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Revision of the $\text{NaBO}_2\text{-H}_2\text{O}$ phase diagram for optimized yield in the H_2 generation through NaBH_4 hydrolysis

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Abstract

The binary phase diagram $\text{NaBO}_2\text{-H}_2\text{O}$ at ambient pressure, which defines the different phase equilibria that could be formed between borates, end-products of NaBH_4 hydrolysis, has been reviewed. Five different solid borates phases have been identified: $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ ($\text{Na}[\text{B}(\text{OH})_4]\cdot 2\text{H}_2\text{O}$), $\text{NaBO}_2\cdot 2\text{H}_2\text{O}$ ($\text{Na}[\text{B}(\text{OH})_4]$), $\text{NaBO}_2\cdot 2/3\text{H}_2\text{O}$ ($\text{Na}_3[\text{B}_3\text{O}_4(\text{OH})_4]$), $\text{NaBO}_2\cdot 1/3\text{H}_2\text{O}$ ($\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$) and NaBO_2 ($\text{Na}_3[\text{B}_3\text{O}_6]$), and their thermal stabilities have been studied. The boundaries of the different Liquid+Solid equilibria for the temperature range from -10 to 80 °C have been determined, confirming literature data at low temperature (20 °C ~ 50 °C). Moreover the following eutectic transformation, $\text{Liq.} \rightarrow \text{Ice} + \text{NaBO}_2\cdot 4\text{H}_2\text{O}$, occurring at -7 °C, has been determined by DSC. The Liquid-Vapour domain has been studied by ebullioscopy. The invariant transformation $\text{Liq.} \rightarrow \text{Vap.} + \text{NaBO}_2\cdot 2/3\text{H}_2\text{O}$ has been estimated at 131.6 °C. This knowledge is paramount in the field of hydrogen storage through NaBH_4 hydrolysis, in which borate compounds were obtained as hydrolysis reaction products. As a

consequence, the authors propose a comparison with previous NaBO₂-H₂O binary phase diagrams and its consequence related to hydrogen storage through NaBH₄ hydrolysis.

Keywords: Hydrogen storage, hydrolysis, sodium borohydride, sodium borate, NaBO₂-H₂O binary phase diagram, thermodynamics.

1. Introduction

Hydrogen stands today as the highest density energy carrier considered as essential to be developed for a spread use of renewable energy source in alternative to fossil fuel resources. Many researches are focused on H₂ storage system and in particular, chemical compounds for solid state storage. Among the promising compounds, NaBH₄, through its hydrolysis (scheme 1 with $y = 0$) permits an attractive theoretical gravimetric storage density of 10.8 wt.% in safe conditions. Most of the researches related to this system focused on improving the slow kinetics of the scheme 1. In this way, intensive works have demonstrated that noble metal catalysts and cobalt based catalysts were very efficient [1-10]. However, it is paramount to note that beyond the kinetically limitations of the hydrolysis reaction, the main issue to be considered is the practical achievable hydrogen storage capacity [11-12] that can be expressed by the gravimetric hydrogen storage capacity (GHSC). GHSC is defined as the percentage of the gravimetric ratio of recovered hydrogen over the reagents (H₂O and NaBH₄)¹. Actually, experimental hydrolysis reaction never lead to anhydrous metaborate ($y = 0$) but to hydrated borate compounds as assumed in scheme 1 for $y \neq 0$. The end products have been denoted as NaBO₂·yH₂O with y, the

¹
$$GHSC = \frac{m_{H_2} \cdot 100}{m_{NaBH_4} + m_{H_2O}} ; m_{H_2O} = f(y) \text{ according to reaction (1)}$$

pseudo hydration degree ² [11,12].

As water is a reagent in the hydrolysis, the amount of water needed to complete the reaction increases with the borate pseudo hydration degree (scheme 1). As a consequence, higher the pseudo hydration degree of borate compounds and lower the GHSC (i.e. GHSC = 10.8 wt.% when $y = 0$; GHSC = 5.5 wt.% when $y = 4$). This aspect has been pointed out in previous works [11-13] but no study allows predicting which borate compounds can be formed in a precise condition, i.e. what is the highest pseudo hydration degree to be expected and consequently the resulting GHSC.

Borates fundamental knowledge comes from the fact that borates constitute the main form of natural resources of boron. In terms of application, they have been mainly studied for its antiseptic properties and its glass former capabilities. The first thermodynamic investigations of the ternary system $\text{H}_2\text{O}-\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ has been published by Dukelski [13] in 1906. He pointed out the existence of borates of different compositions at 30 °C. Among all the borate compounds, anhydrous sodium metaborate, NaBO_2 ³, has a molecular ratio Na_2O to B_2O_3 of 1:1 [14]. This phase, in presence of water, leads to the formation of hydrated borate compounds ($\text{NaBO}_2 \cdot y\text{H}_2\text{O}$). Two stable borate compounds have been reported at 30 °C in the isothermal section of the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ [13]: $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ ⁴ and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ ⁵. Other isothermal sections of this system have also been determined at 0 °C [15], 45 °C [16], 60 °C [17], 90 °C [18] and 100 °C [19]. For each temperature, we focused our investigation on the isoplethal section $\text{NaBO}_2-\text{H}_2\text{O}$ corresponding to the molar ratio $\text{Na}_2\text{O}:\text{B}_2\text{O}_3 = 1:1$.

² It is to note that this notation does not represent the number of real hydration water molecules as discussed in a recent work [21] and detailed in the included footnotes of the present article.

³ Structural formula = $\text{Na}_3[\text{B}_3\text{O}_6]$

Table 1 summarizes the reported compounds as a function of the temperature. $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ was observed to be stable from 0 °C to 45 °C. $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ was characterized in the temperature range 30 ~ 100 °C, but not observed at 0 °C. $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$ was claimed to exist from 45 °C to 100 °C, and $\text{NaBO}_2 \cdot 1\text{H}_2\text{O}$ seems to be stable only for temperatures above 100 °C. However, doubts about the existence and the stability of these two former compounds have been already pointed out [20,21]. Bouaziz [20] has studied in details the binary phase diagram $\text{NaBO}_2\text{-H}_2\text{O}$ in the temperature range (30 ~ 300 °C) confirming results obtained by Dukelski [13] about the stability of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. Moreover, two other hydrates were pointed out in this temperature range: $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$. Even if using similar experimental approaches, Toledano *et al.* [22] have highlighted some differences compared to the work of Bouaziz [20], especially concerning the temperature stability range of $\text{NaBO}_2 \cdot \text{H}_2\text{O}$.

The physical-chemistry knowledge on the different borate compounds was limited to structural characterizations (IR/Raman spectroscopy, TGA and powder X-Ray diffraction): crystallographic investigations have shown that $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ nor $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ crystallize in the triclinic and monoclinic system respectively [23,24]. No crystallographic structure was determined for $\text{NaBO}_2 \cdot 1\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$ (experimental reference patterns were ICDD #00-014-0678 and #000160242, respectively). Note that another borate compound, $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ ⁶, has been characterized in terms of crystallographic structure (space group *Pnma*, a= 8.923 (1), b=7.152 (1), c=9.548 (1) Å [25]. In addition, we recently reported the synthesis of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ ⁷ [21]. However, these two last compounds were observed neither by thermal decomposition of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ [20,22] nor saturated solution studies [26,27]. All the borate species identified in

⁴ Structural formula = $\text{Na}[\text{B}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$

⁵ Structural formula = $\text{Na}[\text{B}(\text{OH})_4]$

⁶ Structural formula = $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$

⁷ Structural formula = $\text{Na}_3[\text{B}_3\text{O}_4(\text{OH})_4]$

the literature have been described as decomposing by non congruent melting and subsequent peritectic reactions which temperatures vary according to the experimental approach used (Table 2).

Very few studies focused on identifying the borate compounds formed after NaBH_4 hydrolysis [11,28]. According to Marrero *et al.*, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ was identified as the stable borate phase formed after NaBH_4 hydrolysis, whatever the reaction conditions were. It is to note that Stepanov *et al.*'s work [28] followed by *ex situ* XRD the borate phase formation after NaBH_4 hydrolysis in air at room temperature, i.e. in presence of vapour and CO_2 . In this case, the formation of other phases than $\text{NaBO}_2 \cdot y\text{H}_2\text{O}$ ($\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ and tincalconite ($\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 3\text{H}_2\text{O}$) located on the adjacent $\text{Na}_2\text{O}:\text{B}_2\text{O}_3 = 1:2$ isoplethic section) can be explained by the presence of CO_2 which modifies the thermodynamic equilibria. The tincalconite formation, resulting from the reaction of borax and carbon dioxide has been highlighted by Krzhizhanovskaya *et al.* [29]. The formation of borax after NaBH_4 hydrolysis can be explained from the reaction of sodium borate crystals and solution with dissolved carbon dioxide from the atmosphere [30]. In other words, NaBH_4 hydrolysis should be performed under reduced CO_2 atmosphere in order to obtain $\text{NaBO}_2 \cdot y\text{H}_2\text{O}$.

At the sight of the present literature review, the stability of borate compounds, $\text{NaBO}_2 \cdot y\text{H}_2\text{O}$, as a function of temperature need to be clarified, particularly in the low water region of the diagram ($0 < y < 2$). Moreover, previous investigations were focused on studying equilibria in closed reactor for temperature higher than 100°C , i.e. under non ambient pressure, in order to avoid the vaporization of the borate solution. The lack of information about borate compounds and identification of the borate phases formed after NaBH_4 hydrolysis led us to conduct the present study. The authors propose a revision of the binary phase diagram $\text{NaBO}_2\text{-H}_2\text{O}$ at ambient pressure, a fundamental knowledge to understand and predict the borate formation through NaBH_4 hydrolysis. Identification of every stable borate compounds was

completed by the investigation of binary phases equilibria obtained under ambient pressure in the binary system $\text{NaBO}_2\text{-H}_2\text{O}$. This study highlights the stability of two new borate compounds: $\text{NaBO}_2\cdot 2/3\text{H}_2\text{O}$ and $\text{NaBO}_2\cdot 1/3\text{H}_2\text{O}$. Finally, a discussion on the achievable GHSC related to phase equilibria formed in the $\text{NaBO}_2\text{-H}_2\text{O}$ system was proposed.

2. Material and methods

As starting materials, commercial $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ from ACROS (white powder > 98 %) was used as received. XRD experiment on this reactant, carried out at ambient temperature evidenced the presence of $\text{NaBO}_2\cdot 2\text{H}_2\text{O}$ (approx. 30 wt.%) in addition to $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$.

2.1. Borate compounds syntheses

Pure $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ was precipitated from a borate solution, $x_{\text{NaBO}_2} = 0.080$ (x_{NaBO_2} is the NaBO_2 molar fraction) cooled from 60 °C to room temperature. Large and well faceted crystals in equilibrium with a saturated solution were obtained after ten hours. Lower hydration degree borates, under powder form, were synthesized by solid state dehydration of commercial $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ under inert atmosphere (Argon) and atmospheric pressure. Thermal treatments were run with a heating rate of 1 °C.min⁻¹ at fixed temperatures of 65 °C, 110 °C, 140 °C, 180 °C and 300 °C ($\Delta T = \pm 1$ °C) for a duration varying from 12 hours to 3 days. In the case of $\text{NaBO}_2\cdot 2/3\text{H}_2\text{O}$, the synthesis was carried out both by solid state dehydration of commercial $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ and NaBH_4 hydrolysis as reported previously in [21].

2.2 Borate compounds characterization

Phases were identified by X-Ray powder diffraction using a Panalytical MPD-Pro diffractometer equipped with a X'celerator detector. Bragg-Brentano configuration was used with the Cu $K_{\alpha 1+\alpha 2}$ radiation ($\lambda_{K\alpha 1} = 1.5406 \text{ \AA}$, $\lambda_{K\alpha 2} = 1.5444 \text{ \AA}$, $\lambda_{K\alpha 1}/\lambda_{K\alpha 2} = 0.5$). X-ray diffraction patterns were recorded between 10 and 60 °(2 θ) with a step size of 0.016 °(2 θ) and an acquisition time of 50 s per step. Polyimide film was covering the sample to prevent from moisture and rehydration. As a consequence, a broad diffusion background was observed at 10-30 °(2 θ) with a characteristic peak at ~21 °(2 θ). In order to correct the physical displacement of the sample compared to the reference plane, silicon powder (ICDD#00-027-1402) was added to the borate powders. *In situ* X-Ray powder diffraction experiments during thermal treatment were carried out using a Panalytical MPD-Pro diffractometer equipped with a Panton HTK 1200 furnace with similar experimental parameters than RT XRD experiments. In this case an open alumina sample holder (16 mm i.d.) was used. Heat treatments were carried out from ambient temperature to 340 °C, with a heating rate of 2 °C.min⁻¹. Diffraction patterns were collected every 5 °C during heating.

2.3. Borate solutions syntheses and characterization

Borate solutions with controlled composition were prepared by dissolving anhydrous sodium metaborate (NaBO₂) in the suitable amount of deionised water.

Boiling temperatures of borate solutions ($0 < x_{\text{NaBO}_2} < 0.400$, $\Delta x_{\text{NaBO}_2} = \pm 10^{-3}$) were determined by ebullioscopy using a Cottrell pump in a closed reactor under atmospheric pressure. Boiling temperatures were measured with an alcohol thermometer ($\Delta T = \pm 0.2 \text{ °C}$). Invariant transformations were studied by Differential Scanning Calorimetry (DSC 821, Mettler-Toledo)

using 40 μL sealed aluminium crucibles. Heating rate was fixed to $0.4\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in the temperature range $-30 \sim 110\text{ }^{\circ}\text{C}$. The working atmosphere was maintained at 10^5 Pa Nitrogen.

3. Results

3.1. Identification of borate compounds by XRD

In a preliminary work, we reported on the thermal analysis of commercial $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ dehydration, carried out by high resolution variable heating rate TGA [31]. The analysis performed in the temperature range from $25\text{ }^{\circ}\text{C}$ to $340\text{ }^{\circ}\text{C}$ evidenced five successive mass losses. The final product was identified as anhydrous sodium metaborate, NaBO_2 , by XRD characterization. Table 3 reports the mass losses and the corresponding transformations temperatures observed during the variable heating rate TGA experiment.

In order to get a better understanding of the $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ dehydration steps, identification of the stable phases formed upon the dehydration steps was realized by *in situ* XRD starting from commercial $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$. A first *in situ* XRD experiment (carried out from 25 to $145\text{ }^{\circ}\text{C}$) pointed out a phase transition at $50\text{ }^{\circ}\text{C}$ assigned to the decomposition of $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ into $\text{NaBO}_2\cdot 2\text{H}_2\text{O}$ (Figure 1). Then, as the temperature increases, $\text{NaBO}_2\cdot 2\text{H}_2\text{O}$ undergoes a phase transition observed around $100\text{ }^{\circ}\text{C}$. The transformation leads to a swelling of the sample, responsible for the loss of the diffracted signal and preventing from identifying the compounds formed. In order to overcome the experimental difficulty due to the large sample volume increase around $100\text{ }^{\circ}\text{C}$, the high temperature range ($110 \sim 340\text{ }^{\circ}\text{C}$) was investigated in a second *in situ* XRD experiment (Figure 2) starting from single phase $\text{NaBO}_2\cdot 2/3\text{H}_2\text{O}$ obtained by thermal treatment of $\text{NaBO}_2\cdot 4\text{H}_2\text{O}$ ($110\text{ }^{\circ}\text{C}$ during 12 h) [21]. Three phases were evidenced by the *in situ* experiment performed in the temperature range $110 \sim 340\text{ }^{\circ}\text{C}$. From $150\text{ }^{\circ}\text{C}$, $\text{NaBO}_2\cdot 1/3\text{H}_2\text{O}$ was

observed in coexistence with $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$. From 190 °C, $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ and NaBO_2 were in coexistence. According to the main Bragg peak intensities, the quantity of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ were inverted in the temperature range 110 ~ 150 °C: thus we suggest that $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ was decomposed to form $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$. The same behaviour was observed with the relative intensity of Bragg peaks of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ and NaBO_2 in the temperature range 190 ~ 280 °C. $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ was no more discernable from 230 °C. Above 280 °C, NaBO_2 was the only phase detected.

In order to supplement *in situ* XRD results, different isothermal treatments have been performed starting from commercial $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$. XRD patterns for compounds heat treated at 65, 110, 140, 180 and 300 °C during 3 days can be found in the Appendix A (Figure A1). XRD pattern for 65 °C evidenced $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ (Figure A1.a) whereas $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ was identified, as single phase, for 110 °C (Figure A1.b), 140 °C (Figure A1.c) and 180 °C (Figure A1.d). Then, NaBO_2 was formed for a thermal treatment carried out at 300 °C (Figure A1.e). The temperature stability range of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and NaBO_2 were in accordance both with *in situ* XRD and variable heating rate TGA experiments (Table 3 and [31]). However, isothermal treatments and XRD characterizations evidenced the formation of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ from 110 to 180 °C. These results constitute the first experimental characterization of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ after heat treatment of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, as this compound was never reported by thermal treatment syntheses [20], TGA analyses [20,22] nor titration [26,27]. Moreover, the formation of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ was observed fifty degrees below the formation temperature determined by variable heating rate TGA (162 °C, Table 3).

3.2. Phase equilibria and transformations in the NaBO₂-H₂O phase diagram

3.2.1. Liquid+Vapour equilibrium

To our knowledge, no result about a Liquid to Vapour transformation has been reported for the NaBO₂-H₂O phase diagram. Previous experiments [20,22] were carried out in closed reactor, i.e. under pressure when temperature exceeds 100 °C. In these experimental conditions, the stability of Liquid+Solid equilibria could have been favoured, the pressure modifying the equilibrium curve Liquid-Vapour.

In the present study, the boundaries of the Liquid+Vapour domain were determined at ambient pressure using ebullioscopy experiments. Figure 3 presents the evolution of the boiling temperature as a function of NaBO₂ molar fraction (x_{NaBO_2}) defining the boiling point curve. These experimental data are also reported on Figure 4. In the water rich domain, boiling temperature increased from 100.0 °C (pure water) to reach a dwell at 131.6 °C for a borate solution with a $x_{\text{NaBO}_2} = 0.280$. Above the boiling point curve, the binary phase equilibrium was established between the liquid solution and vapour. In the concentration range $0 < x_{\text{NaBO}_2} < 0.400$, a temperature dwell was observed at $T = 131.6$ °C indicating a three phases equilibrium. Vaporization of the liquid phase occurred at $T = 131.6$ °C in presence of a third phase: the solid phase NaBO₂·2/3H₂O (see scheme 2). For temperature higher than 131.6 °C, NaBO₂·2/3H₂O was in equilibrium with vapour.

It is to note that the phase transformation occurring at $T = 131.6$ °C was previously observed by variable heating rate TGA (Step 3, $T = 135$ °C, Table 3) and wrongly attributed to the dehydration of a hypothetical borate compound (NaBO₂·1,2H₂O) [31]. Results obtained by ebullioscopy measurements clearly demonstrates that the mass loss observed around 135 °C resulted from the vaporization of the liquid formed after the dehydration of NaBO₂·2H₂O.

3.2.2. Liquid+Solid equilibria

The solubility curve of sodium metaborate (boundary of the Liquid+Solid equilibria) was determined by Nies *et al.* [26] in a temperature range from -10 °C to 120 °C using chemical titration of saturated solutions. These data have been used as published to represent the solubility curve of the binary phase diagram NaBO₂-H₂O (Figure 4). For $T \sim -6$ °C and $x_{\text{NaBO}_2} \sim 0.040$, Nies *et al.* [26] observed a minimum for the solubility curve which corresponds to the eutectic transformation (scheme 3) characterized in the present work by DSC from -30 °C to 30 °C. Different compositions have been studied, i.e. $x_{\text{NaBO}_2} = 0.021, 0.054, 0.095$ and 0.161 by DSC experiments and onset temperatures are presented in Table 4. The sharp endothermic peaks define an average temperature of -7 ± 2 °C for scheme 3 (see for example Appendix B, Figure B1.a). According to phase construction rules, a binary phase domain composed of pure ice and NaBO₂·4H₂O was defined from -30 °C to -7 °C.

According to Nies' work [26], the solubility's values increased from -6 to 120 °C and two breaks were observed along the solubility curve. The first one, around 50 °C, has been characterized in our work for $0.161 < x_{\text{NaBO}_2} < 0.265$ (Table 4), and corresponds to the peritectic decomposition of NaBO₂·4H₂O (scheme 4) as evidenced by *in situ* XRD (Figure 1). The average onset temperature has been measured to 55 ± 2 °C (see for example Figure B1.b in Appendix B), which was in good agreement with literature data (i.e. 53 °C [26]). Thus, a binary phase domain Liquid+NaBO₂·4H₂O was defined by these experiments from -7 °C to 55 °C following the phase construction rules. The second break was related to the peritectic decomposition of NaBO₂·2H₂O (scheme 5), confirmed by *in situ* XRD (Figure 1). This reaction occurs at 103 ± 2 °C after DSC experiments performed at $x_{\text{NaBO}_2} = 0.333$ (Table 4 and Figure B1.c in Appendix B).

Whereas the solubility curve determined by Nies *et al.* [26] at low temperatures and high water content borate solution was in accordance with our experimental data, large discrepancies

were observed at high temperatures between Nies results and our experimental data. For the sake of clarity, experimental results after DSC measurements have been reported on Figure 4. These discrepancies could be partially explained by the tendency to form a metastable state instead of a Liquid+Solid binary phase domain as suggested in recent work [21]. Moreover, the isotherms in Nies *et al.*'s work were obtained, for temperatures above 100 °C, under pressure in order to avoid vaporization of the borate solution. For these reasons, the solubility curve in the temperature range 100.0 ~ 131.6 °C was symbolized in Figure 4 by a dashed line.

3.2.3. Vapour+Solid equilibria

$\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ decomposition temperature has been previously determined by TGA/DSC experiment [21]: peritectic reaction (scheme 6) occurs at 155 ± 2 °C, defining a binary phase domain $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O} + \text{Vapour}$ for $T > 155$ °C. Moreover, variable heating rate TGA experiment (Table 3) indicates a temperature of 250 ± 2 °C for the peritectic decomposition of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ according to the scheme 7. As a consequence, a binary phase equilibrium $\text{NaBO}_2 + \text{Vapour}$ exists for temperature higher than 250 °C. It is to note that regarding equilibria formed with vapour, this phase was assumed to be a rich water phase, almost pure vapour for temperatures higher than 100 °C, as borate compounds' saturation vapour pressure was supposed to be high. As no experimental data was available to highlight this point, vapour domain was represented by a dashed line on Figure 4.

4. Discussion

4.1. Borate compounds formation and stability

Five borate compounds have been identified in the $\text{NaBO}_2\text{-H}_2\text{O}$ system: $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ and NaBO_2 . These compounds were stable at

room temperature (characterized at room temperature by XRD after heat treatment synthesis).

Hydrated borates ($\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$) decomposed by peritectic transformations according to schemes 4 to 7 respectively.

The present results i) refine literature knowledge about $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, ii) highlight the existence and specify the stability domain of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ and NaBO_2 (the two first compounds were observed neither by thermal decomposition of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ [20,22] nor saturated solution studies [26,27]), iii) state on the non existence of $\text{NaBO}_2 \cdot 1\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$ as stable compounds.

Concerning this last point, previous works reporting on the observation of the $\text{NaBO}_2 \cdot 1\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$ compounds were related to non atmospheric pressure studies [20,22,26] and even if referring to similar experimental conditions, discrepancies were observed, in particular in the Toledano *et al.*'s [22] and Bouaziz's [20] works where $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$ stability was discussed. It is also to note that the only crystallographic data available for these compounds [20] were experimental powder XRD patterns as no single crystal characterization of these compounds as well as no single phase synthesis were carried out to our knowledge. The experimental powder XRD patterns were not sufficient enough to provide a clear identification of the compounds. Thus, from the non observation of $\text{NaBO}_2 \cdot 1\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$ after characterization techniques as TGA, DSC and X-ray Diffraction, the authors state on the non existence of these compounds as stable phase in the binary phase diagram $\text{NaBO}_2\text{-H}_2\text{O}$ at atmospheric pressure, i.e. in similar conditions compared to that corresponding to the borate formation through NaBH_4 hydrolysis.

The temperatures of formation of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$, determined by high resolution variable heating rate TGA ($T = 162\text{ }^\circ\text{C}$) and *in situ* XRD ($T = 110\text{ }^\circ\text{C}$), show a fifty degrees gap. The difference in observed temperatures can be attributed to the role of the water partial pressure in

the borate compound formation. Actually, the main configuration difference between the two experiments was the size of the surface exchange between the sample and its gaseous atmosphere: variable heating rate TGA experiment was carried out in a predrilled cap closed crucible, characterized by a low surface exchange (0.35 mm^2), whereas *in situ* XRD characterisations were carried out using a open alumina sample holder with a 201 mm^2 surface exchange. The low surface exchange favours a water partial pressure value close to that of equilibrium conditions. In this work, the dehydration temperature of each compound have been defined using thermal analysis experiments (TGA and DSC), these techniques minimizing the effect of the water partial pressure. To our knowledge, no detailed study on borate compounds' partial pressure has been reported. The present work highlights a decrease of $50 \text{ }^\circ\text{C}$ for the decomposition temperature of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$. Actually, thermal treatment carried out at $110 \text{ }^\circ\text{C}$ during 12 h led to the formation of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ [21] whereas longer treatment (3 days) led to the formation of $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$. Compared to the conventional borate compound formation, i.e. invariant transformation for a given temperature, this work evidences another way for borate compounds formation in which the compound decomposition was due to a decrease of the vapour pressure. Thus, the determination of the vapour pressure related to each borate compound should lead to a better understanding of the dehydration mechanism.

The evidence of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ formation under atmospheric pressure constitutes not only a fundamental difference compared to previous literature studies but a key point for hydrogen storage through NaBH_4 hydrolysis: the formation of these low hydration degree borates, compared to $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ commonly observed [11], constitutes a way of a potential significant increase of the GHSC. Moreover, the present results suggest that the vapour pressure is a significant parameter for the monitoring of the temperature formation of these compounds: as an example, $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$ can be formed at lower temperature by decreasing

the vapour pressure over the compound.

4.2. NaBO₂-H₂O phase diagram

A compilation of all the results is proposed under the form of the binary phase diagram plotted in Figure 4 in the temperature range -30 ~ 300 °C.

This complete revision of the NaBO₂-H₂O binary phase diagram points out main differences compared to the previous ones [20,22] in particular in the rich water part ($x_{\text{NaBO}_2} < 0.333$) and in the low water part ($x_{\text{NaBO}_2} > 0.333$) of the binary phase diagram.

First, in the rich water part of the diagram ($x_{\text{NaBO}_2} < 0.333$), Liquid+Vapour biphasic domain has been described as a function of the NaBO₂ molar fraction in the temperature range 100 ~ 131.6 °C. In this domain, vapour was in equilibrium with a borate saturated solution. At 131.6 °C, the scheme 2 occurred and above 131.6 °C, solid borate compounds were in equilibrium with vapour. Second, concerning the low water part of the binary phase diagram ($x_{\text{NaBO}_2} > 0.333$), the existence of two borate compounds has been pointed out: NaBO₂·2/3H₂O ($x_{\text{NaBO}_2} = 0.666$) and NaBO₂·1/3H₂O ($x_{\text{NaBO}_2} = 0.750$). These compounds were stable until 155 °C and 250 °C respectively and were involved in different phase equilibria.

The synthesis of NaBO₂·2/3H₂O single crystals [21] can be achieved in the binary phase domain Liquid+NaBO₂·2/3H₂O from 103 to 131.6 °C. However, most of the attempts to synthesize the crystallized compound in equilibria with its saturated borate solution felt down in the formation of a metastable gel state. It is to note that for a temperature lower than 103 °C, [B(OH)₄]⁻ ions were present in the solution (see for example the works of Anderson *et al.* for T = 30 °C [32] and Edwards *et al.* [33]). Thus, NaBO₂·4H₂O (Na[B(OH)₄]·2H₂O) and NaBO₂·2H₂O (Na[B(OH)₄]) were observed as the stable phases in equilibrium with saturated borate solution in this temperature range (Figure 4). To our knowledge, there was no available data about the nature of

the polyanions in the saturated borate solution for temperature higher than 103 °C. We suggest that the nature of the main polyanion in presence might be close to $[\text{B}_3\text{O}_4(\text{OH})_4]^{3-}$, this polyanion being the fundamental building block (FBB) of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ [21]. This polyanion could favour the polymerisation between chains or sheets leading to a gel formation. Indeed $[\text{B}_3\text{O}_4(\text{OH})_4]^{3-}$ is based on a B-O cycle, with a maximum out of the plane deviation of O5 of 0.35 Å [21], giving the possibility to form chains and sheets. Second this polyanion contains both hydroxyl groups and bivalent oxygen atoms leading to the possibility of hydrogen bonding formation. A similar behaviour has been observed and explained for other borate system, like metaboric acid $\text{HBO}_2(\text{II})$, where strong hydrogen bonds lead to endless zigzag chains of composition $\text{B}_3\text{O}_4(\text{OH})(\text{OH}_2)$ directed along one axis with H_2 bonds forming links between the chains of different layers as well as between chains of the same layer [30]. To sum up, the nature of the stable polyanion as a function of the temperature could cause differences in the B-O network of the saturated solution: i) for $T < 100$ °C, the presence of $[\text{B}(\text{OH})_4]^-$ would favour the crystallisation of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, ii) for $T > 100$ °C, presence of $[\text{B}_3\text{O}_4(\text{OH})_4]^{3-}$ could lead to the polymerisation of the saturated solution resulting in a metastable viscous gel. Further work is required to evidence the presence of $[\text{B}_3\text{O}_4(\text{OH})_4]^{3-}$ ions in borate solutions at high temperature ($T > 100$ °C) since the formation of metastable gel is a significant technical issue for the implementation of NaBH_4 hydrolysis. Understanding the way the gel state was formed would be very helpful in the search for destabilizing this metastable state since it constitutes a key point for future industrial applications.

As a consequence of this metastable state evidence, we have considered, in the review of the binary phase diagram, a biphasic domain Liquid+ $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ from 105 °C to 131.6 °C but the solubility curve of this domain has been plotted in dashed line, as investigations are still in progress to define this part of the solubility curve (Figure 4).

Beyond the fundamental interest of determining the $\text{NaBO}_2\text{-H}_2\text{O}$ phase diagram in the temperature range $-30 \sim 300\text{ }^\circ\text{C}$, the present work constitutes an invaluable tool for optimisation of the hydrogen capacity of NaBH_4 hydrolysis. Actually the GHSC of NaBH_4 hydrolysis is related to the reaction stoichiometry (ratio $\text{NaBH}_4/\text{H}_2\text{O}$) but the $\text{NaBH}_4/\text{H}_2\text{O}$ ratio can be optimized as a function of the nature of the borate compounds formed. Depending on the temperature and composition, that means depending on the thermodynamic equilibrium described in the $\text{NaBO}_2\text{-H}_2\text{O}$ phase diagram, the ratio of “hydriding” water (trapped in the hydrated borate) over “reacting” water (involved in the hydrolysis) can vary. If x_{NaBO_2} represents the NaBO_2 molar fraction and y the pseudo hydration degree of borate compounds, the empirical relation between x_{NaBO_2} and y , i.e. the relation between the binary phase diagram $\text{NaBO}_2\text{-H}_2\text{O}$ and the NaBH_4 hydrolysis, is given by scheme 8.

In the present work, the phase domains of the diagram were investigated using either borate solutions prepared both from dissolution of anhydrous NaBO_2 and from reaction product of NaBH_4 hydrolysis in order to be as close as possible to the NaBH_4 hydrolysis conditions.

In the next, we discuss the specific consequence deduced from the revised $\text{NaBO}_2\text{-H}_2\text{O}$ phase diagram, supported on the following assumptions regarding the NaBH_4 hydrolysis reaction:

- A complete reaction was assumed, leading to the formation of the stable compounds evidenced in the $\text{NaBO}_2\text{-H}_2\text{O}$ diagram.
- GHSC calculation was only based on the hydrolysis reaction (scheme 1) and does not take into account the overall system required to perform NaBH_4 hydrolysis.

Table 5 presents the theoretical GHSC expected after formation of the borate compounds

evidenced in the present work. Note that in the hypothesis that the final hydrolysis product is a single phase liquid borate solution, the GHSC cannot be higher than 2.56 wt.% at 25 °C [34] with an initial NaBH₄ solution that contains 12.4 g NaBH₄ per 100 g H₂O. This limitation results from the fact that the GHSC was limited by the borate anion solubility (21.6 g NaBO₂ per 100 g H₂O at 25 °C [26]) and not by the BH₄⁻ solubility (35.6 g NaBH₄ per 100 g H₂O at 24 °C, [35]). The authors pointed out that even though the “all liquid” reaction (reactant and final products are purely liquid at 25 °C) appears technologically attractive, the resulting GHSC is very weak and, as suggested in other works [11,12], worthwhile GHSC can only be achieved with solid borate compound as final products. The highest GHSC of NaBH₄ hydrolysis, i.e. 10.8 wt.%, is only achievable by direct formation of anhydrous NaBO₂ and H₂, following the so called “ideal” hydrolysis, i.e. following the reactant ratio NaBH₄:H₂O = 1:2 [36-39]. The conditions to form NaBO₂, deduced from the binary phase diagram, is at high temperature (T > 250 °C) where NaBO₂ coexists with Vapour. Highest GHSC would be observed when the vapour formed would be recovered to hydrolyse unreacted NaBH₄. NaBO₂ also appears, at lower temperature (-30 ~ 250 °C), in the Solid + Solid binary phase domain (NaBO₂·1/3H₂O + NaBO₂). In this case, the presence of NaBO₂·1/3H₂O can lead to a decrease of the GHSC (10.0 wt.%). Moreover, the achieving of pure NaBO₂ implies the overcoming of strong difficulties as, for example, a high temperature reaction or a weak diffusion coefficient in solid state. As a consequence the so called “ideal” hydrolysis reaction, i.e. NaBH₄:H₂O = 1:2 could not be envisaged for a real industrial application.

According to the present work, worth GHSC in the order of 9-10 wt.% can be reached for operating temperature not higher than 132 °C, the final borate compounds being NaBO₂·2/3H₂O or NaBO₂·1/3H₂O. Two ways are proposed to reach such high GHSC: 1) direct synthesis of the

less hydrated compound (described hereafter) or 2) carrying out a 1:6 hydrolysis reaction in order to obtain $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ and then the latter compound is dehydrated to the desired final product, the recovered water becoming available for subsequent hydrolysis. Both ways have their own advantages and drawbacks, the second one requiring for example a two steps process to achieve the theoretical GHSC.

Concerning the direct synthesis of the less hydrated compound, we consider, for the discussion, the synthesis of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ for a 1:4 hydrolysis reaction stoichiometry and a temperature of 70 °C. It is not clear if the reaction first leads to $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ which dehydrates to form the desired product or if the final product is directly formed during the reaction. In other words, what is the chemical pathway leading to $\text{NaBO}_2 \cdot y\text{H}_2\text{O}$ from NaBH_4 hydrolysis? To our knowledge, there was only one study detailing this point [11]. In the Marrero-Alfonso's work [11], reactions were carried out at $T = 100\text{ }^\circ\text{C}$ by reacting NaBH_4 and vapour inside a closed reactor. The final product after reaction was $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ under a variety of reaction conditions. Marrero-Alfonso *et al.* conclude that $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ will be the stable form at temperature up to 105 °C, and that the degree of hydration of the product does not appear to be a direct function of the water/hydride ratio of the hydrolysis [11]. The present work agrees with the latter remark but the temperature has also to be taken into account to predict the nature of the phase formed by NaBH_4 hydrolysis. $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ will not be the stable phase if reaction is carried out at ambient temperature for example, but $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$. Thus Marrero-Alfonso *et al.* mentioned that $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ remained stable even if reaction temperature was slightly in excess of 105 °C whereas our work indicates a peritectic decomposition at 103 °C (scheme 5). The non observation of $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ by Marrero-Alfonso *et al.* for temperature higher than 103 °C could be explained either because the reaction was carried out in a closed reactor, i.e. under pressure, modifying the thermodynamic equilibria or because of the slow dehydration kinetics of $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. The third hypothesis is

$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ could be decomposed *in situ* into a Liquid+Solid following for example the scheme 5. In this case $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ could be formed *in situ*. However, the reaction being carried out in a closed reactor, the overall composition remains constant and from the Liquid+Solid equilibria, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ will be reformed upon cooling. In addition, even for experiments carried out at ambient temperature, one should keep in mind that hydrolysis reaction is exothermic [40] and locally the temperature might be higher than the dehydration temperature of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, especially if the reactor is thermally insulated.

One other fundamental remark concerns the feasibility of the formation of low pseudo hydration degree borate compound through NaBH_4 hydrolysis. According to Figure 4, each compound even the less hydrated one could be formed at ambient temperature. However, regarding the way to perform NaBH_4 hydrolysis, reaction of liquid water and solid NaBH_4 ends up most of the time to local heterogeneities of the reaction stoichiometry [5,41-43]. For a given temperature, the most hydrated stable borate should be first formed, leading to a non equilibrium state with the sequence $\text{H}_2\text{O}/\text{NaBO}_2 \cdot y\text{H}_2\text{O}/\text{NaBH}_4$. Thus, from a microstructure point of view, reaction of water with NaBH_4 grain might lead to the formation of a borate layer at the surface of the NaBH_4 grain. As a consequence, borate compound formation could act as a strong diffusion barrier for water. The conversion of NaBH_4 will end up into very slow kinetics as chemical reaction between two solids (NaBH_4 and $\text{NaBO}_2 \cdot y\text{H}_2\text{O}$) falls into very weak diffusion coefficients leading to incomplete NaBH_4 hydrolysis and as a consequence to a drop of the effective GHSC.

A first approach to overcome this limitation could be to increase the surface/volume ratio, i.e. to decrease the size of the NaBH_4 grain. Recent investigations were focused on synthesizing nanosized chemical hydrides in order to modify thermodynamics of the hydride decomposition in temperature [44,45]. The authors propose to perform NaBH_4 hydrolysis based on nanosized

NaBH₄ powder. The consequence could be an increase of the GHSC as NaBH₄ is mostly consumed but also an increase of the kinetics related to an increase of the specific surface where NaBH₄ hydrolysis could take place. It could be promising to combine this approach with the use of vapour instead of liquid water in order also to avoid local heterogeneity. There is to our knowledge no study combining these two approaches.

A second approach is based on the knowledge of the binary phase diagram NaBO₂-H₂O. As limitations come from a separation of reactants by a borate layer and weak solid state diffusion between two solids, the hydrolysis should be restricted to conditions leading to a Liquid+Solid binary phase domain. The aim is to entirely dissolve NaBH₄ to lead to an equilibrium between a saturated borate solution and NaBO₂·yH₂O crystals. Three different Liquid+Solid domains are identified from Figure 4. Liquid+NaBO₂·4H₂O for a NaBO₂ molar fraction from 0.040 to 0.200 and a temperature range from -7 °C to 55 °C. This domain corresponds to hydrolysis performed with a ratio NaBH₄:H₂O from 1:26 to 1:6 (according to scheme 1 and scheme 8) and lead to the formation of NaBO₂·4H₂O with an associated GHSC of 5.5 wt.% (Table 5). Increasing the temperature, from 55 to 103 °C, a new Liquid+Solid domain was formed: Liquid+NaBO₂·2H₂O. A NaBO₂ molar fraction from 0.138 to 0.333 corresponds to a reaction stoichiometry of 1:8.25 to 1:4 (ratio NaBH₄:H₂O). In this domain, a maximum GHSC of 7.3 wt.% was related to the NaBO₂·2H₂O formation. The last Liquid+Solid domain was observed in Figure 4 for a temperature range 105 ~ 131.6 °C and a NaBO₂ molar ratio (reaction stoichiometry) from 0.258 (1:4.87) to 0.600 (1:2.66). In these conditions, Liquid+NaBO₂·2/3H₂O equilibrium could be formed and the maximum GHSC related to this domain is 9.3 wt.%. In all of these three Liquid+Solid phase domains, the GHSC will be as high as the liquid proportion will be weak. Figure 5 sums up the results concerning the hydrolysis stoichiometry, temperature and expected GSHC according to the above discussion.

To conclude, the three Liquid+Solid binary phase domains (Figure 4) define the reaction conditions to achieve high GHSC through NaBH_4 hydrolysis. The Liquid+ $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ binary phase equilibrium ($100\text{ }^\circ\text{C} < T < 131.6\text{ }^\circ\text{C}$) with, for example, a NaBO_2 molar fraction of 0.6 (i.e. $\text{NaBH}_4\text{:H}_2\text{O} = 1\text{:}2.66$), represents, the highest GHSC that could be expected from NaBH_4 hydrolysis (around 9.3 wt.%) from a Liquid+Solid phase equilibria. Further work is required to make clear the real conditions but the $\text{NaBO}_2\text{-H}_2\text{O}$ binary phase diagram should stand as a reference to predict phases formation through NaBH_4 hydrolysis.

5. Conclusion

A revision of the $\text{NaBO}_2\text{-H}_2\text{O}$ binary phase diagram is proposed in this work. Taking into account that experiments have been carried out under ambient pressure, this diagram stands as a fundamental knowledge in the NaBH_4 hydrolysis. The main result concerns the low water region of the diagram, where two new borate compounds have been identified: $\text{NaBO}_2 \cdot 2/3\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 1/3\text{H}_2\text{O}$. According to their low hydration degree, these compounds seem to be interesting in the NaBH_4 hydrolysis because GHSC could be expected around 10.0 wt.%. Moreover, this work proposes a first approach in the way to use this thermodynamic knowledge to tune the NaBH_4 hydrolysis conditions (temperature and stoichiometry) in order to improve GHSC. Different binary phase equilibria have been defined according to the binary phase diagram, especially the Liquid+Solid domains which determine the hydrolysis conditions to perform complete reactions and achieve highest GHSC through NaBH_4 hydrolysis.

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Figure captions

Figure 1. XRD patterns as a function of the temperature (25-115 °C, 2 °C.min⁻¹). Starting material is commercial NaBO₂·4H₂O. Darker the peak, higher the intensity. Peaks identification was performed by comparison with ICDD reference pattern #01-076-0755 for NaBO₂·4H₂O and #01-081-1512 for NaBO₂·2H₂O.

Figure 2. XRD patterns as a function of the temperature (110-340 °C, 2 °C.min⁻¹). Starting material is NaBO₂·2/3H₂O. Darker the peak, higher the intensity. Peaks identification was performed by comparison with ICDD reference pattern #00-035-0440 for NaBO₂·1/3H₂O and #00-032-1046 for NaBO₂. Peaks identification of NaBO₂·2/3H₂O refers to the work of Andrieux et al. [21].

Figure 3. Evolution of the Liquid+Vapour equilibrium temperature as a function of the NaBO₂ molar fraction, x_{NaBO_2} . Schematic dashed line solubility curve and invariant transformation (NaBO₂·2/3H₂O+Liq.→NaBO₂·2H₂O) were reported to facilitate the visualisation of the different equilibria.

Figure 4. Revised binary phase diagram of the system NaBO₂-H₂O. (●) Solubility curve after

Nies et al. work [26]. (■) Liquid+Vapour equilibrium temperatures after ebullioscopy

experiments. Onset temperatures after DSC experiments for scheme 3 ($\square$), scheme 4 (Δ) and scheme 5 ($\circ$).

Figure 5. GHSC as a function of the hydrolysis reaction stoichiometry (solid line). Temperature and binary phase domains have been reported (dotted lines and greyed areas) according the revised binary phase diagram.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8. Relation between x_{NaBO_2} , the $NaBO_2$ molar fraction and y , the pseudo hydration degree of borate compounds.

$$x_{NaBO_2} = \frac{1}{1+y} \text{ and } y = \frac{1-x_{NaBO_2}}{x_{NaBO_2}} \quad (8)$$

with $0.2 \leq x_{NaBO_2} \leq 1$ and $0 \leq y \leq 4$

Table 1. Literature data on the stability of borate compounds along the vertical section $\text{NaBO}_2\text{-H}_2\text{O}$ of the ternary system $\text{Na}_2\text{O-B}_2\text{O}_3\text{-H}_2\text{O}$ for different temperatures.

T (°C)	Reported stable borate compounds	Ref.
0	$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	[15]
30	$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$; $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$	[13]
45	$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$; $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$; $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$	[16]
60	$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$; $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$	[17]
90	$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$; $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$	[18]
100	$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$; $\text{NaBO}_2 \cdot 1\text{H}_2\text{O}$, $\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$	[19]

Table 2. Identified invariant transformations in the binary phase diagram $\text{NaBO}_2\text{-H}_2\text{O}$.

	Temperature (°C)	Method ^a	Ref.
$\text{NaBO}_2 \cdot 2\text{H}_2\text{O} + \text{Liq.} \longrightarrow \text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	56	P-TGA	[20]
	58	P-TGA	[22]
	53	P-Solubility	[26]
$\text{NaBO}_2 \cdot 1\text{H}_2\text{O} + \text{Liq.} \longrightarrow \text{NaBO}_2 \cdot 2\text{H}_2\text{O}$	105	P-TGA	[20]
	105	P-Solubility	[26]
	112	P-TGA	[22]
$\text{NaBO}_2 \cdot 1/2\text{H}_2\text{O} + \text{Liq.} \longrightarrow \text{NaBO}_2 \cdot 1\text{H}_2\text{O}$	155°C	P-TGA	[20]
	Not observed	P-TGA	[22]
$\text{NaBO}_2 + \text{Liq.} \longrightarrow \text{NaBO}_2 \cdot 1/2\text{H}_2\text{O}$	260	P-TGA	[20]
	306	P-TGA	[22]

^a P refers to closed reactor used for the studies, i.e. experiments were supposed to be carried out under pressure for temperature higher than 100 °C.

Table 3. Dehydration step temperatures and related mass losses, after Chiriac et al. [31].

Dehyd. Step	T (°C)	Mass loss (wt.%) ^b
1	46	48.4
2	90	27.2
3	135	23.8
4	162	16.2
5	250	8.4

^b Mass losses were calculated from NaBO₂ final product.

Table 4. Onset temperatures according to DSC experiments.

X _{NaBO₂}	Onset temperature (°C)		
	Scheme 3	Scheme 4	Scheme 5
0.021	-7.0	-	-
0.054	-4.7	-	-
0.095	-7.2	-	-
0.161	-7.8	52	-
0.200	-	56.7	-
0.230	-	56.0	-
0.265	-	54.1	-
0.333	-	-	103.5

Table 5. Expected GHSC as a function of the borate compounds formed after NaBH₄ hydrolysis.

Compound formed after NaBH ₄ hydrolysis	Pseudo hydration degree, y	Hydrolysis reaction stoichiometry, (2+y)	GHSC (wt.%)
NaBO ₂ ·4H ₂ O	4	6	5.48
NaBO ₂ ·2H ₂ O	2	4	7.28
NaBO ₂ ·2/3H ₂ O	2/3	8/3	9.31
NaBO ₂ ·1/3H ₂ O	1/3	7/3	10.01
NaBO ₂	0	2	10.83

Appendices

Appendix A

Figure A1. XRD patterns on commercial $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ heat treated under inert atmosphere during 3 days at a) 65 °C, b) 110 °C, c) 140 °C, d) 180 °C and e) 300 °C. Comparison with ICDD reference patterns.

Appendix B

Figure B1. DSC curves for a) $x_{\text{NaBO}_2} = 0.161$, b) $x_{\text{NaBO}_2} = 0.230$, c) $x_{\text{NaBO}_2} = 0.333$.

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