

Progress in the catalysts for H₂ generation from NaBH₄ fuel

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ABSTRACT

Over the past decade, sodium borohydride (NaBH₄) has been extensively investigated as a potential hydrogen storage material for fuel cell applications and other energy devices. For NaBH₄-H₂O fuel system the theoretical gravimetric hydrogen storage capacity is 10.8 wt.%, and H₂O provides half of the hydrogen generated. The successful utilization of NaBH₄ in energy system is dependent on the catalysts efficiency for NaBH₄ hydrolysis. In this review, the hydrogen storage technologies, the development of catalyst materials for NaBH₄ hydrolysis, the kinetics and mechanism of BH₄⁻ ions interaction with water on the catalyst surface are analyzed and discussed.

KEYWORDS: sodium borohydride, hydrolysis, catalyst, kinetics, mechanism, cobalt

1. INTRODUCTION

The application of hydrogen (H₂) as an energy carrier makes it necessary to solve an important problem related to the development of a compact system for hydrogen storage and generation, since at room temperature and atmospheric pressure hydrogen is a gas with a very low specific density (0.08 kg/m³). This problem is most topical for power devices with portable fuel cells, where an important factor is the amount of energy extracted from a unit weight and volume of the device, which depends primarily on the choice of hydrogen-containing fuel.

The U.S. Department of Energy has developed the requirements [1] that should be accounted for when devising compact sources of hydrogen for competitive mobile power plants based on fuel cells. Taking into account a complexity of the task and a lack of materials with the required properties, it was planned, starting from year 2004, to increase stepwise the hydrogen content, reduce its cost, and improve the quality of hydrogen generators. By now, numerous studies made it possible to determine the maximum attainable parameters for hydrogen storage systems. System gravimetric capacity 0.075 kg H₂/kg system (or 7.5 wt.% hydrogen), system volumetric capacity 0.07 kg H₂/L system, fuel cost 2-4 \$/gge at pump, operating ambient temperature -40 ÷ +60°C, fuel purity 99.97% (dry basis), start time to full flow 5 s are the targets with potential to meet ultimate targets.

According to the indicated requirements, conventional methods of hydrogen storage in compressed (15-35 MPa) or liquid state (20 K and 0.2 MPa) are unacceptable for compact energy sources due to low content of H₂ in a unit volume, big size of cryogenic units, high power consumption, and explosive risk [2]. The application of materials able to adsorb hydrogen allows increasing H₂ content in the system; therewith, H₂ capacity will grow with a decrease in temperature [3]. In the recent decade, many works were published on hydrogen storage in porous adsorption materials, and advanced materials with improved characteristics were devised; nevertheless, the main problem remains unsolved. It is still unclear how to retain the hydrogen capacity of materials on repeated use.

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Similar problems arise when developing the hydrogen storage systems based on metal hydrides and intermetallic compounds. Besides, these materials are characterized by a low gravimetric hydrogen capacity, which makes it difficult to use them in portable energy sources. Thus, density of intermetallic hydride $\text{LaNi}_5\text{H}_{6.6}$ is equal to 6 g/cm^3 , whereas the hydrogen content is as low as 1.4 wt.% [4]. At present, metal hydride storage cells are employed mainly as lab-scale stationary sources of hydrogen.

Great attention is paid to chemical compounds (hydrocarbons, water and hydrides) as forms of hydrogen storage. The reasons for their application as H_2 sources are high weight and volume contents of hydrogen. At present, main sources of hydrogen are natural gas and oil; in industry, H_2 is conventionally produced by the catalytic conversion of hydrocarbons, mostly methane and its homologs [5]. This method has some drawbacks: this is a multistep and energy intensive process (up to $20 \text{ MJ/m}^3 \text{ H}_2$). At that, the generated hydrogen requires additional purification from carbon oxides for its further use in the low-temperature solid polymer fuel cells with the proton exchange membrane.

In some works, biomass is considered as a renewable source of hydrogen [6]. Unfortunately, no breakthroughs are observed now in this field in spite of the long-term efforts of research teams. Low efficiency of hydrogen generation is still the main drawback.

Water serves as an inexhaustible source of hydrogen, electrolysis being the most common method of its decomposition. In industry, this process is used to obtain hydrogen and oxygen with purity 99.99%. However, this technology requires high energy consumption. For example, 20-22 MJ are needed to produce 1 m^3 of hydrogen. [7].

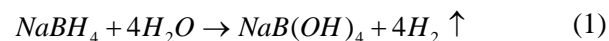
Hydrogen can be generated from water and via the hydrolysis of alkali and alkaline earth metals, aluminum, and their alloys [8]. The interaction of these substances with water proceeds violently and is accompanied by a pronounced heat release; so, hydrogen is usually produced using less active metals-magnesium and aluminum. Their modification with small amounts of transition

metals makes it possible to perform the process at ambient temperatures; however, this strongly increases the cost of resulting hydrogen [9].

Binary and complex hydrides can serve as alternative sources of hydrogen. Currently, these compounds have no competitors with respect to the gravimetric density of H_2 . Although various hydrides are available, when choosing a hydrogen source one should take into account not only the H_2 content, but also some other criteria [10]: physicochemical state, storage safety, accessibility of initial compounds for the synthesis of hydrides, environmental friendliness, thermal effect of the reaction, cost and commercial availability of the hydrides, simplicity of hydrogen generation at ambient temperatures, and a possibility to regenerate the reaction products. In view of these requirements, most researchers [11-14] focused their efforts on studying the hydrogen production from sodium borohydride at ambient temperatures ($0\text{-}60^\circ\text{C}$). The present work reviews publications on the interaction of sodium borohydride (I) with acids and (II) with water in the presence of catalysts. General regularities of hydrogen generation, reaction mechanism and main types of the catalysts are considered.

2. NaBH_4 as hydrogen storage

Among hydrides (Table 1), sodium borohydride (NaBH_4) plays a special role due to high H_2 content, reasonable cost, and stability of its alkaline solutions. Thus, density of hydrogen in sodium borohydride is ca. 0.112 g/cm^3 , which exceeds the density of liquid hydrogen (0.07 g/cm^3). Upon interaction of the hydride with water, hydrogen yield increases twofold due to reduction of water (1).



The resulting hydrogen is saturated only with water vapor [15], so it can be supplied to the anode of a fuel cell without additional purification and humidification.

The hydrolysis of NaBH_4 is accompanied by an increase in pH of the solution due to accumulation of sodium tetrahydroxoborate [16], which loses water upon heating and turns into sodium metaborate NaBO_2 [17]. For this reason, rate of

Table 1. Characteristics of chemical hydrides.

Hydride	H ₂ gravimetric density, m ³ /kg	H ₂ volumetric density, g _{H₂} /cm ³	Reaction type	Reaction enthalpy, kJ/mol H ₂
H ₂ O	1.24	0.111	Electrolysis	285
LiH	1.4	0.098	Thermolysis	181.3
			Hydrolysis	-145
NaH	0.47	0.059	Thermolysis	112.8
			Hydrolysis	-83.37
KH	0.28	0.036	Thermolysis	126.8
			Hydrolysis	-76.57
MgH ₂	0.85	0.11	Thermolysis	74.34
			Hydrolysis	-160
CaH ₂	0.53	0.090	Thermolysis	188.7
			Hydrolysis	-113.12
AlH ₃	1.12	0.147	Thermolysis	7.6
			Hydrolysis	-38.7
LiBH ₄	1.57	0.095	Thermolysis	97
			Hydrolysis	-90
NaBH ₄	1.18	0.112	Thermolysis	91.65
			Hydrolysis	-66.7
KBH ₄	0.83	0.087	Thermolysis	114.85
			Hydrolysis	-45.7
LiAlH ₄	1.18	0.097	Thermolysis	58.15
			Hydrolysis	-150
NaAlH ₄	0.83	0.067	Thermolysis	56.7
			Hydrolysis	-142
NH ₃ BH ₃	2.18	0.144	Thermolysis	59.3
			Hydrolysis	< -50

the reaction in clear water decreases with time [18], whereas in an alkaline medium the hydrolysis of sodium borohydride is suppressed virtually completely, which is of key importance for practical application of aqueous solutions of this hydride as a hydrogen source. The addition of alkali to an aqueous solution of NaBH₄ strongly extends its storage period without noticeable decomposition of the hydride [19, 20]. Additionally, this is accompanied by a decrease in the temperature of “liquid-solid” phase transition for the water-alkaline solutions of NaBH₄. For example, a solution containing 15% of NaBH₄ and 10% of NaOH does not freeze even at 40°C below zero [21]. However, the production of hydrogen

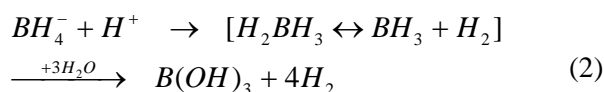
from stabilized alkaline solutions of sodium borohydride is possible only in the presence of catalysts or with the addition of an acid [22, 23].

3. Hydrogen produced by interaction between NaBH₄ and acids

The introduction of organic or mineral acid in a solution of sodium borohydride results in a violent gas emission [23, 24], which ceases completely in a few minutes. Analysis of the composition of generated gas indicates the presence of not only hydrogen, but also diborane. Diborane amount increases as the content of acid is raised; in concentrated acids (sulfuric, phosphoric, etc.) the main process is formation of diborane due to

dimerization of borane. This method is often used to obtain diborane under laboratory conditions [25].

Some authors [26-30] believe that proton of the acid initiates decomposition of BH_4^- via the formation of H_2BH_3 intermediate, which dissociates into molecular hydrogen and borane. The formation of borane BH_3 was confirmed in experiments by its binding into trimethylamine borane [30] and trihydrocyanoborate [31]. Borane hydrolyzes in diluted acids, which increases the fraction of hydrogen in gaseous products. Thus, the total equation for hydrolysis of borohydride ion in an acid medium has the following form [33-35]:



It is virtually impossible to avoid the formation of diborane in the reaction of sodium borohydride with acids. Taking into account high toxicity of diborane, this method of hydrogen production is unacceptable for wide use in portable energy sources with fuel cells.

4. Hydrogen produced by catalytic hydrolysis of NaBH_4

4.1. Effect of the nature of the active component

An obvious benefit of heterogeneous catalysts over acids is that their application excludes the possibility of diborane formation (Table 2). According to chromatographic data, the generated gas contains only water vapor and microadditions of solvents used in the synthesis of sodium borohydride.

In the presence of catalysts, NaBH_4 reacts with water even at room temperature; however, the rate of hydrogen generation depends on the type of catalytic system. Results obtained by different researchers (Table 3) demonstrate that rhodium, ruthenium and platinum are the most active transition metals in hydrolysis of sodium borohydride, whereas cobalt and nickel compounds are the less active ones. Hydrolysis of NaBH_4 is virtually absent in the presence of manganese, molybdenum, aluminum, chromium, zinc, tungsten, gallium, indium, copper, gold, silver, palladium and iron compounds [35]. Hydrogen evolution terminates after reduction of their salts in the reaction medium.

Nevertheless, summarizing the data of Table 3, one cannot make unambiguous conclusions on the effect of metal nature on the rate of hydrogen generation from NaBH_4 aqueous solutions. There are several reasons for disagreement between the activity series of metals reported by different authors. First, different conditions of catalyst synthesis and reduction, differences in the nature of the active component precursor, in the amount of catalyst active phase and types of support. Second, different conditions of comparative testing: temperature, pH of the medium, Me to NaBH_4 ratio, etc. Little attention is paid to this issue owing to the applied nature of the studies, which are aimed mainly at the development of inexpensive cobalt catalysts for sodium borohydride hydrolysis.

4.2. Cobalt catalyst in NaBH_4 hydrolysis

The use of sodium borohydride as a source of hydrogen for portable fuel cells requires the development of active but inexpensive hydrolysis catalysts. This led to intensive investigation of

Table 2. Composition of admixtures in a hydrogen-containing gas obtained by hydrolysis of NaBH_4 in the presence of 1% Rh/ TiO_2 -1. Zvet-500-M gas chromatograph (Russia), Carbon (0.3-0.5 mm) (USA) packed column.

Experiment No.	Content of admixtures, vol.%					
	H_2O	$\text{C}_6\text{H}_5\text{OH}$	CH_3OH	CO_2	CO	B_2H_6
1	0.0026	0.00012	0.00012	-	-	-
2	0.0034	0.000073	-	-	-	-
3	0.0019	0.000059	-	-	-	-
4	0.0023	0.00042	0.00025	-	-	-

Table 3. Activity series of metals according to the data from various research groups.

First author of the paper	Temperature, °C	Catalyst	[NaBH ₄]: [NaOH]	[M] : [NaBH ₄]	Activity of metals
H.I. Schlesinger [36]	25	MnCl ₂ , FeCl ₂ , CoCl ₂ , NiCl ₂ , CuCl ₂	-	1:24	<i>per mole of a metal</i> Co > Ni > Fe > Cu > Mn
M.C. Brown [37]	25	FeCl ₂ , CoCl ₂ , NiCl ₂ , RuCl ₃ , RhCl ₃ , PdCl ₂ , OsO ₄ , IrCl ₄ , H ₂ PtCl ₆	-	1:53	<i>per mole of a metal</i> Rh ≈ Ru > Pt > Co > Ni ≥ Os > Ir > Fe >> Pd
A. Prokopchik [38-41]	20 - 70	Bulk Pt, Pd, Rh and Ru catalysts. Pt, Pd and Rh were prereduced by NaBH ₄ and dried at 100-110°C. Ru is a metallic powder PRU-1	1:43	-	<i>by activation energy</i> Rh > Ru > Pt >> Pd
C.M. Kaufman [32]	21.4	Co, Ni and Cu chlorides, nitrates and carbonates	1:20	1:100 1:200 1:300 1:400	<i>per mole of a metal</i> Ni > Co > Cu
Y. Kojima [42]	20 - 23	Fe/TiO ₂ , Ni/TiO ₂ , Pd/TiO ₂ , Ru/TiO ₂ , Rh/TiO ₂ , Pt/TiO ₂ Initial salts – acetylacetonates of corresponding metals; synthesis was performed under supercritical conditions	-	0.0013 mol of NaBH ₄ and 3.8 mg of catalyst	<i>per gram of a catalyst</i> Pt > Rh > Ru ≈ Pd > Ni ≈ Fe
P. Krishnan [43]	25	Ru/LiCoO ₂ , Pt/LiCoO ₂	1.1:1	1:300	<i>per mole of a metal</i> Pt > Ru <i>per gram of a catalyst</i> Ru > Pt
U.B. Demirci [44]	20	Ru/ZiO ₄ -SO ₄ ⁻ , Pt/ZiO ₄ -SO ₄ ⁻ , Pt/C	1:2.4	1:160	<i>per mole of a metal</i> Ru/ZiO ₄ -SO ₄ ⁻ > Pt/C > Pt/ZiO ₄ -SO ₄ ⁻
Y. Chen [45]	25	Pt/SiO ₂ , Ni/SiO ₂ , Co/SiO ₂ , Ag/SiO ₂ Support was modified with amino groups	-	1:150	<i>per mole of a metal</i> Pt > Ni > Co > Ag
V.I. Simagina [46, 47]	40	Pt/Al ₂ O ₃ , Ru/Al ₂ O ₃ , Rh/Al ₂ O ₃ , Pt/Sibunit, Ru/Sibunit, Rh/Sibunit, Pd/Sibunit, Ni/Sibunit, Co/Sibunit, Pt/TiO ₂ , Ru/TiO ₂ , Rh/TiO ₂ , Pd/TiO ₂ , Ni/TiO ₂ , Co/TiO ₂	-	1:2000	<i>per gram of a metal</i> Rh > Ru > Pt >> Pd ~ Ni ~ Co
J.C. Walter [48]	60	Bulk catalysts Co ₃ B, Ni ₃ B, Ru NaBH ₄ prereduced in an ice bath (~0°C) and heat treated at 200, 300 and 400°C	4.2:1	-	<i>per gram of a catalyst</i> Ru > Co ₃ B > Ni ₃ B
			1:1.2	-	<i>per gram of a catalyst</i> Co ₃ B > Ni ₃ B > Ru
A. Garron [35]			1:1.75	1:5.7	<i>per mole of a metal</i> Pt > Ru ≈ Rh >> Pd Co > Ni > Fe Not active Au, Ag, Cu, Mo, W, Al, Cr, Mn, Zr, Ga, In.

bulk and supported cobalt-containing systems reduced in the sodium borohydride reaction medium [49].

Studies of bulk cobalt catalysts revealed the effect of anion nature on the properties of catalytically active phase forming from various salts in the reaction medium under the action of NaBH₄ [50-52]. In the process, hydrolysis rate is determined not only by the nature of anion, but also by the method of introducing a salt in the reaction medium [53]. If solutions of cobalt salts are added to an aqueous solution of sodium borohydride, their activity will decrease in the following order: CoCl₂ > Co(CH₃COO)₂ ≈ CoSO₄ > CoF₂ > Co(NO₃)₂. At the addition of solid salts to the hydride solution, another dependence is observed: CoCl₂ > CoSO₄ > Co(CH₃COO)₂ > Co(NO₃)₂ > CoF₂. In the first case, the lowest activity of cobalt nitrate can be attributed to the preferential formation of metal hydroxide in an alkaline medium of sodium borohydride, as was shown in [49, 52], which compare phase composition of the deposits forming from CoCl₂ and Co(NO₃)₂ under the action of NaBH₄. In the second case, the low rate of hydrogen generation upon addition of CoF₂ solid salt to a solution of sodium borohydride is caused by a poor solubility of the fluoride in water in comparison with other cobalt salts (the solubilities: CoF₂ - 1.4 g in 100 g of H₂O; CoCl₂ - 36 g in 100 g of H₂O at 25°C) [54]. At a slow dissolution of CoF₂, the amount of catalytically active phase in the reaction medium increases gradually, a maximum rate of hydrogen generation being attained only in 90 seconds.

Unfortunately, differences in the activity of cobalt salts are not explained in the literature in terms of the effect of anion nature on the composition, morphology and structure of the catalytically active phase that forms directly in the reaction medium of NaBH₄. This is related mainly to difficulties in studying this X-ray amorphous Co-containing active component [55-58]. Their diffraction pattern includes a low informative broad line at $2\theta = 45 \pm 2^\circ$ [59, 60], which may be a superposition of the peaks corresponding to cobalt borides of various composition (CoB, Co₂B, Co₃B) and metallic cobalt [55, 61], since their diffraction maxima virtually coincide. Thus, for CoB the most intense reflections are observed at

2θ equal to 34.1, 37.3, 41.3 and 45.6° [62]; for Co₂B at 35.8, 42.8 and 45.8° [63]; for Co₃B at 37, 38, 42.5, 44.1, 44.6, 45.9 and 46.8° [64]; for fcc Co at 44.2°, and for hcp Co at 41.5, 44.5 and 47.4° [65]. Calcination under inert atmosphere of the active phase of bulk cobalt catalyst synthesized by the reduction of cobalt chloride in a NaBH₄ medium leads to appearance of well resolved peaks corresponding to cobalt borides in the diffraction pattern [56, 66].

The formation of borides is indicated also by the chemical analysis that confirms the presence of boron in the composition of catalytically active phase. At that, the Co:B molar ratio may vary from 1.5 to 18 depending on the reduction conditions [49, 58, 60]. Besides, according to XPS, electron density is donated from boron to cobalt, which is a unique feature of cobalt borides [67, 68].

Since cobalt borides and metallic cobalt possess ferromagnetic properties, the measurement of magnetic susceptibility is a more informative method for identifying the phase composition of amorphous cobalt-containing catalysts intended for hydrolysis of sodium borohydride [69]. First, the ferromagnetic state of cobalt-containing catalysts reduced by NaBH₄ is indicated by residual magnetization in a zero field [70]. There is also a nonlinear dependence of their magnetization on the applied magnetic field. It is known that the ferromagnetic state of samples disappears when the temperature begins to exceed the Curie point. According to the literature, the magnetic disordering occurs at different temperatures for metallic cobalt and its borides: Co at > 1000°C, Co₃B at 474°C, Co₂B at 156°C, and CoB is a diamagnetic [69]. Investigation of the temperature dependence of magnetic susceptibility makes it possible to determine the composition of ferromagnetic X-ray amorphous cobalt-containing particles formed in the sodium borohydride reaction medium.

According to the data presented in [71], the Curie point for Co₃O₄ examined after contacting with a sodium borohydride solution falls in the range of 450-500 K. Thus, it can be stated that cobalt oxide transforms under the action of sodium borohydride into amorphous cobalt boride with the approximated Co₂B composition. In the process, the rate of NaBH₄ hydrolysis correlates directly with an increase in the amount of this boride phase in the

reaction medium (Fig. 1). Noteworthy is an increase in magnetic susceptibility of the sample at a temperature above 570 K, which can be attributed to a phase transition leading to the Co₃B crystalline phase and metallic cobalt [58, 72, 73]. According to [56, 74-76], calcination of borides affects their catalytic properties, and formation of metallic cobalt at elevated temperatures becomes the main reason for a loss in activity of the calcined cobalt boride systems.

Modification of the active component with a second metal (Ni, Fe, Cu, Cr, W, Mo) and nonmetal (phosphorus) is a new line in investigation of the cobalt-containing catalysts for sodium borohydride hydrolysis. To attain high activity of the bulk cobalt boride systems, the Italian researchers [77] suggested that cobalt boride should be promoted with phosphorus and found that Co-P-B systems exhibit the highest activity at a boron to phosphorus ratio equal to 2.5. A similar positive effect of phosphorus on the formation rate of hydrogen was found also with cobalt catalysts synthesized by electrochemical deposition of Co on the copper plate surface in the presence of sodium hypophosphite [78].

Doping of bulk cobalt boride with transition metals (Ni, Fe, Cu, Cr, W, Mo) also increases its activity in the hydrolysis of sodium borohydride [79-82]. A synergistic effect was obtained when studying the catalytic properties of Raney cobalt-nickel alloys [83]. It was shown that nickel and cobalt present jointly in a catalytic composition

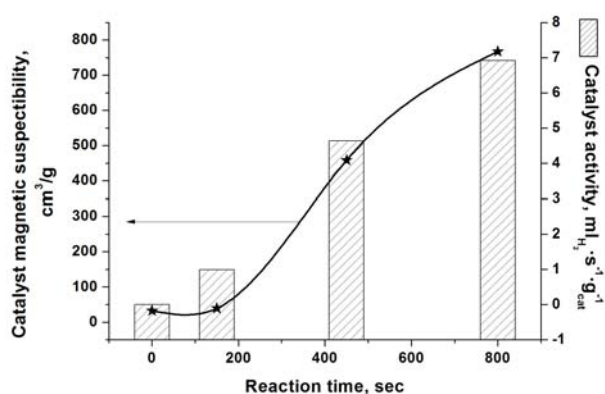


Fig. 1. Catalyst magnetic susceptibility ($H = 3.2$ kOe) and H₂ generation rate as a function of time of NaBH₄ hydrolysis. Catalyst - Co₃O₄; Temperature - 40°C.

increase the hydrogen generation rate as compared to systems containing only one of the metals.

A more detailed comparative study of bimetallic boron-containing systems (Co-Ni-B, Co-Fe-B, Co-Cu-B, Co-Cr-B, Co-Mo-B and Co-W-B) is reported in [80]. Nickel and iron were found to exert the least effect on the catalytic properties of cobalt systems, probably due to formation of low active borides of these metals in the reaction medium of sodium borohydride [35, 83-85]. On the other hand, the presence of additional boron in the composition of the active component may increase electron density of cobalt, thus enhancing the activity of Co-Ni-B and Co-Fe-B catalysts in comparison with monometallic systems. The introduction of a more active ruthenium in the composition of cobalt-nickel and cobalt-iron borides results in a non-additive growth of hydrogen generation rate, which also can be produced by changes in the electronic state of the catalyst active component [84].

Besides, it was noted that doping of cobalt boride with iron, copper, chromium, molybdenum and tungsten increases specific surface area of the catalytic compositions. In the case of Co-Cu-B system, this value was 115 m²/g, which is 5-fold greater than the value typical of cobalt boride. It seems interesting that high specific surface area is retained after the calcination of cobalt-copper catalysts in an argon atmosphere at 400°C [75]. An XPS and SEM study of the Co-Cu-B composition [80] gave grounds to assume the formation of highly dispersed particles of metallic copper in a sodium borohydride medium, which prevent agglomeration of the Co-B particles. A similar role is played by the oxides of iron, chromium, molybdenum and tungsten, which form under the action of NaBH₄ during the synthesis of Co-B catalysts. In addition, Lewis acid sites reside on the surface of these oxides and readily adsorb hydroxide ions from the solution. Saturation of the catalyst with OH⁻ accelerates their interaction with dehydrogenated forms of borohydride ion on the cobalt boride particles, thus increasing the catalyst activity by a factor of 3-4 [80].

A more complicated dependence of the catalytic activity on the presence of second metal was noted for γ -Al₂O₃ supported cobalt-containing catalysts [86]. As demonstrated by experiments,

not only the nature but also the amount of introduced metal can affect the catalytic properties of bimetallic systems. Thus, the addition of up to 5 wt.% zirconium and hafnium to the cobalt catalyst enhances its activity; however, it decreases at a further increase in the content of a modifying metal in the composition. In the case of 20% Co-Y/ γ -Al₂O₃ system, a maximum rate of hydrogen generation is attained at a Co:Y molar ratio equal to 9:1.

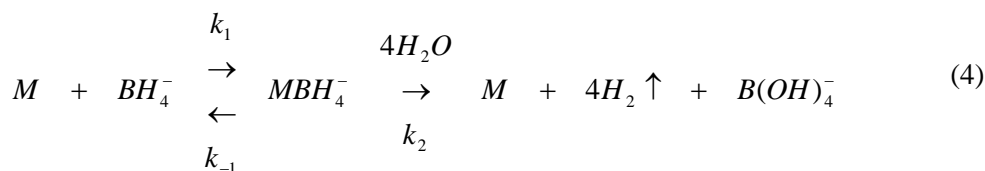
Up to date, doping of the cobalt-containing catalysts with the platinum group metals was not considered in the literature as a special subject; there are some works on the activity of LiCoO₂ modified with platinum, ruthenium and rhodium [87, 88]. Deposition of platinum and ruthenium on LiCoO₂ was shown to produce more than a twofold increase in the hydrogen generation rate as compared with both the initial cobalt compound and the bulk platinum and ruthenium catalysts [57]. This indicates that investigation of cobalt systems modified with the platinum group metals (noble metal) is rather promising for the development of highly efficient catalysts intended for portable hydrogen generators.

Summarizing the data on the cobalt-containing catalysts modified with transition metals [80, 84, 89-91], one can distinguish at least five reasons underlying changes in activity of the modified systems: (I) an increase in specific surface area of the active component; (II) formation of oxides with additional adsorption sites for reactants; (III) changes in the electronic properties of metals; (IV) segregation of a metal on the surface of another metal or (V) redistribution of the electron density between metals in the nascent alloy particles [92].

5. Kinetics of the catalytic hydrolysis of NaBH₄

The kinetic regularities of catalytic process of sodium borohydride hydrolysis were studied over a wide range of catalysts. It was shown that the interaction of water with sodium borohydride on the catalyst surface does not fall into the integer-valued kinetic order with respect to the hydride, its value was found to be less than 1 [93-95]. Besides, analysis of the dependence of hydrolysis rate on the sodium borohydride concentration demonstrated that an increase in the hydride content of a solution raises the reaction rate, which gradually attains its maximum and remains constant at a further addition of NaBH₄. This dependence is most pronounced with rhodium and platinum catalysts at 20°C [38, 40] as well as with ruthenium and palladium catalysts at 40°C [39, 41]. It should be noted that zero order of the reaction with respect to borohydride ion is retained in a wide range of the hydride concentrations both for the bulk and supported catalytic systems: Ru(0) [96, 97], Ni(0) [98, 99], Co-Cr-B [79], 3% Ru/C [100], 1% Pt/LiCoO₂ and 1% Ru/LiCoO₂ [88], 3% Ru/graphite [101], Co/nickel foam and Ni/nickel foam [15], 2% Ru/Y zeolite [102], Co/Y zeolite [103], and Ni-Ru on the ion-exchange resin Dowex® 50WX8 [104].

Analyzing the data obtained, the authors of [42, 105] concluded that the interaction of borohydride ion with the active component [M] is a key step of hydrolysis, and hydrogen generation rate is determined by accessibility of the metal surface to adsorption of BH₄⁻. At that, the total equation for sodium borohydride hydrolysis takes the form [106, 107]:



By now, several methods were suggested to describe the kinetics of interaction between sodium borohydride and water in the presence of heterogeneous catalysts. An empirical approach is often used for this purpose. Several kinetic equations

were proposed taking into account the effect of NaBH₄ concentration and pH of the medium on the rate of hydrolysis. In the case of dilute NaBH₄ solution and ruthenium catalyst based on sulfated zirconium oxide, such equation has the form [44, 93]:

$$r = k[NaBH_4]^{0.23}[NaOH]^{-0.35}[Ru]^{1.27} \quad (5)$$

The following dependence was found for cobalt boride catalytic systems obtained by the reduction of sodium borohydride in the presence of phosphorus compounds [77]:

$$r = k[M]^{1.05}[NaBH_4]^{0.07}[NaOH]^{0.12} \quad (6)$$

As the application of high-concentrated (10-25 wt.%) sodium borohydride solutions is of great practical importance, most of researchers examine the kinetic regularities of hydrogen formation only from solutions with a high content of the hydride [79, 83]. So, a dependence of the reaction rate on NaBH₄ concentration is described by a zero order kinetic equation with respect to the hydride [96, 99]:

$$-\frac{4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[M] \quad (7)$$

As the concentration of sodium borohydride decreases, so does the rate of hydrogen generation, and reaction has the first order with respect to sodium borohydride [108]:

$$-\frac{4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[M][NaBH_4] \quad (8)$$

In [106, 109] the catalytic hydrolysis of NaBH₄ is considered as a complex two-step reaction, one of the steps being reversible (4). Assuming that the process occurs at quasistationary concentration of the short-lived complex MBH_4^- and reaction rate is determined by the rate of MBH_4^- decomposition, a mathematical expression describing the dependence of hydrolysis rate on the hydride concentration and weight of a metal was obtained:

$$\frac{1}{dn_{H_2}/dt} = \frac{1}{K_1 [NaBH_4] \cdot g_{met}} + \frac{1}{K_2 g_{met}}, \quad (9)$$

where g_{met} is the weight of a metal,

$$K_1 = \frac{4k'}{MW_{met}}; \quad K_2 = \frac{4k_2}{MW_{met}}, \quad k' = \frac{k_1 k_2}{k_2 + k_{-1}},$$

and MW_{met} is the average molecular weight of a group of metal atoms entering the composition of one active site.

The authors of [106] believe that such an approach can explain changes in the apparent reaction order from first to zero that occur with

increasing the NaBH₄ concentration in a solution [77], and determine the relative contributions of the first and zero order reactions to the general kinetics of hydrogen generation in the presence of heterogeneous catalysts.

To validate their approach, the authors of [106] demonstrated that results of their experiments presented in the coordinates $\frac{1}{r_{H_2}} - \frac{1}{[NaBH_4]}$ are

described by a linear dependence. However, the experimental data were obtained with simultaneous change of the hydride concentration and amount of the platinum-palladium catalyst from one experiment to other. In these cases, the molar ratio $[NaBH_4]:[M] = 6$ was retained. This approach is used mostly to study the kinetic regularities of complex homogeneous reactions, but it is low informative for describing the kinetics of catalytic processes that take place at the interface of two phases.

Investigating the hydrolysis of sodium borohydride in the presence of cobalt boride (the average particle size of 300 nm), the Chinese researchers [107] suggested that changes in the dependence of hydrogen generation rate on the hydride concentration could be explained within the Michaelis–Menten model. This approach as well as the work [106] are based on the method of quasistationary concentrations with respect to the short-lived complex MBH_4^- , which allows obtaining the following expression for the reaction rate:

$$-\frac{d[NaBH_4]}{dt} = \frac{d[H_2]}{4dt} = \frac{k_2[M_0][NaBH_4]}{K_M + [NaBH_4]}, \quad (10)$$

where $K_M = \frac{k_{-1} + k_2}{k_1}$ is the Michaelis constant.

Experimental investigation of hydrolysis in the presence of cobalt boride catalysts showed that increasing the content of sodium borohydride above 0.04 mol/L does not accelerate the process. The revealed regularity is adequately described by equation (10). At that, the volume of generated hydrogen can be determined quite accurately at any time (t):

if $[NaBH_4] \geq 0.4$ mol/L, then $V_{H_2} = 20.7t$ (the zero order reaction);

if $[\text{NaBH}_4] < 0.4 \text{ mol/L}$, then $V_{H_2} = 994(1 - e^{-0.0027t/V_{p-pa}})$ (the first order reaction).

Thus, the Michaelis–Menten model makes it possible to explain changes in the reaction order upon variation of the hydride concentration and demonstrate that the number of active sites on the catalyst surface plays an essential role [107]. However, the effect of pH of the medium on the hydrogen generation rate is not considered within this approach.

The analysis of publications [38, 41, 48, 77, 83, 96, 100, 102, 104, 110, 111] dealing with the catalytic hydrolysis of sodium borohydride in alkaline solutions does not provide an unambiguous conclusion about effect of sodium hydroxide on the process rate and features. Nevertheless, two trends can be distinguished: (I) an increase in the concentration of alkali is accompanied by a growth of initial rate of hydrogen generation in the presence of cobalt and nickel catalysts [110, 112, 113]; (II) in the case of platinum group metals, an increase in the concentration of sodium hydroxide decreases the initial rate of hydrolysis [39, 44, 93, 101, 114]. Besides, the addition of alkali can alter the dependence of reaction rate on the hydride concentration. Thus, it was observed [108] that in the sodium borohydride concentration range of 0.15 to 0.75 mol/L, the hydrolysis in an aqueous medium was the first order reaction in the presence of cobalt catalyst stabilized by polyvinylpyrrolidone. The introduction of alkali in the reaction medium increased the reaction rate, the process kinetics being described by a zero order reaction. In distinction to the cobalt-containing systems, the addition of NaOH in an aqueous solution of NaBH₄ has no effect on the reaction order of hydrolysis with respect to hydride in the case of ruthenium catalysts containing a sodium form of Y zeolite [102]. It is difficult to explain the reasons of these distinctions without knowledge of a detailed mechanism of the reaction. However, the results obtained clearly demonstrate that catalytic hydrolysis of sodium borohydride is a complex reaction, where the hydroxide ion is an essential participant of the process.

The Lithuanian researchers [39, 40] think that the reduced platinum group metals do not interact with alkali in a NaBH₄ medium. Evidently, an increase in pH enhances the competitive sorption between hydroxide ions and borohydride ions on the surface of active component. This assumption is confirmed by an increase in efficient activation energy of the hydrolysis after addition of alkali, which is observed in the presence of bulk ruthenium catalyst [96]. An increase in apparent activation energy with increasing hydride concentration also indicates a competitive sorption of sodium borohydride and hydroxide ion, and it is observed for nickel and cobalt catalysts [115, 116].

All these examples demonstrate an important role of reactants' adsorption in the hydrolysis of sodium borohydride, which is the main indication of the reactions proceeding by the Langmuir-Hinshelwood mechanism:

$$-\frac{d[\text{NaBH}_4]}{dt} = \frac{d[H_2]}{4dt} = k \cdot \Theta_{\text{BH}_4^-} \cdot \Theta_{\text{H}_2\text{O}}, \quad (11)$$

where Θ is the surface coverage of the active component by initial reactants.

Experimental verification of the Langmuir kinetics for catalytic hydrolysis of NaBH₄ was obtained by the authors of [117, 118], who studied the interaction of sodium borohydride with water in the presence of ruthenium catalysts (3% Ru/C and 3% Ru/Al₂O₃). They considered possible kinetic models of the catalytic hydrolysis: zero order reaction, first order reaction, n-order reaction, and reaction proceeding by the Langmuir-Hinshelwood mechanism. The most correct description of experimental data obtained at different temperatures and concentrations of sodium borohydride was provided by the Langmuir-Hinshelwood model under the condition that surface coverage of the active component with water is included in the reaction rate constant k' :

$$-\frac{d[\text{NaBH}_4]}{dt} = \frac{d[H_2]}{4dt} = k' \cdot \Theta_{\text{BH}_4^-} \quad (12)$$

This hypothesis is based on the assumption that the reaction is performed in an excess of water [117, 118]. However, taking into account the

dependence of catalytic hydrolysis rate on the concentrations of sodium borohydride, sodium hydroxide and water, the authors of [119] made a conclusion that the kinetic equation should include not only the concentration of hydride, but also the concentration of water and sodium hydroxide. Thus, surface of the active component is filled with three adsorbates: borohydride ions, water molecules and hydroxide ions; at that:

$$\Theta_{BH_4^-} + \Theta_{H_2O} + \Theta_{OH^-} = 1 \quad (13)$$

Hence it follows that changes in the concentration of one component should alter the filling with all adsorbates.

Certainly, adsorption of the reaction products on the catalytically active surface should also be considered. However, some experiments [100] showed that the concentration of formed B(OH)₄ has no significant effect on the rate of hydrolysis. In the case of platinum group metals, one should take into account also the chemisorption of hydrogen on the metal surface. Thus, in [120] it was found that hydrogen is present in the samples of platinum, rhodium and palladium blacks obtained by the reduction of their chlorides in a sodium borohydride medium.

Experimental verification of the approach (13) taking into account surface filling of the active component with borohydride ions, water molecules and hydroxide ions in the Langmuir-Hinshelwood model was made when studying the hydrolysis in the presence of bulk copper catalysts [121], which are not characterized by strong hydrogen chemisorption. In the case where a reactant (water) is also a solvent, it can be written [122]:

$$\frac{\Theta_{BH_4^-}}{\Theta_{H_2O}} = a_{BH_4^-} \cdot [BH_4^-] \quad \text{and} \\ \frac{\Theta_{OH^-}}{\Theta_{H_2O}} = a_{OH^-} \cdot [OH^-], \quad (14)$$

where $a_{BH_4^-} = \frac{1}{[H_2O] \cdot e^{-\delta\Delta F_{BH_4^-}/RT}}$ and

$$a_{OH^-} = \frac{1}{[H_2O] \cdot e^{-\delta\Delta F_{OH^-}/RT}}; \quad \delta\Delta F_{BH_4^-} \text{ is the}$$

difference between free energy of the borohydride

ion and water adsorption on copper, and $\delta\Delta F_{OH^-}$ is the difference between free energy of the hydroxide ion and water adsorption on copper.

The rate of sodium borohydride hydrolysis in an alkaline solution can be found from equation (15) using simple numerical transformations:

$$r = k \cdot \Theta_{BH_4^-} \cdot \Theta_{H_2O} = \frac{k \cdot a_{BH_4^-} \cdot [BH_4^-]}{(1 + a_{BH_4^-} \cdot [BH_4^-] + a_{OH^-} \cdot [OH^-])^2} \cdot \quad (15)$$

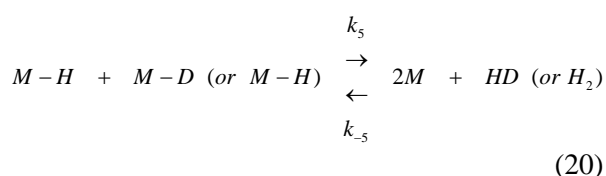
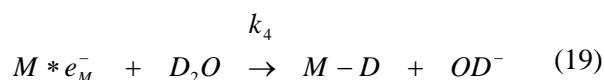
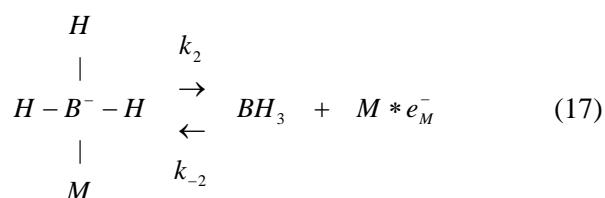
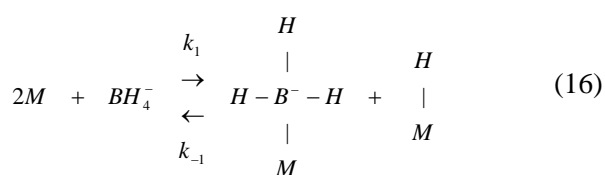
If the concentration of sodium hydroxide in the reaction mixture is low (0.01 mol/L NaOH), the term $a_{OH^-} \cdot [OH^-]$ can be neglected. Then, the experimental data presented in the coordinates $\sqrt{[BH_4^-]/r} - [BH_4^-]$ should be described by a linear dependence. Indeed, this is observed in the presence of bulk copper catalysts, which confirms the validity of the chosen approach for the description of kinetic regularities of NaBH₄ hydrolysis. This confirms the Langmuir kinetics of the catalytic hydrolysis of NaBH₄, whose essential steps are the adsorption of borohydride anion and water on the active component surface.

6. Mechanism of the catalytic hydrolysis of NaBH₄

A study on the interaction of NaBH₄ with heavy water in the presence of nickel and cobalt catalysts showed that both the hydride and water can serve as a hydrogen source, similar to the case of noncatalytic process [123] However, the composition of gaseous products differs significantly. The main product of noncatalytic interaction of NaBH₄ with heavy water is deuterohydrogen - HD (up to 95%) [16]. On the nickel catalyst, the H₂:HD:D₂ molar ratio of gaseous products obtained by hydrolysis is 1.12:1.16:1, whereas with the cobalt catalyst it is equal to 1.17:1.7:1. The increase of the content of deuterated gaseous products is observed with progress in time of reaction; however, if heavy water is supplemented with the same amount of protium water, the content of deuterium in gaseous products decreases nearly by an order of magnitude [123]. Taking in to account a sharp decrease in deuterium content in the gaseous products of the reaction upon dilution of heavy water (D₂O) with protium water (H₂O),

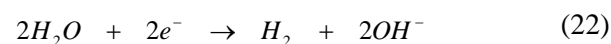
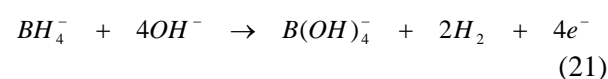
K. A. Holbrook and P. J. Twist made a conclusion that the main role in water activation on the catalyst is played by electrochemical transformations, because they are characterized by very high values of the isotope separation coefficient (5-9) [124]. Meanwhile, for noncatalytic interaction of BH_4^- with water, the $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ ratio is equal to 1.56 [125].

A comparison of kinetic data with qualitative composition of the released gas allowed the authors of [123] to suggest the following mechanism for the catalytic hydrolysis of sodium borohydride:

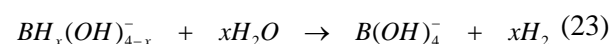


This scheme elucidates the Langmuir kinetics of the catalytic reaction and formation of protium in the case of hydrolysis performed in heavy water. Besides, it includes the electrochemical step of water activation on the catalyst (19), which is expected to proceed on the active sites near the regions of anodic oxidation of the borohydride ion (17). The formed intermediate BH_3 is desorbed from the catalyst surface into the bulk of solution, where it interacts with deuterated hydroxide ion. A further substitution of protons by hydroxide ions in the BH_3OD^- molecule occurs stepwise on the catalyst surface.

The Lithuanian researchers, studying concurrently the hydrolysis of borohydride ion in the presence of bulk catalysts, also supposed the electrochemical mechanism of this catalytic reaction [121]. Their conclusions are based on measuring the potentials of samples, particularly in the absence of external current. In the case of catalytic hydrolysis of borohydride ion on a copper plate with a loose layer of electrochemically deposited copper, its potential in an alkaline solution of NaBH_4 was found to have a more negative value than that of the hydrogen electrode [126]. This is possible only due to anodic oxidation of BH_4^- accompanied by the cathodic evolution of hydrogen from water:



Due to conjugation of these electrochemical processes, a mixed negative potential equal to -0.07 V is established on a copper plate in a 1 M solution of NaOH containing 0.025 M NaBH_4 at 65°C. This potential coincides with the value obtained in the study of copper plate polarization. The experiments showed also that in the range of +0.05 to -0.05 V the apparent rate of hydrogen evolution exceeds the rate of H_2 electrochemical formation by reactions (21) and (22). According to [127], this is caused by a fast noncatalytic interaction of water with the intermediate products like $\text{BH}_n(\text{OH})_{4-n}^-$, which are desorbed from the catalyst surface into the bulk of solution:



Negative potential in an alkaline solution of NaBH_4 is typical also of a copper plate with the strong layer of rhodium electrochemically deposited on its surface from the sulfate electrolyte [128].

All the schemes suggested for the oxidation of borohydride ion with simultaneous reduction of water protons via electrochemical transformations on the catalyst surface [123, 126] imply the involvement of hydroxide ions in the process; their presence in the solution should increase the reaction rate by shifting an equilibrium to the reaction products (18) and (23) [48]. Indeed, an acceleration of hydrogen generation with increasing NaOH content in the solution is observed in the presence of cobalt boride and nickel boride

catalysts [110, 112, 113, 129]. In the case of platinum metals, an increase in pH of the medium decreases the rate of hydrolysis, similar to noncatalytic hydrolysis of sodium borohydride [39, 44, 93, 101, 114]. The authors of [48] explain this fact by strong hydrogen chemisorption on the platinum group metals; so, an increased surface coverage of the catalyst active component with hydrogen decreases the likelihood of borohydride ions adsorption irrespective of the increased concentration of alkali in the reaction medium [130]. Certainly, a large amount of hydrogen on the metal surface is responsible also for shifting the chemical equilibrium in equation (16) toward BH₄⁻ desorption. A ¹¹B NMR spectroscopy study demonstrated that the presence of Pd/C catalyst in a solution initially containing BH₄⁻ and D₂O leads to appearance of partially or completely deuterated borohydride ions with a general formula BH_{4-n}D_n⁻ [131]. The results obtained were attributed to a lower rate of hydrolysis in comparison with the rate of isotopic exchange proceeding concurrently on the palladium surface.

In the case of platinum catalyst, an opposite dependence is observed: the rate of hydrolysis of the borohydride ion in heavy water is higher than the rate of isotopic exchange; so, a small amount (below 10%) of only one product of BH₃D⁻ isotopic exchange was found in the reaction medium [132].

It should be noted that the ¹¹B NMR spectroscopy did not detect any intermediates of BH_{4-n}(OH)_n hydrolysis [133]. According to [132], this may be caused by a short lifetime of these compounds in a solution. Another possible reason for the absence of intermediate products of sodium borohydride hydrolysis is the direct interaction of BH₃ with hydroxide ion on the catalyst surface [40, 106]. At present, these hypotheses have no direct experimental verification in the literature.

The mechanism of catalytic hydrolysis of sodium borohydride proposed by *K. A. Holbrook and P. J. Twist* [123] was used as a basis in [48] to obtain a mathematical expression describing the process kinetics:

$$-\frac{d[BH_4^-]}{dt} = -\frac{d[BH_3]}{dt} = k_3 K_1 K_2 K_5^{1/2} [OH^-] [BH_4^-], \quad (24)$$

$$\text{where } K_1 = \frac{[MBH_3^-][MH]}{[BH_4^-][M]^2}, \quad K_2 = \frac{[BH_3][M]}{[MBH_3^-]}$$

$$\text{and } K_5 = \frac{[M]^2}{[MH]^2}$$

Although the approach to kinetic description of the catalytic hydrolysis of sodium borohydride proceeding with various catalysts is theoretically substantiated, the authors of [48] provide no experimental evidence. Besides, assuming the reaction is carried out in an excess of water, they neglect the step of water interaction with the catalyst active sites (24).

An important role of water activation on the catalytically active surface was shown in the work [132] devoted to the interaction of BH₄⁻ and BD₄⁻ with heavy (D₂O) and protium (H₂O) water in the presence of platinum and palladium catalysts. A comparison of experimental data revealed that the rate of hydrolysis of borohydride ion and its deuterated analog strongly depends on the isotope (protium or deuterium) present in the composition of water. However, rate constants for the reactions of BH₄⁻ and BD₄⁻ in heavy water are very close to each other (k=5.6±0.1×10⁻⁵ mole/s and k=5.0±0.1×10⁻⁵ mole/s, respectively); rate constants for the hydrolysis of BH₄⁻ and BD₄⁻ in protium water also coincide (k=8.8±0.1×10⁻⁵ mole/s and k=8.8±0.2×10⁻⁵ mole/s, respectively).

The observed regularities allowed the authors of [132] to conclude that the limiting step of catalytic hydrolysis of sodium borohydride is decomposition of water rather than dissociation of borohydride ion on the active surface of the catalyst. In addition, theoretical calculations showed that dissociative adsorption of BH₄⁻ on the Pt (111) surface has a low activation barrier [134] in comparison with decomposition of water. As saturation of platinum with hydrogen increases, this may be accompanied either by recombination of hydrogen atoms on the surface and formation of H₂ molecule or by the interaction of adsorbed hydrogen species with hydroxide ion and formation of H₂O. According to [134], the competition of these two processes will be determined by the amount of adsorbed hydrogen, which depends on the concentration of sodium borohydride in a solution. A low content of the

hydride will lead to preferential occurrence of the side reaction of adsorbed hydrogen and hydroxide ion recombination with the formation of water.

Thus, the catalytic hydrolysis of sodium borohydride is a complex process including side reactions. Taking into account the works [123, 126, 132], we made a conclusion that decomposition of adsorbed borohydride ion on the catalyst surface proceeds via electrochemical oxidation of BH_4^- accompanied by water reduction. In the process, activation of water is the limiting step irrespective of its excess in the reaction medium.

The presented analysis of publications on the catalytic hydrolysis of sodium borohydride allows one to assume that a maximum rate of hydrogen generation is expected in the case of metals that, first, possess the highest electric conductivity and, second, have the lowest activation barrier for dissociative adsorption of water not leading to hydroxides. Among transition metals, these two features are inherent in the VIII group metals, such metals being active in the NaBH_4 hydrolysis. Their specific electric resistance decreases in a series $\text{Pd} > \text{Pt} > \text{Ni} > \text{Co} > \text{Ru} > \text{Rh} > \text{Fe}$ [135], the calculated heat of water adsorption on the faces preferentially coming to the surface of metallic particles increases in the following order: $\text{Pd} (111) < \text{Pt} (111) < \text{Ru} (0001) < \text{Rh} (111)$ [136], whereas the activation barrier for water dissociation on the metallic surface increases as $\text{Ni} (211) < \text{Rh} (211) < \text{Co} (0001) \approx \text{Ru} (0001) < \text{Pt} (111) < \text{Pd} (111)$ [137]. Besides, numerical methods [137] were used to show that dissociation of water on

the Rh (211) surface is accompanied by heat release, which is a significant distinction from other platinum group metals (Ru, Pt, Pd, Ir). Thus, among the VIII group metals, the highest activity is expected for rhodium and ruthenium, and the lowest activity – for palladium. This assumption is supported by experimental data reported in [37-41, 46, 47, 138]. It should be noted that nearly in all activity series of metals indicated in Table 3, cobalt and nickel catalysts have a lower activity as compared to platinum systems.

An additional evidence that sodium borohydride hydrolysis proceeds by electrochemical mechanism is sensitivity of the reaction to changes in the electronic state of the active component particles reported in [47, 139, 140]. According to XPS and EXAFS-XANES data, the reduction of Rh/TiO₂ catalyst precalcined at 300°C leads to formation of the electron deficient rhodium particles on the titanium dioxide surface. If reduction in a sodium borohydride solution is performed with the Rh/TiO₂ catalyst calcined at a lower temperature (110-130°C), the charge state of rhodium is equal to that of the bulk metal. Investigation of their catalytic activity during hydrolysis of sodium borohydride showed that activity tends to grow with increasing the heat treatment temperature of unreduced compositions. The authors of [139] think that the presence of electron deficient rhodium particles on the support surface is the main reason for accelerating the decomposition of negatively charged BH_4^- ions and reduction of water (Fig. 2).

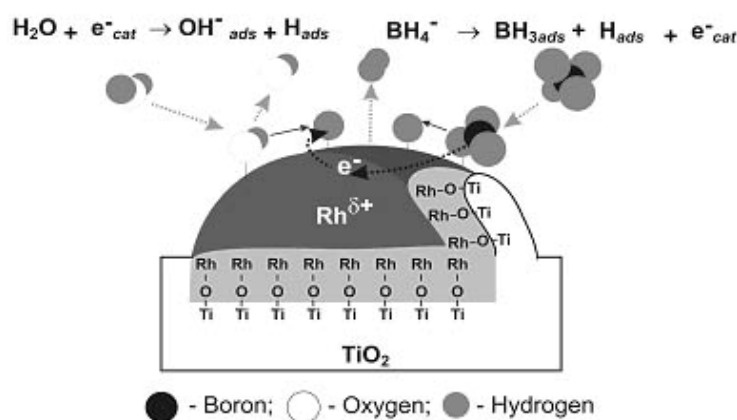


Fig. 2. A scheme of sodium borohydride hydrolysis on the catalyst surface.

CONCLUSION

Main lines of investigation of the sodium borohydride hydrolysis were analyzed. The method of hydrogen production via the interaction of sodium borohydride with acids was found to be unacceptable for operation of fuel cells, since it involves the formation of toxic diborane along with hydrogen. The introduction of the VIII group metals in a sodium borohydride solution provides generation of hydrogen saturated only with water vapor. Among such metals, the most active are ruthenium, rhodium and platinum. However, the majority of works on catalytic hydrolysis of sodium borohydride are devoted to bulk and supported cobalt-containing systems, which are the most inexpensive catalysts for portable hydrogen generators.

Studies on the activity of X-ray amorphous cobalt borides in sodium borohydride hydrolysis revealed that activity depends on the nature of the active component precursor and on the method of its introduction in the reaction medium. It was found that cobalt compounds are reduced under the action of sodium borohydride to form amorphous ferromagnetic borides, which catalyze the hydrolysis. Measurements of magnetic susceptibility can reliably identify the composition of amorphous catalytically active phase of cobalt borides. Crystallization of such catalytic systems during heat treatment leads to decrease of their activity. Modification of cobalt borides with phosphorus and transition metals (Ni, Fe, Cu, Cr, W, Mo) enhances their activity due to increase in specific surface area of the active component, formation of oxides with additional adsorption sites for reactants, changes in the electronic properties of metals, segregation of a metal on the surface of another metal or redistribution of the electron density between metals in the formed alloy particles.

Along with studying the activity of various catalysts in sodium borohydride hydrolysis, the kinetic regularities and reaction mechanism were elucidated. Zero order of the reaction is retained in a wide range of sodium borohydride concentrations; this confirms that the hydrogen generation rate is determined by accessibility of the metal surface to BH₄⁻ adsorption. This is the main feature of reactions proceeding by the Langmuir-Hinshelwood mechanism. However, investigation of the catalytic

hydrolysis of sodium borohydride in heavy water revealed that the process rate does not depend on dissociation rate of borohydride ion on the catalyst surface, rather it is limited by the rate of water decomposition. High values of the isotope separation coefficient, changes in electric potential of the catalyst (copper foil) immersed in a sodium borohydride solution, and high sensitivity to the electronic state of catalyst allow a conclusion that the main role in water activation on the catalyst is played by electrochemical transformations.

Taking into account electrochemical mechanism of the reaction, high activity of the platinum group metals in the hydrolysis of sodium borohydride can be attributed to high electric conductivity, high heat of water adsorption, and low activation barrier of water dissociation. Thus, rhodium is expected to exhibit the highest activity, and palladium—the lowest; this was observed in our works [46, 47, 140].

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