Short communication

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Hydrogen generation by both acidic and catalytic hydrolysis of sodium borohydride

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Abstract: Sodium borohydride tablets have been employed as hydrogen-storage materials. Hydrogen release was performed by acidic hydrolysis where solutions of sulfuric and hydrochloric acids were added to the tablets, and by catalytic hydrolysis where water was added tablets of solid-state NaBH₄/Co composite. In acidic solutions hydrogen evolution occurred instantaneously, and at high concentrations of acids the releasing hydrogen contained an admixture of diborane. Hydrogen evolution from the solid-state NaBH₄/Co composite proceeded at a uniform rate of 13.8±0.1 cm³·min⁻¹, water vapor being the only impurity in the evolving gas.

Keywords: Hydrogen, sodium borohydride, acid hydrolysis, diborane, catalyst hydrolysis

1 Introduction

The development of compact hydrogen sources is an important direction of hydrogen energy research [1-7]. Compact hydrogen sources must provide high yields of hydrogen per unit of mass or volume without any additional heating, as well as purification of hydrogen from compounds that act as catalytic poisons for electrodes of low-temperature proton exchange membrane fuel cells, requirements strongly narrowing the range of hydrogen-generating materials suitable for energy-carrier applications. Binary and complex hydrides of alkali metals most closely satisfy these severe requirements [8-13]. First, they have no rivals in the mass content of hydrogen. For example, potassium borohydride, sodium borohydride and ammonia borane have hydrogen densities of 0.083, 0.112 and 0.145 g·cm⁻³, respectively, which exceeds the value for liquefied hydrogen (0.07 g·cm⁻³). Second, hydride interaction with water increases the hydrogen yield twofold, water being involved in the gas generation.

\[ MH_n + nH_2O \rightarrow M(OH)_n + nH_2 \uparrow, \text{ (1)} \]

where M is an alkali or alkaline-earth metal.

However, hydrolysis of hydrides is not a totally safe process, since it evolves a large amount of heat per mole of hydrogen: LiH - 145 kJ·mol⁻¹; MgH₂ - 160 kJ·mol⁻¹; LiBH₄ - 90 kJ·mol⁻¹; LiAlH₄ - 150 kJ·mol⁻¹; NaBH₄ - 142 kJ·mol⁻¹; AlH₃ - 156 kJ·mol⁻¹; CaH₂ - 140 kJ·mol⁻¹; NaH - 152 kJ·mol⁻¹ [14,15]. Unlike most hydrides, sodium borohydride interaction with water has a comparatively small heat effect (80 kJ per mole of hydrogen) so that its complete conversion can be achieved either at temperatures above 110 °C and in the presence of vapors of hydrochloric or acetic acids [16], or over metal catalysts [17,18] which opens the possibility of the control of the process of hydrogen generation. Inexpensive but active cobalt catalysts are most often used [19,20]. Acid catalysts prepared by modifying the support with sulfuric [21], boric, and citric [22] acids are also efficient in hydrogen generation from solutions of sodium borohydride.

Along with the catalytic sodium borohydride hydrolysis, hydrogen generation by adding inorganic or organic acids to a solution of this hydride has also been discussed in the literature [23-25]. It has been demonstrated that the addition of a weak solution (0.25 M) of phosphoric acid to sodium borohydride in the presence of a copper catalyst which has a low activity leads to a substantial growth in the hydrogen generation rate [26]. Nevertheless in dilute solutions of acids, complete conversion of this hydride could not be achieved without catalysts and increased concentrations of acids were used to increase...
the hydrogen yield and the rate of gas generation [27]. An XRD analysis of the non-gaseous products of the interaction of sodium borohydride with acids has shown them to be sodium borates and sodium salts of the corresponding acids [28]. According to a chromatographic analysis, the hydrogen-containing gas did not contain any impurities even in the case of hydrochloric acid [29]. This result is doubtful and needs additional investigation since hydrogen chloride easily evaporates and is always present above a hydrochloric acid solution.

Despite the convenience of aqueous sodium borohydride solutions for hydrogen generation by acidic and catalytic hydrolysis, in storage the sodium borohydride slowly interacts with water even in the presence of sodium hydroxide [30-32]. This not only leads to a reduction in hydrogen content but also to changes in the character of the in situ reduction of cobalt catalysts because of the forming sodium tetrahydroxoborate [33].

Considering the instability of sodium borohydride solutions it was suggested that this hydride in the form of tablets may be stored and used for hydrogen generation [34-37]. The advantages of such an approach are: high content of hydrogen (up to 10 wt %), the absence of an alkali, no losses of hydrogen in storage, simplicity of operation using water from any natural source, as well as the possibility to vary the rate of gas generation by varying the amounts of the added inexpensive cobalt catalyst [38]. It is important to consider the composition of the gas evolving from the NaBH₄ tablet when used as a hydrogen source since impurities can poison fuel cell electrodes catalytically. To date, little attention has been paid to this issue in the literature. Also, there have been no publications comparing the efficiencies of hydrogen generation from solid-state compositions of NaBH₄ by acidic and catalytic hydrolysis.

The aims of this work are (I) to compare the kinetic regularities of hydrogen generation from sodium borohydride tablets in solutions of acids with different concentrations and from NaBH₄/Co tablets upon addition of water and (II) to determine the qualitative composition of the forming hydrogen-containing gas.

2 Methods

To prepare the tablets, a powder of sodium borohydride (CAS No 16940-66-2, 98 wt%) – 0.0352 g and a mechanical mixture of this hydride – 0.0352 g with a cobalt catalyst – 0.0117 g ((4Co:2B)cataylst in equation (2)) were pressed in a PRG-400 hydraulic press (Russia). The cobalt catalyst was prepared by the reduction of cobalt chloride (CAS No 7791-13-1, 97 wt%) in a 0.12 M aqueous solution of sodium borohydride at 40 °C with constant stirring at 400 rpm. The Co:NaBH₄ mole ratio was 1:25.

\[4CoCl₂ + 8NaBH₄ + 18H₂O → \]
\[(4Co : 2B)_{catalyst} + 6B(OH)₃ + 8NaCl + 25H₂ \uparrow \quad (2)\]

After gas evolution the black ferromagnetic catalyst precipitate was separated from the reaction medium, washed with acetone (CAS No 67-64-1, 99 wt%) and dried in a vacuum box at 70 °C for 2 hr. The synthesized cobalt catalyst was stored in desiccators under argon to prevent its oxidation by air. The reduction of the cobalt catalyst by sodium borohydride leads to the formation of spherical particles (average size 30 nm) consisting of a core of amorphous cobalt-boron and an oxygen-containing shell (thickness 3-5 nm). In an earlier study the molar ratio of the elements in such cobalt-boron catalysts was found to be Co:B:H=3:2:1.5:1.4:1 [39]. The physicochemical properties of the prepared cobalt catalyst have been described in detail elsewhere [39,40].

The elemental composition of the catalyst was identified by atomic-emission spectroscopy with inductively-coupled plasma on an Optima 4300V instrument (Germany). The relative error of determination of cobalt and boron did not exceed 5 %.

For the hydrogen generation kinetic study, the tablets were placed into a temperature-controlled glass reactor at 40 °C and then 5 cm³ of water or an acid solution of a given concentration (H₂SO₄ – from 6.2 to 98 wt%, CAS No 7664-93-9; HCl – 34 wt%, CAS No 7647-01-0) was added. The volume of the evolving gas was determined volumetrically using a gas burette and reduced to normal conditions (N refers to normal conditions, i.e., 0°C, 1 atm). Each experiment was repeated three times and the average values were taken to construct the kinetic dependences. The relative experimental error did not exceed 2 %.

The qualitative analysis of the hydrogen-containing gas was performed on a Nicolet 380 IR-spectrometer (Thermo Scientific, USA). The spectrometer was equipped with a gas cell with an optical path length of 10 cm. The scan space was from 900 to 4000 cm⁻¹, the resolution was 1 cm⁻¹. Each spectrum was averaged over 64 scans. The absorption bands were assigned using the NIST Chemistry WebBook [41].

3 Results and Discussion

The kinetics of hydrogen evolution upon the addition of sulfuric or hydrochloric acids to tablets of sodium
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The interaction of sodium borohydride with acids has been demonstrated to proceed very swiftly (Fig. 2). The reaction was completed within 10 seconds. Addition of a diluted sulfuric acid solution (6.2 wt %) led to the evolution of 83 Ncm\(^3\) of hydrogen-containing gas which corresponds to complete hydride conversion. An IR analysis has shown that the evolved gas (Fig. 3) did not contain impurities other than water vapor since in the IR spectrum only the vibrations of deformational vibrations H–O–H at 1600 cm\(^{-1}\) are observed [42-44].

Unlike the heterogeneous catalysts [45,46], the acids are reagents which are used up during reaction. For smaller volumes of acids more concentrated solutions were used [27,28]. Our investigations (Fig. 2) have shown that the volume of the evolving gas decreased with an increasing concentration of sulfuric acid. First of all, this may be caused by the formation of diborane, the presence of which, in the hydrogen-containing gas, was confirmed by IR spectroscopy (Fig. 3). IR spectra of gaseous products formed in the presence of a highly-concentrated acid show a series of absorption bands at 970, 1170, 1600, 1870, 2520 and 2610 cm\(^{-1}\) characteristic of diborane (Table 1).

The obtained results are in good agreement with the mechanism of interaction of sodium borohydride with acids in diluted and concentrated solutions. According to [50-53], in an acid medium the interaction of a proton with the borohydride anion occurs via the formation of an intermediate complex \(\text{H}_2\text{BH}_4\) (or \(\text{H}^+\text{BH}_4^-\)) which decomposes to form molecular hydrogen and borane.
Table 1. Vibration frequencies of diborane [47-49].

<table>
<thead>
<tr>
<th>Frequency, cm(^{-1})</th>
<th>Intensity</th>
<th>Symmetry*</th>
<th>Mode</th>
<th>Character of diborane vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>960...980</td>
<td>strong</td>
<td>B(_{2u})</td>
<td>(n_{14})</td>
<td></td>
</tr>
<tr>
<td>1160...1180</td>
<td>very strong</td>
<td>B(_{3u})</td>
<td>(n_{18})</td>
<td></td>
</tr>
<tr>
<td>1580...1610</td>
<td>very strong</td>
<td>B(_{3u})</td>
<td>(n_{17})</td>
<td></td>
</tr>
<tr>
<td>1860...1880</td>
<td>strong</td>
<td>B(_{2u})</td>
<td>(n_{13})</td>
<td></td>
</tr>
<tr>
<td>2510...2570</td>
<td>very strong</td>
<td>B(_{2u})</td>
<td>(n_{15})</td>
<td></td>
</tr>
<tr>
<td>2610...2630</td>
<td>strong</td>
<td>B(_{1u})</td>
<td>(n_{8})</td>
<td></td>
</tr>
</tbody>
</table>

* B – antisymmetric with respect to the main axis of symmetry.
- hydrogen; – boron.

\[ H_2BH_3 \leftrightarrow BH_3 + H_2 \uparrow \] (3)

The formation of borane (BH\(_3\)) has been confirmed experimentally by converting it to trimethylamine borane [54] and sodium trihydrocyanoborate [55]. In concentrated acids (sulfuric, phosphoric and others) dimerization of borane was observed.

\[ 2BH_3 \rightarrow B_2H_6 \uparrow \] (4)

Such an approach has often been employed to prepare diborane under laboratory conditions [58]. Hence, in highly concentrated solutions the interaction between the acid and sodium borohydride is described by the equation [56,57]:

\[ 2NaBH_4 + H_2SO_4 \rightarrow Na_2SO_4 + B_2H_6 + 2H_2 \uparrow \] (5)

\[ 2NaBH_4 + 2HCl \rightarrow 2NaCl + B_2H_6 + 2H_2 \uparrow \] (6)

In this case, the hydrogen sources are sodium borohydride and acid.

In dilute acids BH\(_3\) was instantly hydrolized which increased the hydrogen content in the forming gas [59], since water is an additional source of hydrogen:

\[ BH_3 + 3H_2O \rightarrow B(OH)_3 + 3H_2 \uparrow \] (7)

Hence, in dilute solutions the reaction between the acid and hydride can be described as follows [28]:

\[ 2NaBH_4 + 6H_2O + H_2SO_4 \rightarrow Na_2SO_4 + 2B(OH)_3 + 8H_2 \uparrow \] (8)
$NaBH_4 + 3H_2O + HCl \rightarrow NaCl + B(OH)_3 + 4H_2 \uparrow$ (9)

Thus, in our work, when the concentration of sulfuric acid was reduced (Fig. 2) the dimerization of borane was suppressed by the hydrolysis of borane in excess water. This is also the reason for the reduction of diborane in the hydrogen-containing gas.

It should be noted that the gas forming in highly concentrated solutions of sulfuric and hydrochloric acids also contains, apart from the diborane, impurities of sulfur oxides and hydrogen chloride, respectively. The presence of sulfur oxides is indicated by observation of the absorption band at 1410 cm$^{-1}$ [60] while the presence of hydrogen chloride follows from the absorption at 2600 to 3100 cm$^{-1}$ [61,62]. The presence of such impurities means that the hydrogen-containing gas must be purified before it can be used in fuel cell applications.

In the presence of a cobalt catalyst the sodium borohydride hydrolysis proceeded at a uniform rate and was completed within 6 minutes (Fig. 2) to produce 83 Ncm$^3$ of the gas. In this case, the hydrogen sources are sodium borohydride and water:

$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_3 + 4H_2 \uparrow$$ (10)

At the onset of the reaction the $NaBH_4/Co$ tablets dissolved, accompanied by a growth in the reaction rate (Fig. 2). After 30 sec the rate of the catalytic interaction of hydride with water became constant and was equal to 13.8±0.1 cm$^{-1}$·min$^{-1}$. The quantity of the hydride remaining in the reaction medium did not influence the process rate, indicating that the reaction was zero-order in sodium borohydride. Similar behavior of sodium borohydride hydrolysis has been observed not only in the presence of a cobalt catalyst [63-66], but also in the presence of ruthenium [67-70], nickel [71-73], platinum [74] and bimetallic Ni-Co [75], Ni-Ru [76], Co-Mn [77] catalysts. The main reason for the constant rate of reagent conversion may be the limited quantity of catalyst in the reaction medium. By varying the content of the cobalt catalyst in the tablets it is possible to set required rates of hydrogen generation as was demonstrated in [38]. It should be noted that according to IR spectroscopy data (Fig. 3) only water vapor was present as an impurity in the forming hydrogen which allowed its use in a proton exchange membrane fuel cell without humidification [78].

### 4 Conclusions

The kinetic regularities of the release of hydrogen from sodium borohydride tablets upon addition of sulfuric or hydrochloric acids, and from tablets that are a mixture of sodium borohydride and a cobalt catalyst upon addition of water have been studied. It was demonstrated that in solutions of acids the conversion of the hydride proceeded swiftly. The reaction time was less than 10 seconds. In the 6.2 wt% solution of sulfuric acid the released gas contained only water vapors. In more concentrated solutions a quantity of diborane was observed that increased with increasing acid content. This shows that in highly concentrated acid solutions the dimerization of borane (as an intermediate) takes place, giving the presence of diborane in the hydrogen-containing gas. Apart from diborane, in highly concentrated solutions of sulfuric and hydrochloric acids the gas released also contained impurities of sulfur oxides and hydrogen chloride, respectively.

Sodium borohydride interaction with water in the presence of a cobalt catalyst proceeded at a uniform rate and was completed within 6 min. It was demonstrated that in this case water vapor was the only impurity in the released hydrogen allowing the hydrogen to be supplied to the anode space of a proton exchange membrane fuel cell without purification and humidification. Control over the hydrogen generation rate is possible by varying the cobalt catalyst content in tablets.

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### References


