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CO$_2$-promoted hydrolysis of KBH$_4$ for efficient hydrogen co-generation

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ARTICLE INFO

ABSTRACT

Hydrolysis of metal borohydrides in the presence of CO$_2$ has not been studied so far, although carbon dioxide contained in air is known to accelerate hydrogen generation. KBH$_4$ hydrolysis promoted by CO$_2$ gas put through an aqueous solution was studied by time-resolved ATR-FTIR spectroscopy, showing a transformation of BH$_4^-$ into B$_4$O$_5$(OH)$_4^{2-}$, and a drastically accelerated hydrogen production which can be completed within minutes. This process can be used to produce hydrogen on-board from exhaust gases (CO$_2$ and H$_2$O). We found a new intermediate, K$_9$[B$_4$O$_5$(OH)$_4$]$_3$(CO$_3$)(BH$_4$)·7H$_2$O, forming upon hydrolysis on air via a slow adsorption of the atmospheric CO$_2$. The same intermediate can be crystallized from partly hydrolyzed solutions of KBH$_4$ + CO$_2$, but not from the fully reacted sample saturated with CO$_2$. This phase was studied by single-crystal and powder X-ray diffraction, DSC, TGA, Raman, IR and elemental analysis, all data are fully consistent with the presence of the three different anions and of the crystallized water molecules. Its crystal structure is hexagonal, space group P-62c, with lattice parameters $a = 11.2551(4)$, $c = 17.1508(8)$ Å. Formation of the intermediate produces 16 mol of H$_2$ per mole of adsorbed CO$_2$ and thus is very efficient both gravimetrically and volumetrically. It allows also for an elimination of carbon dioxide from exhaust gases.

Introduction

Running out of fossil fuels, humankind is facing the problem of new sustainable energy carriers. Hydrogen can be the cleanest energy carrier, currently used in mobile applications via proton-exchange membrane fuel cells (PEMFCs) [1]. However, there are challenges regarding its storage [2]. In particular, the efficient storage of pressurized and liquefied hydrogen has technical problems of high pressures (350–700 bar) and cryogenic temperatures (−253 °C),

respectively [2]. That is why during recent years the attention was paid to the solid state hydrogen storage in the form of complex metal hydrides [3–5]. Hydrogen can be released from them either by thermolysis or via hydrolysis. Mobile applications require low decomposition temperatures, suitable for PEMFC (60–120 °C) [6], and high hydrogen content. For the year 2017 the system targets set by the U.S. Department of energy are 5.5 wt. % of hydrogen and gravimetric density of 40 g/l [7]. These and other limitations (hydrogen purity, reversibility etc.) decrease the number of potentially applicable systems

giving the priority to light complex hydrides, like borohydrides [8,9]. Several metal borohydrides $M(BH_4)_n$ ($n = 1$, $M = Li^+$, Na^+ [10,11]; $n = 2$, $M = Be^{2+}$, Mg^{2+}, Ca^{2+} [12–14] and $n = 3$, $M = Al^{3+}$, Ti^{3+} [15,16]) have been studied as potential hydrogen storage media. Their high desorption temperatures of about 470 °C for $LiBH_4$, and 290–500 °C for $Mg(BH_4)_2$ and toxicity of $Al(BH_4)_3$ with $Be(BH_4)_2$ make them unpractical for thermal hydrogen desorption. Alkali metal borohydrides, MBH_4, were also intensively studied with respect to hydrogen release by hydrolysis, where hydrogen can be generated in accordance with the following simplified reaction [17]:

$$MBH_4 + (2 + n)H_2O \rightarrow MBO_2 \cdot nH_2O + 4H_2 \qquad (1)$$
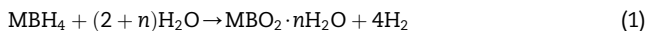
Depending on hydrolysis conditions, such as temperature, $LiBH_4$ gives different products [18,19]: $LiBO_2$, $LiBO_2 \cdot H_2O$, $LiBO_2 \cdot 2H_2O$, the latter also known as $Li[B(OH)_4]$ [20]. $NaBH_4$ attracted the biggest attention due to its higher stability and ease to handle as compared with $LiBH_4$ (the latter reacts vigorously with water at room temperature), and high hydrogen content of 10.6 wt. %, contrary to 7.4 wt. % in KBH_4 [21]. Aqueous solutions of $NaBH_4$ are usually chemically stabilized by rendering solutions basic and do not generate significant amounts of H_2 under ambient conditions [22]. However, $NaBH_4$ hydrolysis rate can be dramatically accelerated upon the addition of certain heterogeneous catalysts [23,24]. Among the conventional catalysts studied for the reaction, ruthenium-based catalysts were proposed to be most effective for promoting H_2 generation [25,26]. The hydrolysis of KBH_4 was also reported [27], showing the lowest hydrolysis rate without the use of catalysts.

Acid is known to accelerate hydrolysis of borohydrides [28]. However, the hydrolysis of metal borohydrides in the presence of CO_2 has not been studied so far, even though its influence on the hydrogen release rate from aqueous solution of $NaBH_4$ has been noticed already in 1962 [23]: the influence of CO_2 on $NaBH_4$ hydrolysis in open air was assigned to the lowering of the pH of the solution. Our work is dedicated to the hydrolysis of KBH_4 in open air, attempting to clarify the role of CO_2, as well as to the hydrolysis reaction promoted by CO_2 gas put through the reaction mixture. Such process is interesting due to its potential of producing hydrogen on-board, making use of the exhaust gases (CO_2 and H_2O) from hydrocarbon fuels. The co-generation of hydrogen may thus improve the energy density of the system, as well as allow for CO_2 sequestration.

We found that CO_2 boosts up the hydrolysis reaction rates, transforming in solution the borohydride ions, BH_4^-, into tetraborates, $B_4O_5(OH)_4^{2-}$. Analysis of solid residues reveals a new complex intermediate, $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4) \cdot 7H_2O$. This substance was studied by single-crystal and powder X-ray diffraction, DSC, TGA, Raman, IR spectroscopy and elemental analysis, all the results are consistent with the presence of three different anions and of the crystallized water molecules.

Experimental part

Hydrolysis reaction on open air. A ~190 g/l water solution of potassium borohydride (95% purity, Sigma Aldrich) was left at 4 °C in an open flask for approximately one year. The solution

was found completely dried and transparent needle-like hexagonal crystals were observed, see Fig. 1. Microscopy analysis revealed that the sample was almost single-phase, with only a small fraction of cubic crystals corresponding to the original KBH_4. The needle-like crystals, which formed the largest part of the solid phase, were hand-picked from the mixture for further characterization. They were found to be well soluble in water.

Single-crystal synchrotron X-ray diffraction. Synchrotron radiation with $\lambda = 0.69790$ Å and a MAR345 detector were used for the data collection (SNBL/ESRF) at room temperature. The structure was solved by direct methods and refined by a full matrix least-squares technique on F^2 using SHELXL97 program [29]. The experimental details for the two alternative compositions from structure analysis are presented in a Table 1. The further characterization by other methods (see below) suggested a $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4) \cdot 7H_2O$ composition of the complex with disordered BH_4^-, which gives slightly better R values compared to the initially assumed $K_9[B_4O_5(OH)_4]_3 \cdot BO_3 \cdot 8.2H_2O$ composition (left column in the Table 1).

Hydrolysis reaction promoted by CO_2. As both elementary and IR analyses indicate the crystals to contain the carbonate anion (see below), we attempted to repeat this synthesis under a CO_2 atmosphere. The same phase was obtained albeit by a much faster hydrolysis of KBH_4 under partial CO_2 pressure. 5 ml portions of 190 g/l aqueous solution of KBH_4 were exposed to CO_2 gas at room temperature. Hydrogen was readily desorbed from the solution on contact with CO_2, and the reaction was completed within minutes. Different portions of incompletely and completely hydrolyzed (saturated with CO_2) solutions were dried and the resulting powder was analyzed by X-ray powder diffraction. The completely hydrolyzed sample did not contain the $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4) \cdot 7H_2O$ phase, while it was the major crystalline phase in the incompletely hydrolyzed samples.

Addition of aqueous solutions of sodium hydrogen carbonate ($NaHCO_3$) to potassium borohydride leads to a vigorous hydrogen evolution, indicating that the hydrogen carbonate is

Fig. 1 – The optical microscopy image of a hexagonal crystal of $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4) \cdot 7H_2O$.

Table 1 – Experimental details of crystal structure analysis.		
Formula	Hypothetical composition $K_9[B_4O_5(OH)_4]_3BO_3 \cdot 8.2H_2O$	True composition $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4) \cdot 7H_2O$
Formula mass	1122.62	1124.26
T [K]	296 (2)	
λ [Å]	0.69790 (synchrotron)	
Space group	$P\text{-}62c$	
Z	2	
Cell parameters [Å]	$a = 7.8585$ (2)	
	$c = 15.7136$ (8)	
V [Å^3]	1881.54 (13)	
ρ_{calc} [g·cm^{-3}]	1.982	1.984
μ [mm^{-1}]	1.146	1.144
F(000)	1126	1132
θ range max [°]	29.87	
Reflections collected	11,935	
Independent reflections	1949 [$R_{int} = 0.0982$]	
Data/restraints/parameters	1949/0/106	1949/0/107
Goodness-of-fit	1.131	1.134
R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0411$, $wR_2 = 0.1165$	$R_1 = 0.0381$, $wR_2 = 0.1084$
R indices (all data)	$R_1 = 0.0419$, $wR_2 = 0.1169$	$R_1 = 0.0390$, $wR_2 = 0.1088$

the strong enough acid to promote the acid-catalyzed BH_4^- hydrolysis, yielding the carbonate anion and hydroxyborates.

X-ray powder diffraction. In line with the crystal structure model, the X-ray powder diffraction analysis of the separated and ground hexagonal crystals and of the mixture with cubic KBH$_4$ were made. The diffraction experiments were done with 0.5 mm glass capillaries, MAR345 image plate diffractometer with Mo Kα radiation. The received data images were azimuthally integrated by the program Fit2D [30], using LaB$_6$ calibrant, followed by a calculation intensity uncertainties. Phase analysis was done using Rietveld method with Fullprof Suite software [31].

Infrared and Raman spectroscopy was performed to verify the crystal structure model. The infrared spectra were recorded on Shimadzu Benelux FTIR-84005 spectrometer between 400 and 4000 cm^{-1} using pressed pellets of the sample powder with dried KBr. Raman spectroscopy analysis was done using a Raman Thermo Scientific with a 532 nm DXR laser between 200 and 3500 cm^{-1}.

Time-resolved online ATR–FTIR spectra were recorded on a ReactIR 15 spectrometer (Mettler-Toledo) equipped with a diamond probe with a resolution of 4 cm^{-1}. Spectra were collected continuously at 1 min intervals. CO$_2$ gas was put through a 190 g/l water solution of KBH$_4$ during the 4 h of the measurements. Changes of the spectra were recorded during the first 90 min.

Thermal analyses were done using TGA/SDTA 851 Mettler and DSC 821 Mettler in the temperature range 25–500 °C with a heating rate of 10 °C/min and under a 0.5 ml/min nitrogen flow to avoid oxidizing reactions.

Elemental analysis. The determination of carbon, hydrogen and nitrogen quantity was made using microanalysis at MEDAC Ltd (England).

Results and discussion

Crystal structure and phase analysis. The X-ray single crystal analysis of the hexagonal crystals allowed to establish a new crystal structure with a $P\text{-}62c$ space group shown on Fig. 2a. Although structure solution first suggested a composition of $K_9[B_4O_5(OH)_4]_3BO_3 \cdot 8.2H_2O$, containing two types of anions: tetraborate and orthoborate, with four independent co-crystallized water molecules, a slightly different picture was obtained by a combination of techniques. In particular, Raman analysis suggested the presence of carbonate anion, and IR as well as Raman analysis clearly revealed the presence of a borohydride group. This forced us to revise the structural assignment of the molecular entities, changing the orthoborate to a carbonate, and one of the poorly resolved water molecules to a borohydride group orientationally disordered around the −6 axis. The resulting formula is charge neutral, $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4) \cdot 7H_2O$, and the calculated content of carbon is 1.08 weight %, close to the measured value of 1.11%. The fit to the single-crystal diffraction data is furthermore slightly better than for the original model (compare the two columns in Table 1). The compound is thus stabilized by a very small amount of the atmospheric CO$_2$ that slowly reacted with the borohydride solution yielding CO_3^{2-} anions.

The X-ray powder diffraction pattern of the separated and ground crystals is shown in the bottom of Fig. 2b. It fits very well with that of the crystal structure model described above. According to the Rietveld refinement, the sample hydrolyzed on open air contains a $K_9[B_4O_5(OH)_4]_3(CO_3)$ (BH$_4$)·7H$_2$O intermediate as a major phase (bottom Fig. 2b) and traces of potassium tetraborate dihydrate $K_2[B_4O_5(OH)_4] \cdot 2H_2O$ [32]. The same intermediate was also observed after incomplete hydrolysis of KBH$_4$ under CO$_2$ (middle pattern in the Fig. 2b). Structure determination is difficult to perform due to the low resolution; however K$_2$CO$_3$, KHCO$_3$, as well as other known K–B–O–H compounds listed in the Pearson's crystal database crystal are not present in the mixture. It likely involves tetraborate and (hydrogeno)carbonate anions, since all the borohydride is hydrolyzed.

The new compound $K_9[B_4O_5(OH)_4]_3(CO_3)$ (BH$_4$)·7H$_2$O is a complex salt, containing isolated tetraborate $[B_4O_5(OH)_4]^{2-}$, tetrahydroborate BH_4^- and carbonate CO_3^{2-} anions, Fig. 2a. The
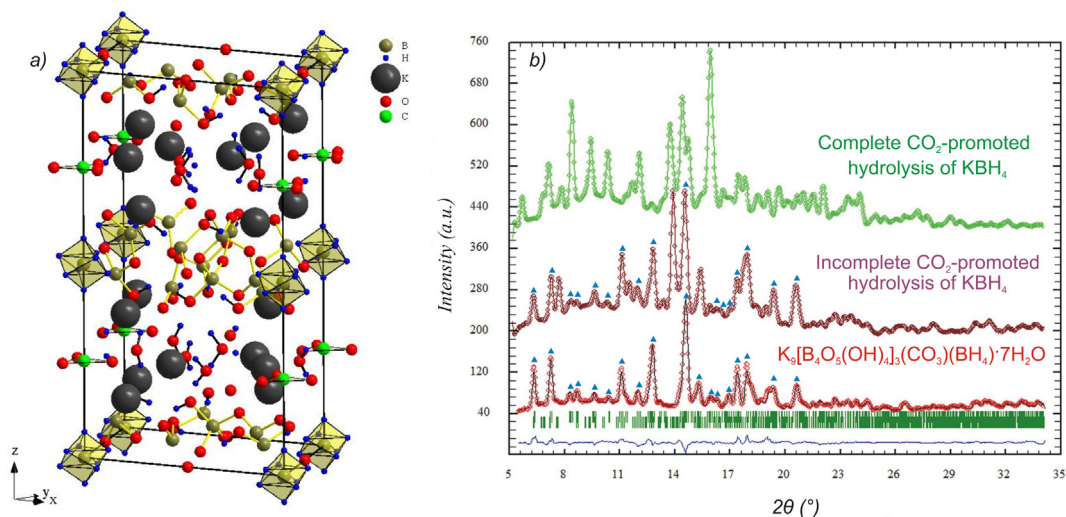
Fig. 2 — a) The crystal structure of $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot 7H_2O$, space group P-62c, cell parameters: $a = 11.2551(4)$, $c = 17.1508(8)$ Å; b) Powder diffraction patterns from the samples in KBH_4–H_2O–CO_2 system. The bottom pattern shows the Rietveld fit for the sample hydrolyzed on open air, the peaks of $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot 7H_2O$ are highlighted by the blue triangles. The peak positions of the minor phase, $K_2[B_4O_5(OH)_4]\cdot 2H_2O$, are marked by the second raw of green bars. The middle pattern from a partly reacted KBH_4–H_2O–CO_2 contains $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot 7H_2O$ as the major phase, and the top pattern shows no title phase in the fully hydrolyzed product. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tetraborate ion is common in alkali metal-B-O-H chemistry, present in borax [33] and in its potassium-based analogue $K_2[B_4O_5(OH)_4]\cdot 2H_2O$ [34]. The geometry of the tetraborate anion is not affected by the presence of carbonate and borohydride, as it is practically identical to the one in $K_2[B_4O_5(OH)_4]\cdot 2H_2O$. More complex polymeric anions contain fragments identical to tetraborate, as in the infinite 1D anion found in $K_4[B_{10}O_{15}(OH)_4]$ [35].

In the title structure, the CO_3^{2-} anion has a trigonal prismatic coordination by K atoms, capped on the square sides, increasing the coordination number to 9. These three extra contacts correspond to the shortest K … O distances of 2.725(3) Å and to the linear B–O … K arrangement. The structure contains two independent K cations, coordinated to 9 and 10 oxygen atoms from both anions and from four independent water molecules, designated Ow1-Ow3. The K … Ow distances range from 2.706(4) to 3.468(1) Å; the latter contact corresponds to the weakly bound Ow3 site, populated by 49(1)%. The hydrogen atoms of the hydroxyl groups and the localized H-atoms of water molecules Ow1 and Ow2 form short and well directed hydrogen bonds. Unlike in the hydrated $NaBH_4$ [36,37], there are no dihydrogen bonds formed between O-H$^{\delta+}$ and H$^{\delta-}$-B.

Infrared and Raman spectroscopy. The infrared and Raman spectra of the complex include typical anions' characteristic peaks (Fig. 3). Most of the Raman and IR shifts correspond to the tetraborate anion $[B_4O_5(OH)_4]^{2-}$ known from borax $Na_2[B_4O_5(OH)_4]\cdot 6H_2O$ and potassium tetraborate dyhydrate $K_2[B_4O_5(OH)_4]\cdot 2H_2O$: ($B_{tetr}$-O) 573, 826, 944, 1006; (B_{trig}-O) 1337 cm^{-1} [38—40]. The characteristic shifts of tetrahydroborate BH_4^- anion are close to those of KBH_4: 1226, 2188, 2267, 2290 and 2346 cm^{-1} [41,42]. The strong Raman

shift at 1050 cm^{-1} is typical for the carbonate anion (1040-1100 cm^{-1}) [27].

The evolution of the time-resolved ATR-FTIR spectra are shown on Fig. 4. During the bubbling of CO_2 through the water solution of KBH_4 the intensity of the BH_4^- band near 1100 cm^{-1} is going down to practically zero in 30—40 min, while the intensity of HCO_3^- (~1630 cm^{-1}) does not change significantly. The new peaks appear at 930-1000 and 1320-1420 cm^{-1}, and are identified as $[B_4O_5(OH)_4]^{2-}$ anion or similar derivatives forming during the hydrolysis [28,43]. In contrast to CO_2-promoted hydrolysis, the KBH_4 solution kept at room
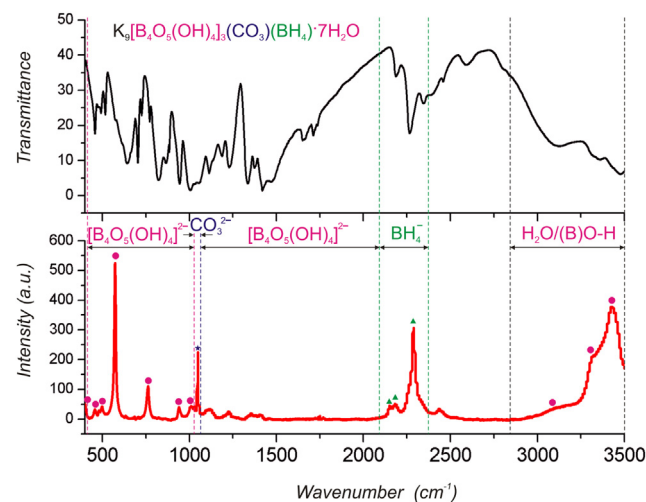

Fig. 3 — The infrared (top) and Raman (bottom) spectra of $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot 7H_2O$ at RT.
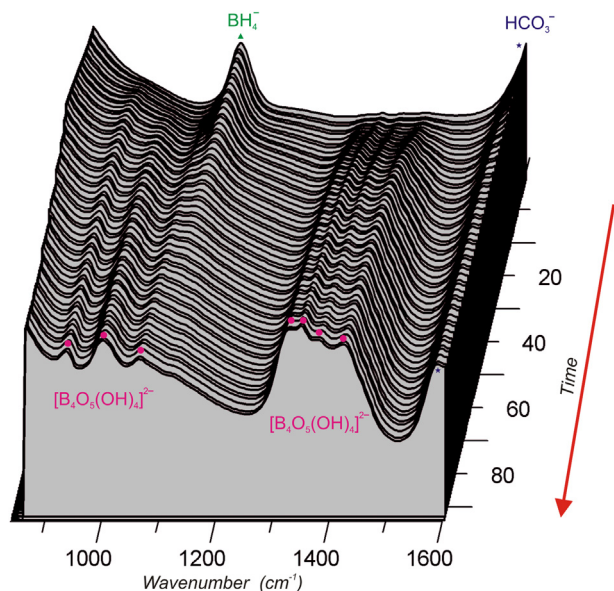
Fig. 4 – The time-resolved online ATR-FTIR (adsorption) plot.

temperature without access of CO_2 (closed even from air) retains BH_4^- bands after 24 and even 96 h, see Fig. S1.

Thermal analysis. The title compound steadily gives mass loss starting from room temperature up to 350 °C. From TGA and DSC curves in Fig. 5, we can discern only one big decomposition step, of about 19.3 wt. % of mass loss. The latter is higher than the expected loss of 7 water molecules (11.2 wt. %) and rather corresponds to the loss of $12H_2O$ (19.2 wt. %). The phenomena of releasing water both from crystalline and coordinated water (dehydration) as well as from complex anions containing OH (dehydroxylation) was known so far only for hydrated borates [44].

Conclusion

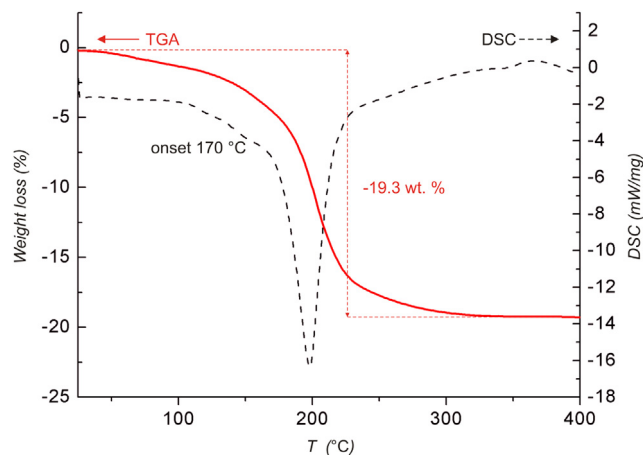Hydrolysis of potassium borohydride in the presence of CO_2 yields an intermediate, containing three anions: the

Fig. 5 – Thermal analysis of $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot7H_2O$ crystals.

borohydride is almost fully hydrolyzed into tetraborate, with 1/13 of unreacted BH_4^- co-crystallized in the solid, along with a minor amount of the carbonate. The same $K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot7H_2O$ solid is obtained by a slow reaction of atmospheric CO_2 with a water solution of KBH_4, as well as upon bubbling the gas through the solution. The latter drastically increases the rate of hydrogen production, and thus enables to hydrolyze KBH_4 on demand, by controlling the CO_2 gas flow. This prompts us to suggest borohydride hydrolysis promoted by CO_2 as a convenient system for the co-generation of hydrogen using spent fossil fuel gases ($CO_2 + H_2O$). The structural data and the studies in solution, in particular by time-resolved FTIR measurements allow us to suggest the following reaction for the formation of the intermediate:

$$13KBH_4 + 37H_2O + 3CO_2 \rightarrow K_9[B_4O_5(OH)_4]_3(CO_3)(BH_4)\cdot7H_2O$$
$$+ 2K_2CO_3 + 48H_2$$

$$(2)$$
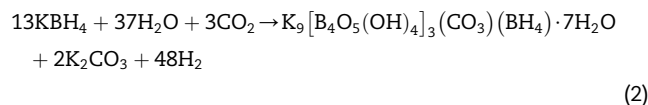
It produces 16 mol of H_2 per mole of the adsorbed CO_2 and thus is gravimetrically very efficient. This reaction shows gravimetric hydrogen release of 8.4 wt.%, higher than the total hydrogen content in KBH_4 (7.5 wt%). Thus it allows converting efficiently carbon dioxide into fuel, H_2. Regarding the yield of H_2 per KBH_4, it reaches 92.3% compared to the complete hydrolysis of all the BH_4 groups. Carbon dioxide in water solution is a cheap and mild acid which drastically accelerates the hydrolysis of borohydrides. In particular, the hybrid system with CO_2/H_2O exhaust gases used for hydrolysis of borohydrides can achieve two targets: the generation of hydrogen for PEMFCs as an additional source of energy and the capture of carbon dioxide.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2014.09.068.

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