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# The hydrogen cycle with the hydrolysis of sodium borohydride: A statistical approach for highlighting the scientific/technical issues to prioritize in the field

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ABSTRACT

The 2000–2013 literature (through 260 research articles) dedicated to the field of "the hydrogen cycle with hydrolysis of sodium borohydride" was statistically analyzed. The objectives were (i) to emphasize the imbalance of the efforts dedicated to different aspects of the hydrogen cycle, (ii) to highlight the scientific/technical issues to prioritize from now on, and (iii) to revive an image tarnished since 2007. The statistical analysis was performed in terms of form and content. With respect to the form, it stands out for example that: the principal journal in the field is *International Journal of Hydrogen Energy*; the Chinese institutions are the most active; Turkey is also much involved while the most abundant reserves of boron can be found in this country. In terms of content, it is shown that there is unequivocal imbalance in the efforts dedicated to *e.g.* catalysis, borates recycling and scale-up. Huge attention has been focused on catalysis. The other topics were somehow neglected. Catalysis is not a critical issue anymore. Hence, recycling definitely merits much more interest, particularly to address the cost issue. A potential solution to explore is suggested herein. Scale-up is also imperative as it is the only way to demonstrate the technological potential of "the hydrogen cycle with hydrolysis of sodium borohydride", to which one can optimistically believe. All of these aspects, among others, are discussed herein.



## Introduction

Hydrogen storage is a critical key issue of the near-future *hydrogen economy*. Of the solutions under investigation, solid- or liquid-state materials have shown attractive features such as safe handling, high hydrogen densities and fast kinetics of hydrogen release [1]. Sodium borohydride $NaBH_4$ (10.8 wt% H and 113 g H $L^{-1}$) is a typical example. The pristine material is stable under inert conditions over a wide range of temperature (up to *ca.* 450 °C) [2], but in the presence of a protic solvent (*e.g.* water and methanol) it spontaneously dehydrogenates by

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solvolysis [3]. Accordingly, hydrolysis and also alcoholysis of sodium borohydride have been much investigated since the late 1990s and the prototyping works of the company *Millennium Cell Inc.* (Eatontown, New Jersey, USA; founded in 1998; closed down in 2009) [4,5].

The reaction of sodium borohydride hydrolysis (Eq. (1)) is exothermic ($\Delta H = -210$ kJ mol$^{-1}$) [6]. The formation of the tetrahydroxyborate anion ($pK_a$ of $B(OH)_3/B(OH)_4^- = 9.2$) basifies the aqueous medium which has the effect to drastically reduce the hydrogen generation kinetics [7]; the positive side of this is that the aqueous solution of sodium borohydride can be stabilized by making it alkaline by addition of hydroxide ions [8]. Basification is however useless when sodium borohydride is stored in solid-state (pure or mixed with a catalyst) [9,10]. A metal-based catalyst (generally heterogeneous), or an acid, is then used to start-and-stop the hydrogen generation by hydrolysis [11]. Such properties have been used as scientific rationales to emphasize the technological potential of the hydrolysis of sodium borohydride as on-board hydrogen generator [4,5,12].

$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2 \quad (1)$$

Thenceforward, many efforts have been dedicated to the hydrolysis of sodium borohydride [13], with special attention to the catalyst, and in a lesser extent, to the hydrogen cycle with sodium borohydride (Fig. 1). This is the core topic of the present article. Unlike the classical review articles published in the field, it aims at giving a statistical and infographical analysis of the open literature while highlighting (*i*) the imbalance in the efforts dedicated to each aspect of the aforesaid hydrogen cycle and (*ii*) the scientific/technical issues to prioritize in short-term so that a further step would be taken towards effective implementation, and then commercialization.

## Method

For the present statistical analysis, 260 research articles [4–6,9,10,14–268] dealing with at least one aspect of the hydrogen cycle with sodium borohydride were brought together and classified. Four restrictions were nevertheless applied. First, the publication date was restricted to the period 2000–2013. Second, the articles were all from peer-reviewed international journals. Third, the proceedings and extended abstracts of congresses were discarded. Fourth, the review-type articles were also discarded (they are nevertheless cited to support the overall discussion).

The *Five Ws*, *who*, *where*, *when*, *what*, *why*, to which an additional question, *how*, can be added, enable effective information-gathering and it is in that sense that they were used to prepare a chart allowing collecting the data needed for the statistical analysis. The six questions were addressed as follows: *who* for information about the corresponding author(s), the number of co-authors, the journals, the journals area, and the publishing houses; *when* for the publication dates; *where* for the laboratories and companies, as well as the countries of origin; *what*: for science-related information, like the keywords proposed by the authors (the keywords were classified by "themes"), the main topic of the articles (the topics were defined according to the main subject focused by the reported work; then, "themes" and "topics" were distinguished), and the details about catalysis, kinetics, by-products, recycling processes, storage capacities and scale-up; *why* for setting the authors' main objective(s) in the context of the hydrogen cycle with sodium borohydride; *how* for details about the articles form in terms of type, number of pages, number of cited references, *etc.*

The charts (handwritten) were then completed by scrutinizing the 260 articles one after the other. They were afterwards compiled by using the software Microsoft Excel. The as-obtained statistical data were analytically exploited and used

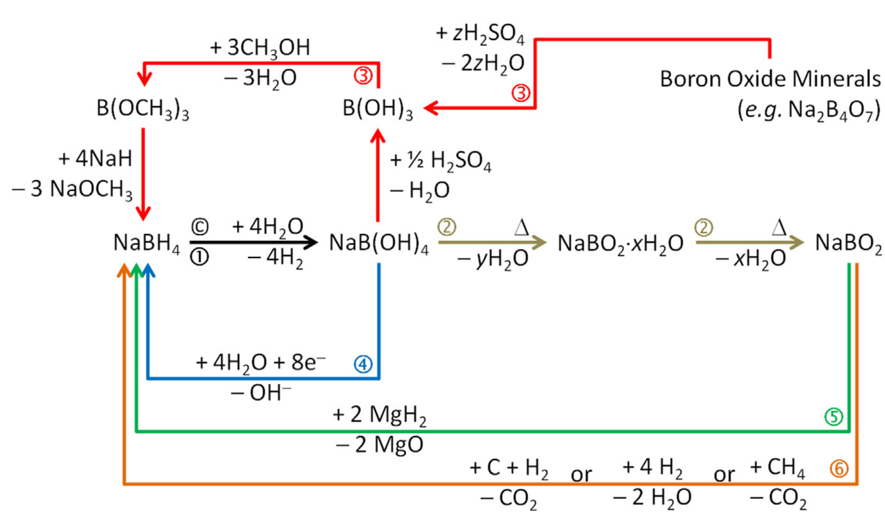


**Fig. 1 – Hydrogen cycle with sodium borohydride, with: ① the catalyzed hydrolysis reaction where the catalyst is denoted with the symbol ©; ② the thermal dehydration of sodium tetrahydroxyborate $NaB(OH)_4$ with $x + y = 2$; ③ the Brown-Schlesinger process; ④ the electrochemical process; ⑤ the modified Bayer process; ⑥ the reduction process with three different reducing agents.**