

## Short communication

Olga V. Netskina\*, Tihon N. Filippov, Oksana V. Komova, Valentina I. Simagina

# Hydrogen generation by both acidic and catalytic hydrolysis of sodium borohydride

<https://doi.org/10.1515/cse-2018-0006>

Received October 9, 2018; accepted October 16, 2018

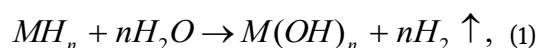
**Abstract:** Sodium borohydride tablets have been employed as hydrogen-storage materials. Hydrogen release was performed by acidic hydrolysis where solutions of sulfuric and hydrochloric acids were added to the tablets, and by catalytic hydrolysis where water was added tablets of solid-state  $\text{NaBH}_4/\text{Co}$  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  $\text{NaBH}_4/\text{Co}$  composite proceeded at a uniform rate of  $13.8 \pm 0.1 \text{ cm}^3 \cdot \text{min}^{-1}$ , 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  $0.145 \text{ g} \cdot \text{cm}^{-3}$ , respectively, which exceeds the value for liquefied hydrogen ( $0.07 \text{ g} \cdot \text{cm}^{-3}$ ). Second, hydride interaction with water increases the hydrogen yield twofold, water being involved in the gas generation.



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:  $\text{LiH} - 145 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{MgH}_2 - 160 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{LiBH}_4 - 90 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{LiAlH}_4 - 150 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{NaAlH}_4 - 142 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{AlH}_3 - 156 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{CaH}_2 - 140 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $\text{NaH} - 152 \text{ kJ} \cdot \text{mol}^{-1}$  [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  $110 \text{ }^\circ\text{C}$  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

\*Corresponding author: Olga V. Netskina, Laboratory of Hydrides Investigation, Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5, Novosibirsk, 630090, Russia, [netskina@catalysis.ru](mailto:netskina@catalysis.ru)  
Tihon N. Filippov, Photocatalysis group, Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5, Novosibirsk, 630090, Russia

Oksana V. Komova, Valentina I. Simagina, Laboratory of Hydrides Investigation, Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5, Novosibirsk, 630090, Russia

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].

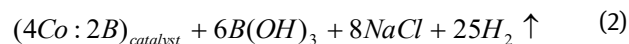
Considering the instability of sodium borohydride solutions it was suggested that this hydride in the form of tablets may be stored and used for hydrogen generation [34-37]. The advantages of such an approach are: high content of hydrogen (up to 10 wt %), the absence of an alkali, no losses of hydrogen 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 NaBH<sub>4</sub> 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 NaBH<sub>4</sub> 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 NaBH<sub>4</sub>/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)*catalyst* 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:NaBH<sub>4</sub> mole ratio was 1:25.



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:O: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 cm<sup>3</sup> of water or an acid solution of a given concentration (H<sub>2</sub>SO<sub>4</sub> – 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<sup>-1</sup>, the resolution was 1 cm<sup>-1</sup>. 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

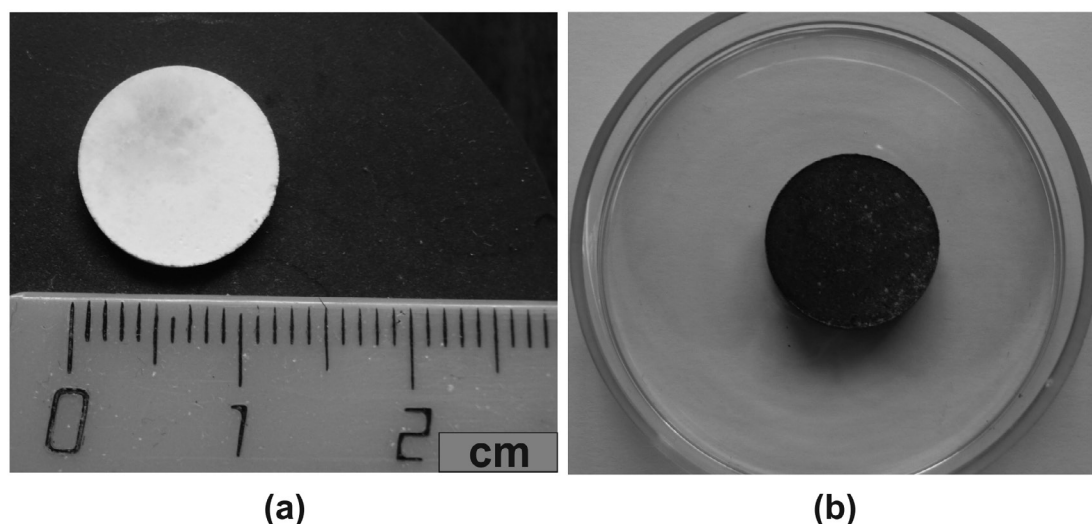


Figure 1. Solid-state (a)  $\text{NaBH}_4$  and (b)  $\text{NaBH}_4/\text{Co}$  tablets.

borohydride (Fig. 1a) was compared with that upon the addition of water to tablets of a solid-state  $\text{NaBH}_4/\text{Co}$  composite (Fig. 1b).

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  $83 \text{ Ncm}^3$  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  $1600 \text{ cm}^{-1}$  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  $2610 \text{ cm}^{-1}$  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  $\text{H}_2\text{BH}_3$  (or  $\text{H}^+\times\text{BH}_4^-$ ) which decomposes to form molecular hydrogen and borane.

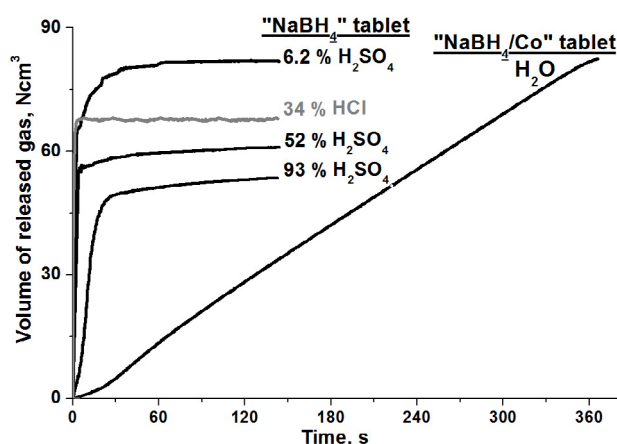


Figure 2. Acidic and catalytic hydrolysis of sodium borohydride.

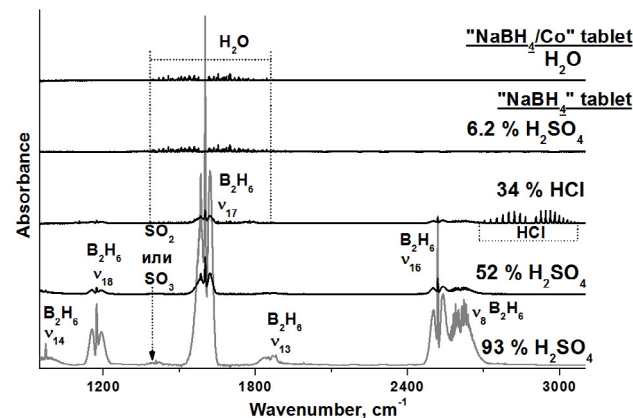
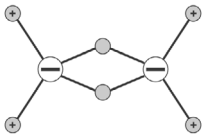
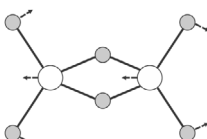
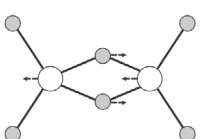
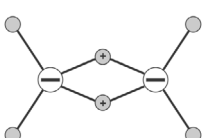
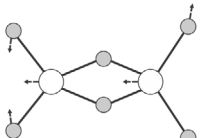
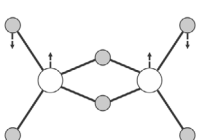


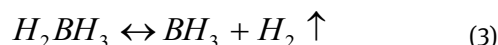
Figure 3. IR spectra of hydrogen-containing gas generated by acidic and catalytic hydrolysis of sodium borohydride.

**Table 1.** Vibration frequencies of diborane [47-49].

Frequency, cm <sup>-1</sup>	Intensity	Symmetry*	Mode	Character of diborane vibration
960...980	strong	B <sub>2u</sub>	n <sub>14</sub>	
1160...1180	very strong	B <sub>3u</sub>	n <sub>18</sub>	
1580...1610	very strong	B <sub>3u</sub>	n <sub>17</sub>	
1860...1880	strong	B <sub>2u</sub>	n <sub>13</sub>	
2510...2570	very strong	B <sub>3u</sub>	n <sub>16</sub>	
2610...2630	strong	B <sub>1u</sub>	n <sub>8</sub>	

\*B – antisymmetric with respect to the main axis of symmetry.

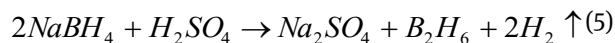
– hydrogen; – boron.



The formation of borane (BH<sub>3</sub>) 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.

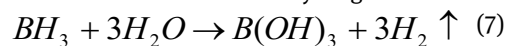


Such an approach has often been employed to prepare diborane under laboratory conditions [58]. Hence, in highly concentrated solutions the interaction between the acid and sodium borohydride is described by the equation [56,57]:

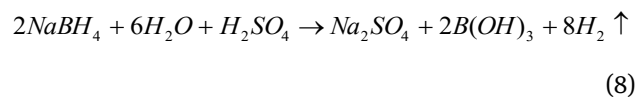


In this case, the hydrogen sources are sodium borohydride and acid.

In dilute acids BH<sub>3</sub> was instantly hydrolyzed which increased the hydrogen content in the forming gas [59], since water is an additional source of hydrogen:



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





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  $1410\text{ cm}^{-1}$  [60] while the presence of hydrogen chloride follows from the absorption at  $2600$  to  $3100\text{ cm}^{-1}$  [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  $83\text{ Ncm}^3$  of the gas. In this case, the hydrogen sources are sodium borohydride and water:



At the onset of the reaction the  $\text{NaBH}_4/\text{Co}$  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  $13.8 \pm 0.1\text{ cm}^3 \cdot \text{min}^{-1}$ . 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 it 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.

**Acknowledgements:** This work was conducted within the framework of the budget project No. 0303-2016-0015 for Boreskov Institute of Catalysis. The authors are grateful to Tayban E.S. for providing kinetic experiments.

## References

- [1] Abdalla A.M., Hossain S., Nisfindy O.B., Azad A.T., Dawood M., Azad A.K., Hydrogen production, storage, transportation and key challenges with applications: A review, *Energ. Convers. Manage.*, 2018, 165, 602-627.
- [2] Züttel A., Hydrogen storage methods, *Naturwissenschaften*, 2004, 91, 157-172.
- [3] Niaz S., Manzoor T., Pandith A.H., Hydrogen storage: Materials, methods and perspectives, *Renew. Sust. Energ. Rev.* 2015, 50, 457-469.
- [4] Zacharia R., Rather S.U., Review of solid state hydrogen storage methods adopting different kinds of novel materials, *J. Nanomater.*, 2015, 2015, 914845.
- [5] Durbin D.J., Malardier-Jugroot C., Review of hydrogen storage techniques for on board vehicle applications, *Int. J. Hydrogen Energy*, 2013, 38, 14595-14617.

- [6] Pukazhselvan D., Kumar V., Singh S.K., High capacity hydrogen storage: Basic aspects, new developments and milestones, *Nano Energy*, 2012, 1, 566-589.
- [7] Jiang H.-L., Singh S.K., Yan J.-M., Zhang X.-B., Xu Q., Liquid-Phase chemical hydrogen storage: Catalytic hydrogen generation under ambient conditions, *ChemSusChem*, 2010, 3, 541-549.
- [8] Mohtadi R., Remhof A., Jena P., Complex metal borohydrides: Multifunctional materials for energy storage and conversion, *J. Phys.: Condens. Matter.*, 28 (2016) 353001.
- [9] Ley M.B., Jepsen L.H., Lee Y.-S., Cho Y.W., Bellosta Von Colbe J.M., Dornheim M., Rokni M., Jensen J.O., Sloth M., et al., Complex hydrides for hydrogen storage - New perspectives, *Mater. Today*, 2014, 17, 122-128.
- [10] Yadav M., Xu Q., Liquid-phase chemical hydrogen storage materials, *Energy Environ Sci.*, 2012, 5, 9698-9725.
- [11] Chen P., Hydrogen storage: Liquid and chemical, In: A. Sayigh (Ed.), *Comprehensive Renewable Energy: Fuel Cells and Hydrogen Technology*, Elsevier Ltd., Amsterdam, 2012.
- [12] Li H.-W., Yan Y., Orimo S.-I., Züttel A., Jensen C.M., Recent progress in metal borohydrides for hydrogen storage, *Energies*, 2011, 4, 185-214.
- [13] Jain I.P., Jain P., Jain A., Novel hydrogen storage materials: A review of lightweight complex hydrides, *J. Alloys Compd.*, 2010, 503, 303-339.
- [14] Kong V.C.Y., Foulkes F.R., Kirk D.W., Hinatsu J.T., Development of hydrogen storage for fuel cell generators. I: Hydrogen generation using hydrolysis hydrides, *Int. J. Hydrogen Energy*, 1999, 24, 665-675.
- [15] Fakioglu E., Yurum Y., Veziroglu T.N., A review of hydrogen storage systems based on boron and its, *Int. J. Hydrogen Energy*, 2004, 29, 1371-1376.
- [16] Akkuş M.S., Murathan H.B., Özgür D.Ö., Özkan G., Özkan G., New insights on the mechanism of vapour phase hydrolysis of sodium borohydride in a fed-batch reactor, *Int. J. Hydrogen Energy*, 2018, 43, 10734-10740.
- [17] Demirci U.B., Akdim O., Andrieux J., Hannauer J., Chamoun R., Miele P., Sodium borohydride hydrolysis as hydrogen generator: Issues, state of the art and applicability upstream from a fuel cell, *Fuel Cells*, 2010, 10, 335-350.
- [18] Liu B.H., Li Z.P., A review: Hydrogen generation from borohydride hydrolysis reaction, *J. Power Sources*, 2009, 187, 527-534.
- [19] Demirci U.B., Miele P., Cobalt in  $\text{NaBH}_4$  hydrolysis, *Phys. Chem. Chem. Phys.*, 2010, 12, 14651-14665.
- [20] Zhong H., Ouyang L.Z., Ye J.S., Liu J.W., Wang H., Yao X.D., Zhu M., An one-step approach towards hydrogen production and storage through regeneration of  $\text{NaBH}_4$ , *Energy Storage Materials*, 2017, 7, 222-228.
- [21] Manna J., Roy B., Sharma P., Efficient hydrogen generation from sodium borohydride hydrolysis using silica sulfuric acid catalyst, *J. Power Sources*, 2015, 275, 727-733.
- [22] Nabid M.R., Bide Y., Fereidouni N., Boron and nitrogen co-doped carbon dots as a metal-free catalyst for hydrogen generation from sodium borohydride, *New J. Chem.*, 2016, 40, 8823-8828.
- [23] Kim H.J., Shin K.-J., Kim H.-J., Han M.K., Kim H., Shul Y.-G., Jung K.T., Hydrogen generation from aqueous acid-catalyzed hydrolysis of sodium borohydride, *Int. J. Hydrogen Energy*, 2010, 35, 12239-12245.
- [24] Akdim O., Demirci U.B., Miele P., Acetic acid, a relatively green single-use catalyst for hydrogen generation from sodium borohydride, *Int. J. Hydrogen Energy*, 2009, 34, 7231-7238.
- [25] Balbay A., Sahin O., Hydrogen production from sodium borohydride in boric acid water mixtures., *Energ. Source Part A.*, 2014, 36, 1166-1174.
- [26] Balbay A., Saka C., Effect of phosphoric acid addition on the hydrogen production from hydrolysis of  $\text{NaBH}_4$  with Cu based catalyst, *Energ. Source Part A.*, 2018, 40, 794-804.
- [27] Javed U., Subramanian V.(R.), Hydrogen generation using a borohydride-based semi-continuous milli-scale reactor: Effects of physicochemical parameters on hydrogen yield, *Energy Fuels*, 2009, 23, 408-413.
- [28] Murugesan S., Subramanian V.(R.), Effects of acid accelerators on hydrogen generation from solid sodium borohydride using small scale devices, *J. Power Sources*, 2009, 187, 216-223.
- [29] Abdul-Majeed W.S., Arslan M.T., Zimmerman W.B., Application of acidic accelerator for production of pure hydrogen from  $\text{NaBH}_4$ , *Int. J. Ind. Chem.*, 2014, 5, 15.
- [30] Minkina V.G., Shabunya S.I., Kalinin V.I., Martynenko V.V., Stability of aqueous-alkaline sodium borohydride formulations, *Russ. J. Appl. Chem.*, 2008, 81, 380-385.
- [31] Minkina V.G., Shabunya S.I., Kalinin V.I., Martynenko V.V., Smirnova A.L., Stability of Alkaline Aqueous Solutions of Sodium Borohydride, *Int. J. Hydrogen Energy*, 2012, 37, 3313-3318.
- [32] Netskina O.V., Komova O.V., Mukha S.A., Simagina V.I., Aqueous-alkaline  $\text{NaBH}_4$  solutions: The influence of hydride decomposition on catalytic properties of  $\text{Co}_3\text{O}_4$ , *Catal. Commun.*, 2016, 85, 9-12.
- [33] Netskina O.V., Komova O.V., Simagina V.I., Odegova G.V., Prosvirin I.P., Bulavchenko O.A., Aqueous-alkaline  $\text{NaBH}_4$  solution: The influence of storage duration of solutions on reduction and activity of cobalt catalysts, *Renewable Energy*, 2016, 99, 1073-1081.
- [34] Liu B.H., Li Z.P., Suda S., Solid sodium borohydride as a hydrogen source for fuel cells, *J. Alloys Compd.*, 2009, 468, 493-498.
- [35] Liu C.-H., Kuo Y.-C., Chen B.-H., Hsueh C.-L., Hwang K.-J., Ku J.-R., Tsau F., Jeng M.-S., Synthesis of solid-state  $\text{NaBH}_4/\text{Co}$ -based catalyst composite for hydrogen storage through a high-energy ball-milling, *Int. J. Hydrogen Energy*, 2010, 35, 4027-4040.
- [36] Netskina O.V., Ozerova A.M., Komova O.V., Odegova G.V., Simagina V.I., Hydrogen storage systems based on solid-state  $\text{NaBH}_4/\text{Co}_x\text{B}$  composite: Influence of catalyst properties on hydrogen generation rate, *Catal. Today*, 2015, 245, 86-92.
- [37] Netskina O.V., Komova O.V., Prosvirin I.P., Pochtar' A.A., Ozerova A.M., Simagina V.I., Solid-State Hydrogen-Generating Composites Based on Sodium Borohydride: Effect of the Heat Treatment of Boron-Cobalt Catalysts on the Hydrogen Generation Rate, *Russ. J. Appl. Chem.*, 2017, 90, 1666-1673.
- [38] Simagina V.I., Ozerova A.M., Komova O.V., Odegova G.V., Kellerman D.G., Fursenko R.V., Odintsov E.S., Netskina O.V., Cobalt boride catalysts for small-scale energy application, *Catal. Today*, 2015, 242, 221-229.
- [39] Netskina O.V., Ozerova A.M., Komova O.V., Kochubey D.I., Kanazhevskiy V.V., Ishchenko A.V., Simagina V.I., The effect of heat-treatment temperature of cobalt-boron catalysts on their

- activity in sodium borohydride hydrolysis, *Top. Catal.*, 2016, 59, 1431–1437.
- [40] Netskina O.V., Kochubey D.I., Prosvirin I.P., Malykhin S.E., Komova O.V., Kanazhevskiy V.V., Chukalkin Yu.G., Bobrovskii V.I., Kellerman D.G., Ishchenko A.V., et al., Cobalt-boron catalyst for  $\text{NaBH}_4$  hydrolysis: The state of the active component forming from cobalt chloride in a reaction medium, *Mol. Catal.*, 2017, 441, 100–108.
- [41] NIST Chemistry WebBook: NIST Standard Reference Database, No 69, 2018. <https://webbook.nist.gov/chemistry>.
- [42] Devlin J.P., Sadlej J., Buch V., *Infrared Spectra of Large H<sub>2</sub>O Clusters: New Understanding of the Elusive Bending Mode of Ice*, *J. Phys. Chem. A*, 2001, 105, 974–983.
- [43] Roscioli J.R., Diken E.G., Johnson M.A., Horvath S., McCoy A.B., Prying Apart a Water Molecule with Anionic H-Bonding: A Comparative Spectroscopic Study of the  $\text{X}\cdot\text{H}_2\text{O}$  ( $\text{X} = \text{OH}, \text{O}, \text{F}, \text{Cl}, \text{and Br}$ ) Binary Complexes in the 600–3800  $\text{cm}^{-1}$  Region, *J. Phys. Chem. A*, 2006, 110, 4943–4952.
- [44] Brubach J.-B., Mermet A., Filabozzi A., Gerschel A., Roy P., Signatures of the hydrogen bonding in the infrared bands of water, *J. Chem. Phys.*, 2005, 122, 184509.
- [45] Brack P., Dann S.E., Upul Wijayantha K.G., Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride  $\text{NaBH}_4$  solutions, *Energy Sci. Eng.*, 2015, 3, 174–188.
- [46] Simagina V.I., Komova O.V., Netskina O.V., Nano-sized cobalt catalysts for hydrogen storage systems based on ammonia borane and sodium borohydride, In: A.A. Gromov, U. Teipel (Eds.), *Metal Nanopowders: Production, Characterization, and Energetic Applications*, Wiley-VCH, Verlag, 2014.
- [47] Bell R.P., Longuet-Higgins H.C., The normal vibrations of bridged  $\text{X}_2\text{Y}_6$  molecules, *Proc. R. Soc. London, A*, 1945, 183, 357–374.
- [48] Price W.C., The absorption spectrum of diborane, *J. Chem. Phys.*, 1948, 16, 894–902.
- [49] Song Y., Murli C., Liu Z., In situ high-pressure study of diborane by infrared spectroscopy, *J. Chem. Phys.*, 2009, 131, 174506.
- [50] Davis R.E., Swain C.G., General acid catalysis of the hydrolysis of sodium borohydride, *J. Am. Chem. Soc.*, 1960, 82, 5949–5950.
- [51] Kreevoy M.M., Hutchins J.E.C.,  $\text{H}_2\text{BH}_3$  as intermediate in tetrahydridoborate hydrolysis, *J. Am. Chem. Soc.*, 1972, 94, 6371–6376.
- [52] Olah G.A., Westerman P.W., Mo Y.K., Klopman G., Electrophilic reactions at single bonds. VII. Hydrogen-deuterium exchange accompanying protolysis (deuterolysis) of the borohydride and aluminum hydride anion with anhydrous strong acids. The intermediacy of pentahydroboron ( $\text{BH}_3$ ) and pentahydroaluminum ( $\text{AlH}_3$ ) and their structural relationship with the methonium ion ( $\text{CH}_3^+$ ), *J. Am. Chem. Soc.*, 1972, 94, 7859–7862.
- [53] Willen R., Possible mechanisms of the reaction between tetrahydridoborate and hydrogen ion: A permutational analysis, *J. Chem. Soc., Dalton Trans.*, 1979, 1, 33–40.
- [54] Davis R.E., Boron hydrides. IV. Concerning the geometry of the activated complex in hydrolysis of borohydride ion by trimethylammonium ion, *J. Am. Chem. Soc.*, 1962, 84, 892–894.
- [55] Levine L.A., Kreevoy M.M., Solvent isotope effects on tetrahydridoborate hydrolysis, *J. Am. Chem. Soc.*, 1972, 94, 3346–3349.
- [56] Schlesinger H.I., Brown H.C., Metallo Borohydrides. III. Lithium Borohydride, *J. Am. Chem. Soc.*, 1940, 62, 3429–3435.
- [57] Brown H.C., Schlesinger H.I., Sheft I., Ritter D.M., Addition Compounds of Alkali Metal Hydrides. Sodium Trimethoxyborohydride and Related Compounds, *J. Am. Chem. Soc.*, 1953, 75, 192–195.
- [58] Duke B.J., Gulbert J.R., Read I.A., Preparation and purification of diborane, *J. Chem. Soc. A*, 1964, 540–542.
- [59] Weiss H.G., Shapiro I., Diborane from the sodium borohydride-sulfuric acid reaction, *J. Am. Chem. Soc.*, 1959, 81, 6167–6168.
- [60] Dunn J.P., Koppula P.R., Stenger H.G., Wachs I.E., Oxidation of sulfur dioxide to sulfur trioxide over supported vanadia catalysts, *Appl. Catal. B*, 1998, 19, 103–117.
- [61] Liu Y.-T., Tsai M.-T., Liu C.-Y., Tsai P.-Y., Lin K.-C., Shih Y.H., Chang A.H.H., Photodissociation of gaseous acetyl chloride at 248 nm by time-resolved fourier-transform infrared spectroscopy: The  $\text{HCl}$ ,  $\text{CO}$ , and  $\text{CH}_2$  product channels, *J. Phys. Chem. A*, 2010, 114, 7275–7283.
- [62] Robertson E.G., Medcraft C., Puskar L., Tuckermann R., Thompson C.D., Bauerecker S., McNaughton D., IR spectroscopy of physical and chemical transformations in cold hydrogen chloride and ammonia aerosols, *Phys. Chem. Chem. Phys.*, 2009, 11, 7853–7860.
- [63] Zhao J.Z., Ma H., Chen J., Improved hydrogen generation from alkaline solution using carbon-supported Co-B as catalysts, *Int. J. Hydrogen Energy*, 2007, 32, 4711–4716.
- [64] Andrieux J., Swierczynski D., Laversenne L., Garron A., Bennici S., Goutaudier C., Miele P., Auroux A., Bonnetot B., A multifactor study of catalyzed hydrolysis of solid  $\text{NaBH}_4$  on cobalt nanoparticles: thermodynamics and kinetics, *Int. J. Hydrogen Energy*, 2009, 34, 939–951.
- [65] Rakap M., Ozkar S., Intrazeolite cobalt (0) nanoclusters as low-cost and reusable catalyst for hydrogen generation from the hydrolysis of sodium borohydride, *Appl. Catal. B*, 2009, 91, 21–29.
- [66] Zhang X., Zhao J., Cheng F., Liang J., Tao Z., Chen J., Electroless-deposited Co-P catalysts for hydrogen generation from alkaline  $\text{NaBH}_4$  solution, *Int. J. Hydrogen Energy*, 2010, 35, 8363–8369.
- [67] Amendola S.C., Sharp-Goldman S.L., Janjua M.S., Kelly M.T., Petillo P.J., Binder M., An ultrasafe hydrogen gas generator: aqueous, alkaline borohydride solutions and Ru Catalyst, *J. Power Sources*, 2000, 85, 186–189.
- [68] Hsueh C.-L., Chen C.-Y., Ku J.-R., Tsai S.-F., Hsu Y.-Y., Tsau F., Jeng M.-S., Simple and fast fabrication of polymer template-Ru composite as a catalyst for hydrogen generation from alkaline  $\text{NaBH}_4$  solution, *J. Power Sources*, 2008, 177, 485–492.
- [69] Liang Y., Dai B.H., Ma L.P., Wang P., Cheng H.M., Hydrogen generation from sodium borohydride solution using a ruthenium supported on graphite catalyst, *Int. J. Hydrogen Energy*, 2010, 35, 3023–3028.
- [70] Ozkar S., Zahmakiran M., Hydrogen generation from hydrolysis of sodium borohydride using Ru(0) nanoclusters as catalyst, *J. Alloys Compd.*, 2005, 404–406, 728–731.
- [71] Hua D., Hanxi Y., Xiping A., Chuansin C., Hydrogen production from catalytic hydrolysis of sodium borohydride solution using nickel boride catalyst, *Int. J. Hydrogen Energy*, 2003, 28, 1095–1100.
- [72] Metin O., Ozkar S., Hydrogen generation from the hydrolysis of sodium borohydride by using water dispersible, hydrogen-phosphate-stabilized nickel (0) nanoclusters as catalyst, *Int. J. Hydrogen Energy*, 2007, 32, 1707–1715.

- [73] Liu B.H., Li Z.P., Suda S., Nickel- and cobalt-based catalysts for hydrogen generation by hydrolysis of borohydride, *J. Alloys Compd.*, 2006, 415, 288-293.
- [74] Guella G., Patton B., Miotello A., Kinetic features of the platinum catalyzed hydrolysis of sodium borohydride from  $^{11}\text{B}$  NMR measurements, *J. Phys. Chem. C*, 2007, 111, 18744-18750.
- [75] Ingersoll J.C., Mani N., Thenmozhihal J.C., Muthaiah A., Catalytic hydrolysis of sodium borohydride by a novel nickel-cobalt-boride catalyst, *J. Power Sources*, 2007, 173, 450-474.
- [76] Liu C.H., Chen B.H., Hsueh C.L., Ku J.R., Jeng M.S., Tsau F., Hydrogen generation from hydrolysis of sodium borohydride using Ni-Ru nanocomposite as catalysts, *Int. J. Hydrogen Energy*, 2009, 34, 2153-2163.
- [77] Mitov M., Rashkov R., Atanassov N., Effects of nickel foam dimensions on catalytic activity of supported Co-Mn-B nanocomposites for hydrogen generation from stabilized borohydride solutions, *J. Mater. Sci.*, 2007, 42, 3367-3372.
- [78] Vasu G., Tangirala A.K., Viswanathan B., Dhathathreyan K.S., Continuous bubble humidification and control of relative humidity of  $\text{H}_2$  for a PEMFC system, *Int. J. Hydrogen Energy*, 2008, 33, 4640-4648.