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Reaction mechanisms of the hydrolysis of sodium borohydride: A discussion focusing on cobalt-based catalysts[☆]

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ABSTRACT

In the field of hydrolysis of sodium borohydride, most of the works deal with metal-based catalysis and catalytic performance. Knowledge of reaction mechanisms, especially when a cobalt-based catalyst is used, is limited. This review has therefore two objectives. It aims at surveying the reaction paths and the related kinetic models proposed hitherto, and at discussing the mechanisms that could take place on $\text{Co@B}_\alpha\text{O}_\beta(\text{OH})_\gamma$, an original catalytic phase with a core@shell-type structure. It stands out that the nature of the catalytic surface of cobalt is not well known and that a sophisticated kinetic model is necessary to efficiently predict the reaction mechanisms.

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R É S U M É

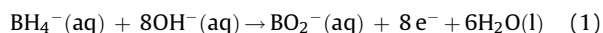
Les travaux de cette dernière décennie sur l'hydrolyse du borohydrure de sodium ont principalement concerné la catalyse métallique et les performances catalytiques. Les mécanismes réactionnels, surtout en présence de cobalt, sont en revanche peu connus. Cet article est donc destiné à dresser l'état de l'art des mécanismes réactionnels et des études cinétiques, ainsi qu'à discuter de ces mécanismes en présence de la nouvelle phase catalytique $\text{Co@B}_\alpha\text{O}_\beta(\text{OH})_\gamma$. Il ressort de cette analyse que l'état de surface des catalyseurs au cobalt est encore sujet à controverse et qu'un modèle cinétique sophistiqué est nécessaire pour mieux prédire les mécanismes réactionnels.

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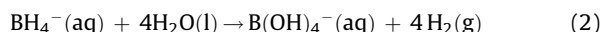
1. Introduction

In the field of liquid-phase chemical hydrogen storage, aqueous alkaline solutions of sodium borohydride (sodium tetrahydroborate, NaBH_4) have shown to be attractive, especially for low-temperature fuel-cell applications. The solution can be used “directly” as a liquid fuel of a direct borohydride fuel cell that is a technology based

on the anodic electro-oxidation of the borohydride anions BH_4^- [1]:



Otherwise, the solution can be used as the “indirect fuel” of the fuel cell, in fact as a hydrogen carrier for fuel cell [2]. In this case, the couple $\text{NaBH}_4\text{--H}_2\text{O}$ is dehydrogenated by hydrolysis (Eq. (2)) in the presence of a metal-based catalyst [3]; the as-generated hydrogen is then oxidized at the anode of a fuel cell [2]:



The advantageous features of this reaction are as follows. First, the gravimetric hydrogen density of

[☆] The present article is dedicated to Dr. François Garin (CNRS, Strasbourg, France), who has recently retired.

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$\text{NaBH}_4 \cdot \text{H}_2\text{O}$ (Eq. (2)) is 7.3 wt% H, which is a high capacity if compared to solid- and liquid-state hydrogen storage materials taken in near-ambient conditions [4]. Higher densities (up to 9 wt% H) can be achieved at higher temperatures ($> 80^\circ\text{C}$) when solid sodium borohydride and steam are used [5]. Second, the reaction is spontaneous, thus exothermic, with ΔH between -210 and -250 kJ mol^{-1} [6]. To avoid uncontrolled generation of hydrogen, the solution is generally stabilized by adding some sodium hydroxide NaOH (e.g., 0.1–5 M) into it [7]. With such a stabilized aqueous solution, dehydrogenation of sodium borohydride by hydrolysis requires then a catalyst [8]. Third, the liberated hydrogen is pure [9].

The development of the hydrolysis of aqueous alkaline solutions of sodium borohydride is however hindered by an important issue, which is related to the formation of the tetrahydroxyborate anion $\text{B}(\text{OH})_4^-$. Indeed, it is highly crucial to recycle this by-product back into the starting material, i.e. BH_4^- . The hydrogen cycle with sodium borohydride must be closed [10]. Yet, the strength/energy of the B–O bond in $\text{B}(\text{OH})_4^-$ is comparable to that of the C–O bond in CO_2 and, therefore, the conversion of $\text{B}(\text{OH})_4^-$ into BH_4^- is thermodynamically difficult [11]. Actually, the inefficiency and the high cost needed for such a process have made the US Department of Energy (US DOE) recommend, in 2007, a no-go for sodium borohydride for on-board automotive applications [12]. Another reason for this decision has been motivated by the low effective storage capacities achieved [13]. Despite everything, aqueous alkaline solutions of sodium borohydride are considered to be attractive for mobile/portable applications, e.g. niche applications [14].

During the past 13 years dedicated to hydrolysis of sodium borohydride, priority has been given to searching for active metal-based catalysts [3], and especially cobalt-based catalysts [15]: e.g., cobalt halides that lead to *in situ* formation of aggregated nanoparticles when put into contact with sodium borohydride (a strong reducing agent) [16]; *ex situ*-prepared cobalt nanoparticles and nanostructures [17]; cobalt deposited on powdery supports, like, e.g., alumina Al_2O_3 , titanium oxide TiO_2 or even clay [18]; cobalt deposited on shaped substrates like, e.g., nickel foam, polycarbonate membrane or copper foil [19]; cobalt alloyed with other elements like, e.g., phosphorus, molybdenum or chromium [20]; and so on. For more details, the reader is invited to refer to the reviews cited in reference [3]. It is worth noting that despite the huge work dedicated to cobalt in hydrolysis of sodium borohydride, the catalytically active form of the metal that is really involved in the reaction is rather unknown [15].

From a fundamental point of view, one can claim that knowledge of the hydrolysis mechanisms, especially those occurring on the surface of cobalt catalysts, is quite poor. In our opinion, this is due to three main reasons [15]. The first one is related to the difficulty to perform *in situ* and *operando* characterizations, which are essential to follow any evolution of the cobalt catalyst surface at the molecular level during the reaction. Actually, vigorous bubbling of hydrogen and precipitation of borates make any characterization very difficult. The second reason is related to the (very) fast kinetics of hydrolysis, which is

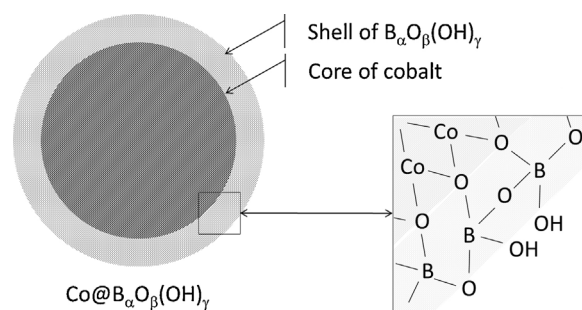


Fig. 1. Schematic representation of $\text{Co}@B_\alpha O_\beta(\text{OH})_\gamma$, a core@shell-type structure where the core is a cobalt compound and the shell (poly)borates. Adapted from [15,21].

generally concomitant with an important temperature increase (due to ΔH between -210 and -250 kJ mol^{-1} [6]). The third reason is that the nature of the catalytically active phase of cobalt is still unknown. Cobalt–boron alloys, cobalt borides, metal cobalt, cobalt oxides and so on have been suggested up to now. Recently, we have demonstrated that the catalytic surface of cobalt is not stable and is modified in the course of the hydrolysis reaction, leading to the deactivation of the catalyst [21]. This is a further complication. We have shown that the surface of fresh cobalt supported on nickel foam is initially clean (i.e. free of surface-adsorbed species), but after hydrolysis, the surface is covered by a film consisting of strongly-adsorbed (poly)borates. This is consistent with Kim et al.'s observation about nickel filamentary catalysts [22]. Consequently, we have suggested that the catalytically active phase of cobalt is a core@shell-type structure where the core is cobalt and the shell (poly)borates (Fig. 1).

Despite the aforementioned difficulties, which can be simply explained in terms of experimental problems, mechanistic schemes have been tentatively elaborated and proposed in the open literature. In some of those works, kinetic studies based on known kinetic models (e.g., Langmuir–Hinshelwood and Michaelis–Menten models) were conducted in order to gain new insight into hydrolysis mechanisms. These studies are reported and discussed in details herein. In this context, we propose a short review aiming at (i) reporting the hydrolysis mechanisms proposed up to now as well as the kinetic models used for this purpose, and (ii) discussing their reliability on the basis of the original phase of the catalytic cobalt (core@shell-type structure) we found.

2. Kinetic studies and models

There are various kinetic models that can be used to fit the experimental data (generally the volume or mole number of hydrogen as a function of time) of metal-catalyzed hydrolysis of aqueous alkaline solution of sodium borohydride and then to give a first interpretation of the reaction mechanisms. To date, five different models have been considered: the *n*th-order kinetics, where *n* is equal to 0, 1 or 2; the power law; the Langmuir–Hinshelwood model; the Michaelis–Menten one; and the semi-empirical kinetics. These models were surveyed in 2011 by Retnamma et al. [23], who especially showed

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