obtained in the absence of water [21]. Huynh et al. isolated and characterized a solid-state methanolysis by-product [51]. By XRD analyses, a derivative of $NaB(OCH_3)_4$ was found; the following structure was suggested: $[Na_2(B(OCH_3)_4)_2(CH_3OH)_2]_4$. Its stability in water was scrutinized; it was observed that hydrolysis takes place resulting in the formation of a hydrated sodium tetraborate salt with the structure $Na_2[B_4O_5(OH)_4].8/3H_2O$. In this way, methanol (CH_3OH) was recovered.

In such a context, our efforts have focused on methanolysis of $NaBH_4$, specifically on the by-products stemming from this reaction. For a technology that has commercial objectives, implying then large volumes of spent fuel, it is necessary to better understand the by-products as well as to think about economically viable recycling processes. We performed a systematic work on spent fuel stemming from the methanolysis of $NaBH_4$. The reaction was performed at the scale of few grams, unlike what is generally reported in the literature, in order to be closer to the technological application. In addition, the reaction was proceeded at different $NaBH_4/CH_3OH$ ratios to check the nature of the spent fuel depending on the amount of CH_3OH and to find the suitable conditions for implementation. Our results have shown the formation of $NaB(OCH_3)_4$ only for the ratio 4, which corresponds to the stoichiometric conditions and is the optimal one for a conversion of 100% of $NaBH_4$ with attractive H_2 generation rates (331 mL(H_2) min^{-1}). Otherwise, the methanolysis products obtained for the other ratios, namely 2, 8, 16 and 32, were recovered to be analyzed and identified. In a second part of the work, we analyzed the hydrolytic evolution of $NaB(OCH_3)_4$ at ambient conditions. It was found to evolve into 4 equivalents of CH_3OH, for which the close is thus closed, and into $NaB(OH)_4$. The latter product was separated and used to highlight the experimental conditions of its transformation into $NaBO_2$. In that respect, the appropriate conditions to transform $NaB(OCH_3)_4$ into $NaBO_2$ while recovering CH_3OH have been defined and are discussed in the form of a triangle recycling scheme. This is reported herein.

2. Experimental procedure

Sodium borohydride ($NaBH_4$; ≥98% purity Merck) and anhydrous methanol (CH_3OH; ≥99.9% Sigma Aldrich) were used as received. They were stored under inert atmosphere.

Methanolysis by-products were prepared as follows. $NaBH_4$ (3 g) was transferred in a three-neck flask (100 mL). Hydrogen evolution (Eq. 2) was started by adding a volume of methanol. The amount of the alcohol was varied such as x = 2, 4, 8, 16, 32, where x is the mole number of CH_3OH per mole of $NaBH_4$. In other words, the reaction was stoichiometric for x = 4 (Eq. 2); we performed one experiment at sub-stoichiometry (x = 2), and three other ones at over-stoichiometry (x = 8, 16, 32). The reaction temperature was set at 20 ± 2 °C. The three-neck flask was connected to an inverted burette (to measure the volume of the evolving H_2), via a cold trap used to condensate any vapor.

After the H_2 evolution experiment, the methanolysis spent fuel was recovered. A white solid was obtained for x = 2, 4 and 8. For x = 16, a white viscous liquid was found to form, and the excess of CH_3OH was removed as follows. The liquid was hold at room temperature (under a hood) for 72 h, leading to the formation of white solid powder. For $x = 32$, a colorless liquid was obtained. After extraction of CH_3OH in excess in a similar way, a white solid powder was recovered. The powders were put under vacuum at 40 °C before they were stored in a desiccator. Their morphology was scrutinized by scanning electron microscope (SEM, Zeiss EVO® LS 10).

The crystal structure of the white solid powders was analyzed by powder X-ray diffraction (XRD; Philips Panalytical X'Pert-Pro, CuKα). Pattern matching was performed using the database available proposed by the PANalytical X'Pert HighScore Plus (PDF-4 2018 RDB) software. The molecular structure was investigated by Fourier transform infrared spectroscopy (FTIR, ATR equipped Perkin Elmer Spectrum One, 4 cm^{-1}). The samples were analyzed by ^{11}B nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCE-300; probe head BBO10, 96.29 MHz, D_2O or CD_3CN in a capillary tube). Anhydrous N,N-dimethylformamide ($HCON(CH_3)_2$, Merck) was used to dissolve the solids. Some of the samples were further analyzed by Raman spectroscopy (Horiba Jobin Yvon LabRAM 1B; laser Ar/Kr 100 mW 647.1 nm).

Solid $NaB(OCH_3)_4$ (recovered for the experiment such as $x = 4$) were then put in water to investigate their possible evolution into e.g. $NaB(OH)_4$ by hydrolysis:

$$NaB(OCH_3)_4\,_{(aq)} + 4H_2O\,_{(l)} \rightarrow NaB(OH)_4\,_{(aq)} + 4CH_3OH\,_{(l)} \qquad (3)$$

Typically, $NaB(OCH_3)_4$ (2.46 g) and H_2O (1.25 g) were loaded in a glass batch reactor. The reaction mixture was heated at 80 ± 2 °C, under stirring (500 rpm), and for 90 min. Upon hydrolysis, the slurry was isolated and dried at 60 °C under vacuum atmosphere for 4 h. The as-obtained white solid was analyzed by XRD. Its thermal stability was analyzed by thermogravimetric (TG) analysis and differential thermal (DT) analysis (SII Nanotechnology – SII6000 Exstar TG/DTA 6300; aluminum crucible; temperature range of 50-700°C; heating rate of 10°C min^{-1}) under either oxidative (O_2) or inert (N_2) atmosphere. These TG and DT analyses allowed us choosing the temperatures 300 and 500 °C for calcination of the hydrolysis white solids; alumina high temperature crucibles were used. The as-calcined solids were analyzed by XRD. The formation of $NaBO_2$ was actually targeted:

$$NaB(OH)_{4\ (s)} \rightarrow NaBO_{2\ (s)} + 2H_2O_{\ (g)} \tag{4}$$

Based on Eq. 3, CH_3OH was predicted to form. It was identified by analyzing the slurry using gas chromatography (Perkin Elmer Clarus 580 GC apparatus with split injector and FID detector; 30 m column ID BPX5 with i.d. and film thickness of 0.25 mm and 0.25 µm respectively). The oven temperature program was as follows: initial temperature of 40 °C; heating rate of 15 °C min^{-1} until 70°C; 3 min at 70 °C; heating rate of 45 °C min^{-1} until 250 °C; 5 min at 250 °C. The injector and detector temperatures were, respectively, 100 and 300 °C. The flow rate of the carrier gas (H_2) was set at 0.5 mL min^{-1}.

3. Result and Discussion

3.1. Towards sodium tetramethoxyborate $NaB(OCH_3)_4$

At sub-stoichiometric and stoichiometric conditions, i.e. for x = 2 and x = 4 (Eq. 2), a solid formed by methanolysis of $NaBH_4$. In the former case, the presence of some unreacted $NaBH_4$ is likely. A repeated experiment where the volume of H_2 was collected showed a partial conversion of $NaBH_4$, calculated to be as low as about 40% (Figure S1). This is also consistent with the NMR, XRD and FTIR results reported hereafter. In the case of x = 4, all of the $NaBH_4$ are ideally supposed to react with 4 equiv CH_3OH to form $NaB(OCH_3)_4$. This was verified by measuring the volume of the generated H_2 (Figure S1); the H_2 generation rate was calculated (for a conversion ≤ 50%) to be 331 mL(H_2) min^{-1}. A solid was also recovered upon the completion of the reaction involving x = 8. The three solids were observed by SEM (Figures S2 to S4). They consist of an irregularly-shaped matrix. The surface of the solids obtained for x = 2 is rougher, likely because of the presence of some unreacted $NaBH_4$. The surface of the solids obtained for x = 4 and x = 8 are smoother and comparable, and they may indicate similar products. A white viscous liquid was obtained for x = 16, and for the higher ratio, x = 32, a colorless liquid was recovered. Actually, at over-stoichiometric conditions, the excess of methanol, that is, the fraction that did not react with $NaBH_4$, acts as solvent. This excess of methanol was then extracted and white solids were recovered. By SEM (Figures S5 and S6), smaller structures (about 400-600 nm) were observed. They are irregularly-shaped and agglomerated. The smaller size may be a result of the solvent extraction and the related crystallization of the methanolysis product.

The methanolysis solid by-products were first considered for analysis by ^{11}B NMR spectroscopy. D_2O as deuterated solvent was found to be inappropriate because of e.g. bubbling of the solid obtained for $x = 2$. Note that this confirmed the presence of some unreacted $NaBH_4$ (quintet at -39.2 ppm) upon hydrolysis in sub-stoichiometric conditions. N,N-Dimethylformamide is a good solvent for $NaBH_4$, and the borates are also slightly soluble in it. It was therefore used to dissolve the methanolysis solid by-products. The ^{11}B NMR analyses were performed using CD_3CN as deuterated solvent (Figure 1). The presence of some unreacted $NaBH_4$ for the reaction at $x = 2$ (i.e. sub-stoichiometry) is confirmed. Borates ($\delta = 3$ ppm) formed when methanolysis was performed in stoichiometric and over-stoichiometric conditions (total conversion of $NaBH_4$). According to Huynh et al. [51], the signal may be ascribed to methanolated methoxyborate like $[Na_2(B(OCH_3)_4)_2(CH_3OH)_2]_4$.

The solids were analyzed by XRD (Figure 2). The presence of unreacted $NaBH_4$ (ref. 00-009-0386) for the reaction performed at $x = 2$ is confirmed. No trace of a crystalline phase of $NaB(OCH_3)_4$ was detected, suggesting the formation of an amorphous by-product. There are few peaks, of very low intensity, that have not been identified and indexed. Pattern matching has not given any relevant result. They are likely to belong to one or more unidentified intermediate species or to an unidentified product; compounds with one to four B–O bonds (for example $NaBH_3(OCH_3)$ and $NaBH_2(OCH_3)_2$), including oligomeric borates made of 2 to 5 boron atoms, are possible species. The pattern of the by-product obtained at $x = 4$ well matches that of the referenced structure (ref. 00-012-0863) belonging to $NaB(OCH_3)_4$. This is in agreement with the results reported by Fernandes et al. [21]. The XRD patterns of the other by-products (i.e. obtained at $x = 8$, 16 and 32) are different. There are similar to the pattern reported by Huynh et al. [51] found for $[Na_2(B(OCH_3)_4)_2(CH_3OH)_2]_4$ (tetragonal, s.g. I_4), synthesized by reacting $NaBH_4$ in an excess of methanol (anhydrous). To sum up our observations, a minimum of 4 equiv CH_3OH is required for methanolysis completion and the reaction results in the formation of $NaB(OCH_3)_4$. In an excess of CH_3OH, the by-product is a complex of both $[B(OCH_3)_4]^-$ and CH_3OH, like the species $[Na_2(B(OCH_3)_4)_2(CH_3OH)_2]_4$.

The solids were analyzed by FTIR (Figure 3). The observed bands have been indexed with database available in the literature [52–54]. The spectrum of the solid obtained at $x = 2$ shows well-defined sharp bands at e.g. 2500-2100 cm^{-1} (B–H stretching), ascribed to unreacted $NaBH_4$ [55]. There are also bands at wavenumbers typical of O–H stretching (3600-3000 cm^{-1}) and B–O stretching (1000-750 cm^{-1}) modes, indicating some conversion of $NaBH_4$ into a borate intermediate (amorphous to X-ray). The spectrum of the solid obtained at $x = 4$ is comparable to the fingerprint of $NaB(OCH_3)_4$ [56]. All of the bands can be ascribed to B–O stretching/deformation, C–O stretching and C–H stretching/deformation modes. The spectra of the solids obtained at $x = 8$, 16 and 32 (Figures 3, and S7 to S9) look like that of a methoxyborate by-product like $NaB(OCH_3)_4$. The O–H deformation mode at around 1600 cm^{-1} (as well as the bands due to O–H stretching) indicates the presence of CH_3OH [51], in agreement with the conclusions made from the analysis of the XRD patterns.

The sample obtained at $x = 4$, i.e. $NaB(OCH_3)_4$, was selected for further analyses. Its thermal stability was analyzed under oxidative and inert atmospheres (Figure S10). A comparable behavior was found. The sample decomposes starting from 30 °C. It undergoes four successive weight losses up to 700 °C, with a main one between 60 and 300 °C. The total weight loss is slightly higher than 45 wt%. In other words, $NaB(OCH_3)_4$ is not thermally stable.

3.2. Towards sodium metaborate $NaBO_2$

$NaB(OCH_3)_4$ (i.e. the solid obtained at $x = 4$) readily reacts with water. Total conversion was found to occur for a $H_2O/NaB(OCH_3)_4$ molar ratio $n \geq 4$. The formation of CH_3OH was verified by GC–FID (Figure S11). The hydrolytic boron product was heated at 60°C, under vacuum, to remove water. A white solid was recovered.

The hydrolysis solid was analyzed by XRD (Figure 4). Monoclinic $NaB(OH)_4$ (ref. 04-011-2875) was found to be the main crystallographic phase. The presence of another hydrated borate (e.g. $Na_2B_4O_7{\cdot}5H_2O$, ref. 00-007-0277) is likely. The FTIR spectrum (Figure 5) is consistent with the formation of such hydrated borates [57–59]. The ^{11}B NMR spectrum (Figure 6) of the solid dissolved in deuterated water shows two signals at positive chemical shifts suggesting two borate species [60], which might be due to equilibrium between the *B*O_3 (due to e.g. H_3BO_3) and *B*O_4 environments (i.e. $B(OH)_4^-$) [61].

The hydrolysis solid was heated, up to 300°C. The XRD pattern (Figure 4) indicates a lightly crystalline solid. The few peaks of small intensity were found to indicate the formation of $NaBO_2$ (ref. 00-037-0115). However, the presence of crystalline $Na_2B_4O_{10}$ (ref. 00-022-1347) cannot be discarded as suggested by the pattern matching. The FTIR spectrum (Figure 5) shows an evolution towards dehydration, which is featured by O–H bands with decreased intensity. The ^{11}B NMR spectrum (Figure 6) is comparable to that of the sample heated at 60 °C.

A last heat-treatment was performed at 500°C. Only the rhombohedral $NaBO_2$ phase (ref. 01-076-0750) was identified (Figure 4), consistently with ref. [62]. $NaB(OH)_4$ is known to lose structural water from about 150 °C [57], resulting in the formation of $NaBO_2$. Temperatures of $NaBO_2$ formation of 300 and 400 °C were reported [57,62]. This is quite consistent with our XRD observations. The FTIR spectrum is also consistent with this observation (Figure 5). The ^{11}B NMR spectrum (Figure 6) of $NaBO_2$ dissolved in deuterated water shows one signal at 4.5 ppm, ascribed to a *B*O_4 environments such as for $B(OD)_4^-$.

The solids heated at 60, 300 and 500 °C were analyzed by Raman spectroscopy (Figure 7). The first two solids show bands due to symmetric (700-950 cm^{-1}) and asymmetric (350-1100 cm^{-1}) stretching of B–O bonds. The bands at about 750 cm^{-1} may be attributed to $B(OH)_3$ species, and that at 942 cm^{-1} to $B(OH)_4^-$ [63]. The band peaking at 1076 cm^{-1}, which is the only one observed for the sample heated at 500 °C, is assigned to $NaBO_2$. These results confirm the XRD, FTIR, and NMR data discussed above, that is, the complete transformation of $NaB(OCH_3)_4$ into $NaBO_2$ via $NaB(OH)_4$.

3.3. Towards a neutral cycle with $NaBH_4$

What emerges from the patterns and spectra reported above is that the hydrogen cycle with $NaBH_4$ can be neutral. In other words, the methanolysis by-product could be recycled through a stepwise process to form $NaBH_4$ back. This is illustrated in Figure 8.

Methanolysis of $NaBH_4$ is an efficient process for H_2 release, resulting in formation of $NaB(OCH_3)_4$ as main by-product when the reaction is realized in stoichiometric conditions (Eq. 2). Typically, 1 equiv $NaBH_4$ reacts with 4 equiv CH_3OH and transforms into 1 equiv $NaB(OCH_3)_4$ while liberating 4 equiv H_2. Such a reaction is very interesting for two reasons. First, all of the atoms are effectively used resulting in an "atom economy" in good agreement with one of the green chemistry principles. Second, the aforementioned stoichiometry implies an effective gravimetric hydrogen capacity of 4.8 wt% for the couple $NaBH_4$-CH_3OH, and this is a clearly promising capacity. In addition, the H_2 generation rate was calculated to be 331 $mL(H_2)\ min^{-1}$ (without catalyst), which is one of the best performance for an uncatalyzed solvolysis reaction involving a hydride and a protonic solvent; some examples are shown in Table 1 [21,22,30,64–74].

The as-formed $NaB(OCH_3)_4$ can be readily hydrolyzed into $NaB(OH)_4$, and 4 equiv CH_3OH are generated. The cycle is then neutral in CH_3OH. With respect to $NaB(OH)_4$, it is easily converted, under heating up to 500 °C in our conditions, into $NaBO_2$ while releasing 2 equiv H_2O. The other 2 equiv H_2O are generated during reduction of $NaBO_2$ into $NaBH_4$. Hence, the cycle is neutral in H_2O.

As mentioned just above, $NaBO_2$ has to be reduced into $NaBH_4$. This may be done by using 4 equiv H_2 or a reducing agent carrying H^- such as MgH_2 [18,75,76]. Another original procedure, recently reported [77], could be to make react $NaBO_2$ with CO_2 in aqueous solution, the as-forming $Na_2B_4O_7{\cdot}10H_2O$ and Na_2CO_3 being afterwards ball-milled with Mg under ambient conditions to form $NaBH_4$ in a yield close to 80 %. In any case, the cycle is then neutral in H_2. It is worth mentioning that regeneration of $NaBH_4$ starting from $NaBO_2$ has been demonstrated, but the processes developed so far need to be further improved to make one/few of them cost-effective [78]. Another challenge, with these processes, will be to develop them while the cycle of each reactant and product is neutral. Otherwise, the scheme of the recycling process could be considered differently for the third part, namely transformation of $NaB(OH)_4$ into $NaBH_4$ via $NaBO_2$. In the recent years, Ouyang and co-workers reported few regeneration routes using $NaBO_2{\cdot}xH_2O$ (with x = 2 or 4) as starting borate. Ball-milling $NaBO_2{\cdot}xH_2O$ with MgH_2 at room temperature and atmospheric pressure was found to lead to $NaBH_4$ back with a yield as high as 90% [79]. In another work, Mg was used instead of MgH_2 and $NaBH_4$ was regenerated with yields of 64-68% [80]. The formation of $NaBH_4$ was explained by the involvement of reaction intermediates like MgH_2 and $NaBH_3(OH)$.

4. Conclusion

In the present work, we have proposed a neutral cycle for the hydrogen storage system based on the couple $NaBH_4$-$4CH_3OH$. Upon methanolysis, this couple releases 4 equiv H_2 in such a way that the effective gravimetric hydrogen capacity is as high as 4.8 wt%, which is quite attractive from an implementation point of view. It is worth mentioning the H_2 generation rate that has been achieved without any catalyst, namely, 331 $mL(H_2)\ min^{-1}$. The methanolysis by-product is $NaB(OCH_3)_4$. By using 4 equiv H_2O, $NaB(OCH_3)_4$ can be readily hydrolyzed to $NaB(OH)_4$. The process generates 4 equiv CH_3OH, making the cycle neutral in CH_3OH. Then, $NaB(OH)_4$ can be converted, under heating up to 500 °C, into $NaBO_2$ which is the most common starting material for regenerating $NaBH_4$. In a further step, $NaBO_2$ could be reduced into $NaBH_4$ while using 4 equiv H_2 or e.g. 4 equiv MgH_2. The cycle would be neutral in H_2. Each of the $NaB(OH)_4$ heating and $NaBO_2$ reduction processes generates 2 equiv H_2O, making the cycle neutral in H_2O also. The cycle summarized above is thus also neutral in the B element; indeed the starting $NaBH_4$ is targeted to be regenerated by recovering all of the formed $NaB(OH)_4$ via its total conversion into $NaB(OH)_4$ and then $NaBO_2$. In that respect, all of the atoms involved in this cycle are used and re-used, resulting in an “atom economy” in good agreement with one of the green chemistry principles. In conclusion, the strategy we propose will help us in building a closed pathway from $NaBH_4$ to its spent fuel without disturbing the environmental balance.

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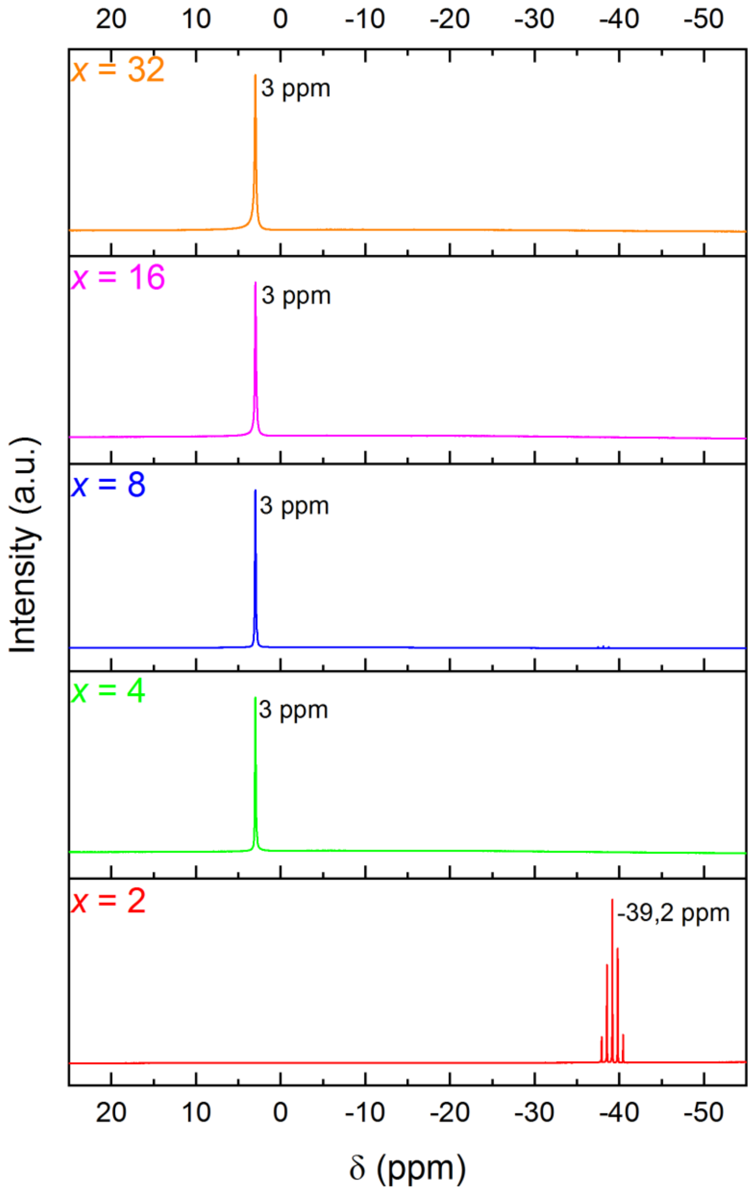

Figure 1. ^{11}B NMR spectra of the solids recovered after methanolysis of $NaBH_4$ such as x = 2, 4, 8, 16 and 32. The solids were dissolved in N,N-dimethylformamide (with CD_3CN).

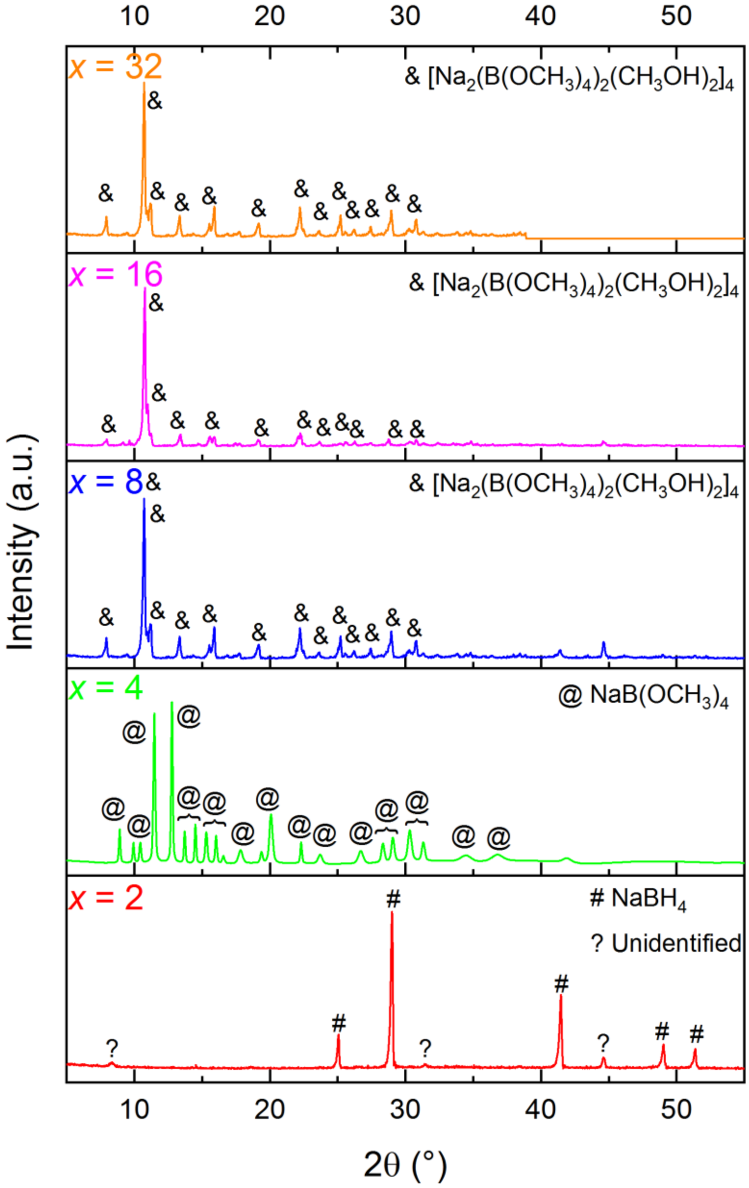

Figure 2. XRD patterns of the solids recovered after methanolysis of $NaBH_4$ such as *x* = 2, 4, 8, 16 and 32. The peaks have been indexed as shown. The structures indicated by # and @ were found to match with referenced patterns (respectively: $NaBH_4$ ref. 00-009-0386, and $NaB(OCH_3)_4$ ref. 00-012-0863). The structure indicated by & corresponds to that of $[Na_2(B(OCH_3)_4)_2(CH_3OH)_2]_4$ reported elsewhere [51]. There are also few unidentified peaks (as shown by the symbol ?).

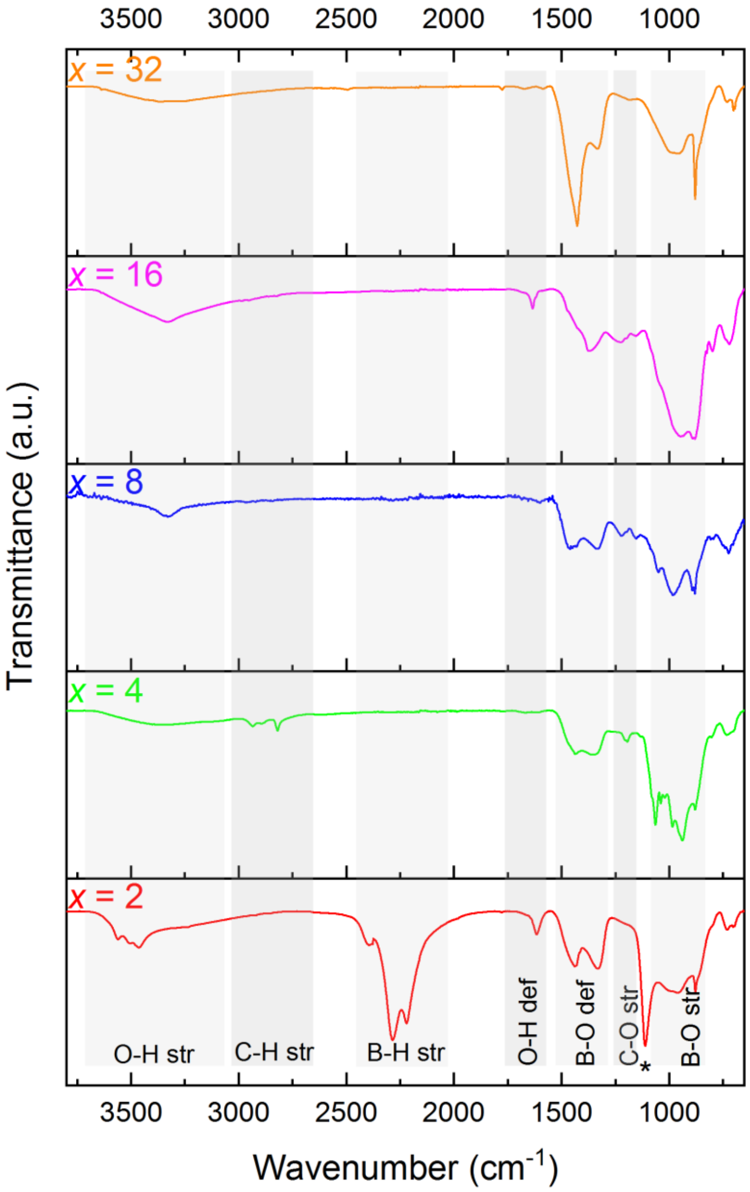

Figure 3. FTIR spectra of the solids recovered after methanolysis of NaBH$_4$ such as *x* = 2, 4, 8, 16 and 32. The bands have assigned. The symbol * is attributed to the B–H bending mode. The spectra for *x* = 8, 16 and 32 are also shown in Figures S7 to S9.

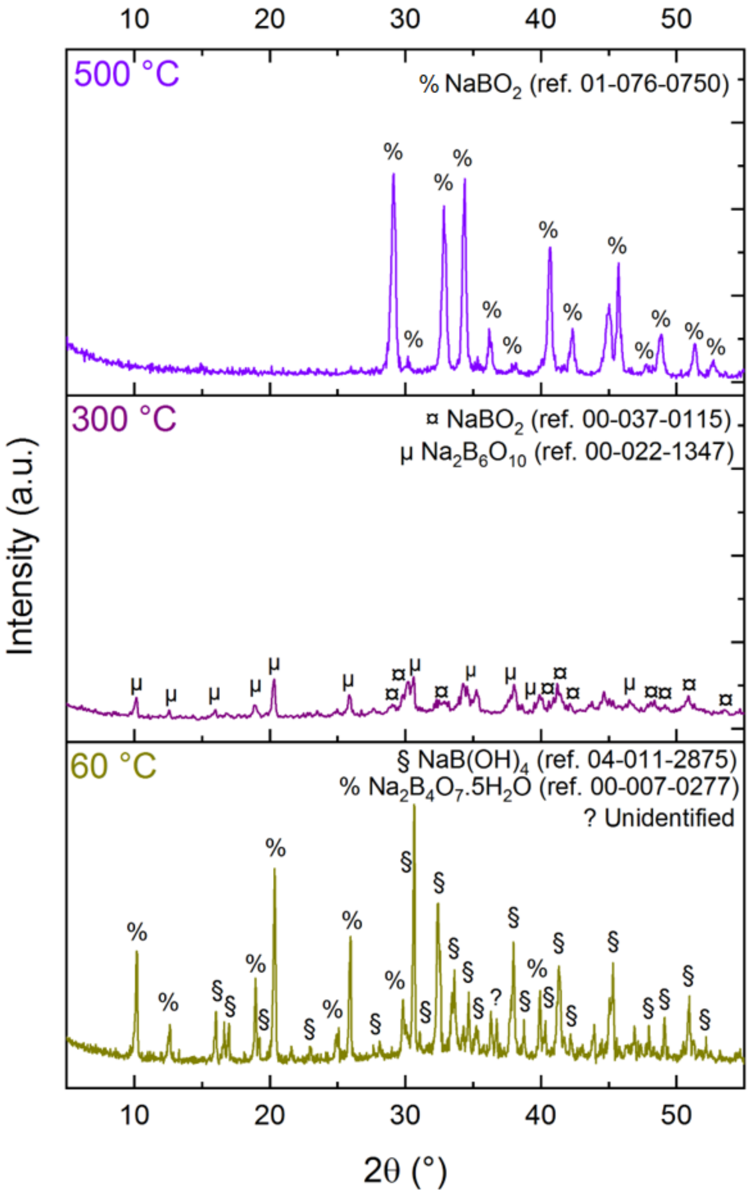

Figure 4. XRD patterns of the hydrolysis product of NaB(OCH$_3$)$_4$ (i.e. x = 4) heated at 60, 300, and 500 °C. The peaks have been assigned, when possible, as shown in the figure. There are few peaks (shown by the symbol ?) that have not been assigned because of unsuccessful pattern matching.

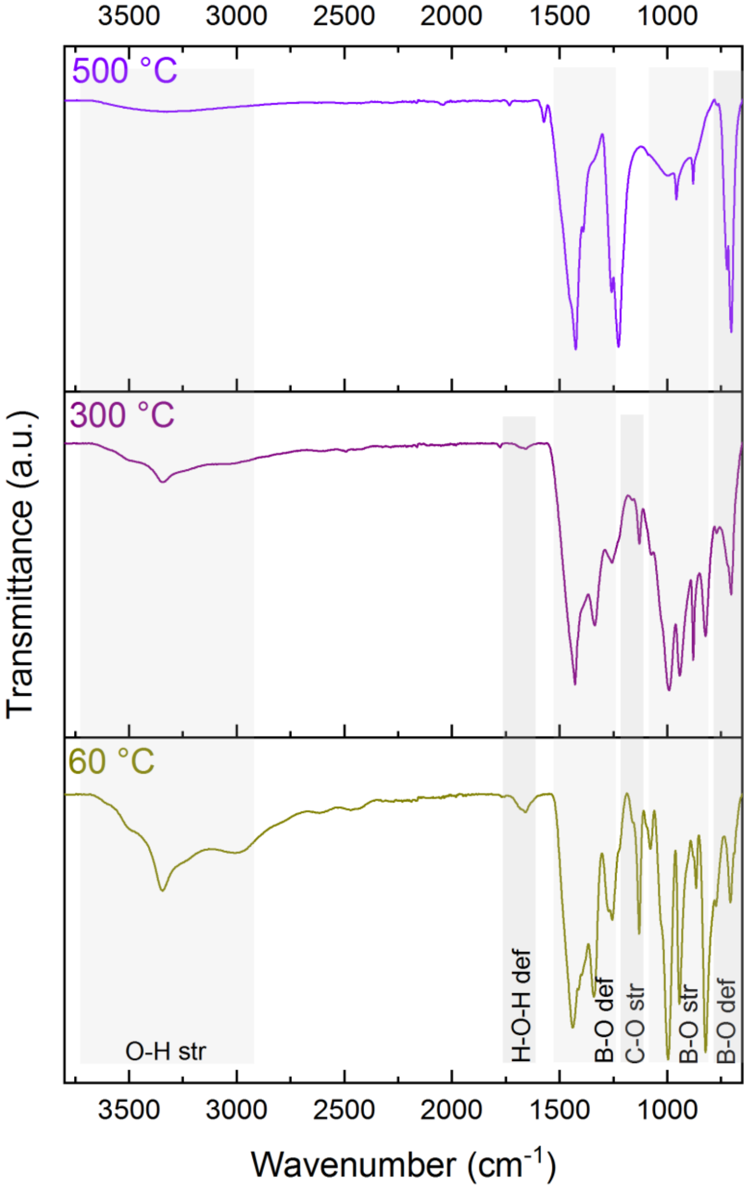

Figure 5. FTIR spectra of the hydrolysis product of $NaB(OCH_3)_4$ (i.e. $x = 4$) heated at 60, 300, and 500 °C. The bands have assigned.

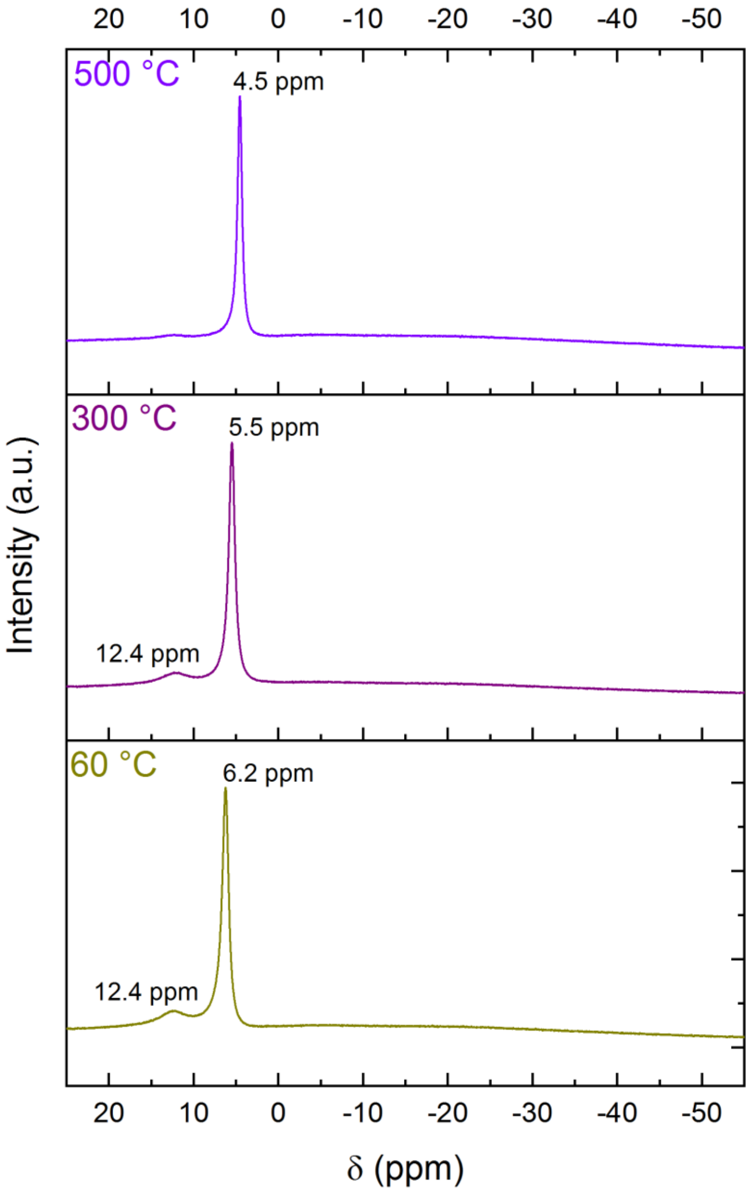

Figure 6. ^{11}B NMR spectra of the hydrolysis product of $NaB(OCH_3)_4$ (i.e. $x = 4$) heated at 60, 300, and 500 °C. They were dissolved in deuterated water for analysis.

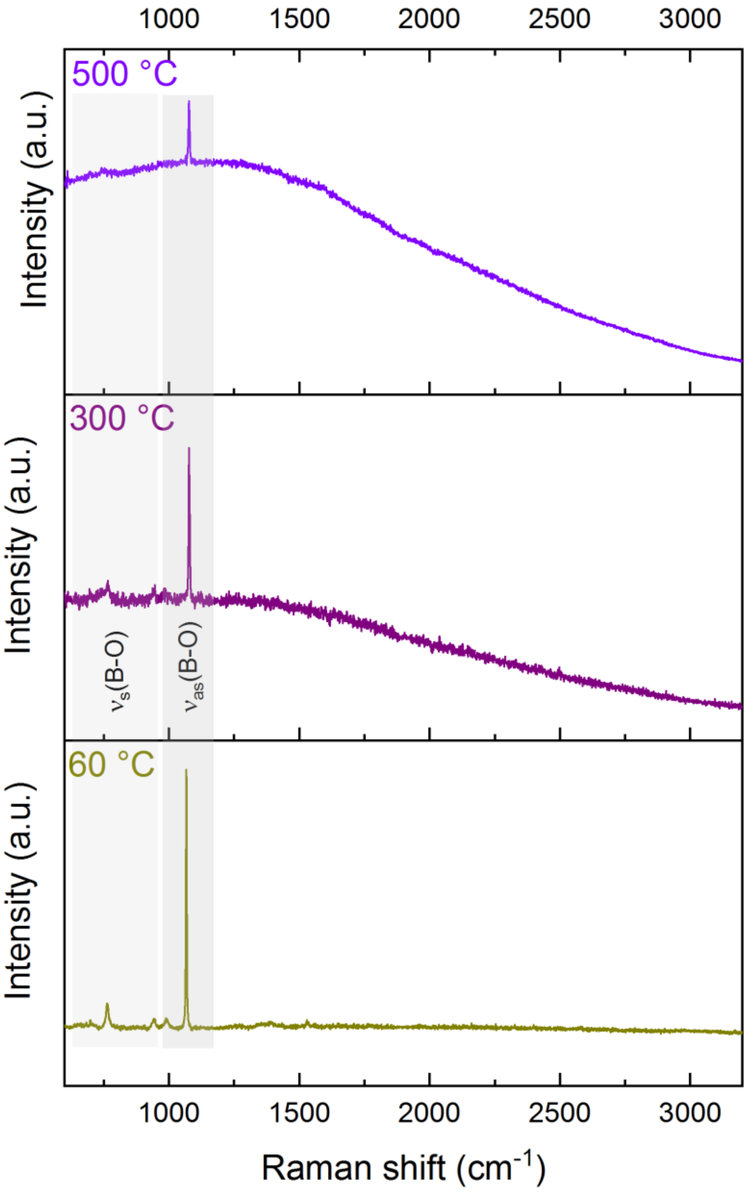

Figure 7. Raman spectra of the hydrolysis product of $NaB(OCH_3)_4$ (i.e. $x = 4$) heated at 60, 300, and 500 °C. The bands have assigned.

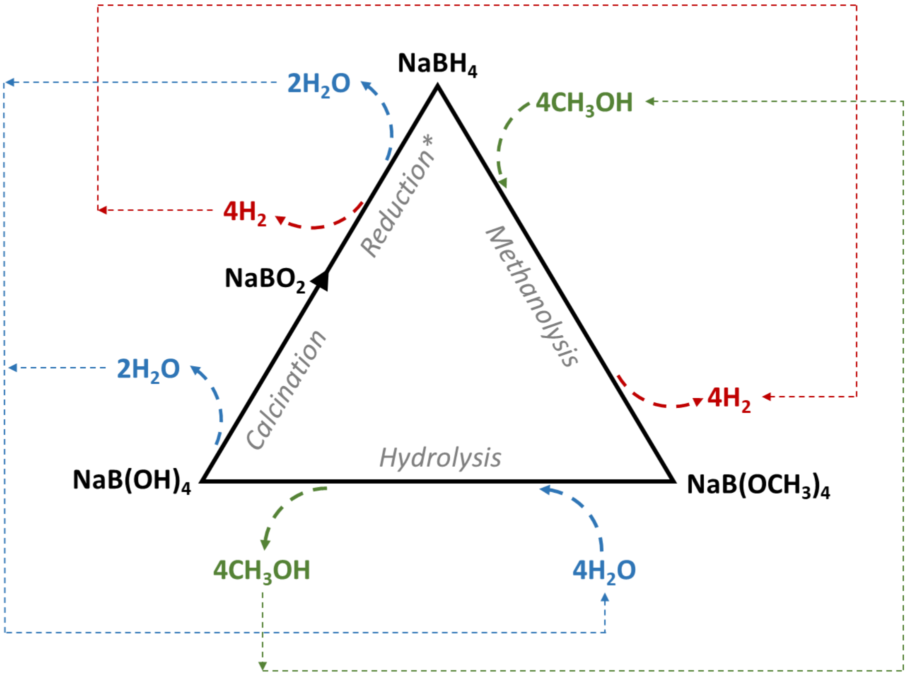

Figure 8. Triangular scheme of the recycling process of the spent fuel stemming from methanolysis of $NaBH_4$ and subsequent hydrolysis of $NaB(OCH_3)_4$. The reduction process transforming $NaBO_2$ to $NaBH_4$ requires a reducing agent such H_2 or MgH_2; here the scheme has been illustrated with H_2.

Table 1. Comparison of the H_2 generation rates (HGR) for a series of hydride-protonic solvent couples (spontaneous solvolysis reactions without the presence of a catalyst or of an acid).

Hydride	**Protonic solvent**	**T (°C)**	**HGR (mL H_2 min^{-1})**	**Ref.**
$LiBH_4$	H_2O	23	2	[64]
$NaBH_4$	H_2O	20-30	<2	[22,65–67]
$NaBH_4$	CH_3OH	5	37	[30]
$NaBH_4$	CH_3OH	20	331	This work
$NaBH_4$	CH_3OH	45	480	[21]
$NaBH_4$	CH_3CH_2OH	25	<0.1	[68]
KBH_4	H_2O	30	55	[69]
KBH_4	CH_3CH_2OH	30	60	[69]
MgH_2	H_2O	25	20	[70]
CaH_2	H_2O	20	3	[71]
NH_3BH_3	H_2O	20	<0.1	[64]
NH_3BH_3	CH_3OH	20	<0.1	[72]
$LiNH_2BH_3$	H_2O	20	546	[73]
$NaNH_2BH_3$	H_2O	20	381	[74]