

# Hydrogen Generation by Reforming of Sodium Hypophosphite on Cobalt-Boron Oxides Containing Catalyst

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## Abstract

Cobalt-Boron oxides containing catalyst  $\text{CoO}\cdot\text{B}_2\text{O}_3$  ( $\text{CoB}_2\text{O}_4$ ) are synthesized for hydrogen generation by catalytic reforming of basic solution of sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ ) and identified by chemical and X-ray analysis. Reforming is performed in temperature range of  $30^\circ\text{C}$  -  $80^\circ\text{C}$ . Reaction rate constants at each value of temperature ( $k^{30^\circ\text{C}} = 8.53 \times 10^{-4} \text{ s}^{-1}$ ;  $k^{40^\circ\text{C}} = 1.62 \times 10^{-4} \text{ s}^{-1}$ ;  $k^{50^\circ\text{C}} = 3.06 \times 10^{-3} \text{ s}^{-1}$ ;  $k^{60^\circ\text{C}} = 5.06 \times 10^{-3} \text{ s}^{-1}$ ;  $k^{80^\circ\text{C}} = 1.39 \times 10^{-2} \text{ s}^{-1}$ ), temperature coefficient of rate of chemical reaction ( $\gamma = 0.917$ ) and activation energy ( $E_A = 49.59 \text{ kJ}\cdot\text{mol}^{-1}$ ) are calculated.

## Keywords

Cobalt-Boron Oxide, Hydrogen, Catalyst, Reforming, Sodium Hypophosphite

## 1. Introduction

The rapid depletion of traditional energy sources (crude oil, natural gas, coal, etc.) forces scientists to work on problems of development of alternative energy sources. An unlimited amount of hydrogen is a very attractive candidate as an ecologically friendly source of energy. Hydrogen, used in fuel cells as fuel and obtained by catalytic reforming of natural gas or crude oil, contains carbon monoxide. Even a small amount of CO poisons electrodes containing Pt and Pd and negatively effects performance of fuel cell. Storage and transportation of hydrogen are also an issue. Storage of hydrogen under high pressure, in a liquid form or cryoadsorbed form cannot satisfy demands of safety. The most promising way to store hydrogen is to keep it bound in hydrides of different metals [1]-[9].

In this work we present the possibility of utilization of sodium hypophosphate

( $\text{NaH}_2\text{PO}_2$ ) as a source of hydrogen for fuel cells. In a process of chemical nickel-plating at temperatures of  $80^\circ\text{C}$  -  $95^\circ\text{C}$ , hydrogen is generated due to interaction of  $\text{NaH}_2\text{PO}_2$  with water. This process takes place with high rate only on metals which exhibit catalytic activity at a high temperature. For this purpose, the surface is usually treated with solution of  $\text{SnCl}_2$  and activated with compounds of  $\text{Pd}^{2+}$ .  $\text{Sn}^{2+}$  ions on the surface reduce  $\text{Pd}^{2+}$  ions to metal Pd, thin catalytic layer of which uniformly covers the treated surface. For example, total reaction of reduction of  $\text{Ni}^{2+}$  ions reduction on surfaces activated by metal palladium can be presented as [10]-[16]:



Therefore selection of commercially competitive and efficient catalysts, which will be active at low temperature for hydrogen generation from sodium hypophosphite, is problem.

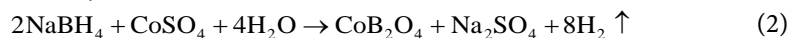
The goal of the present work is synthesis of highly active catalyst  $\text{CoO}\cdot\text{B}_2\text{O}_3$  for generation of hydrogen from solution of  $\text{NaH}_2\text{PO}_2$ .

## 2. Experimental

### 2.1. Reagents and Methods of Analysis

$\text{NaOH}$ ,  $\text{NaH}_2\text{PO}_2$ ,  $\text{CoSO}_4$ ,  $\text{NaBH}_4$  grade of "Chemically pure reagents" were used. Solutions were prepared using distilled water.

To synthesize boron containing cobalt catalyst, 20 mL of 0.6 M  $\text{NaBH}_4$  solution was added dropwise under stirring at temperature of  $90^\circ\text{C}$  (exothermic process) to 20 mL of 1 M  $\text{CoSO}_4$  solution under stirring (stirring rate 800 rpm) at temperature of  $90^\circ\text{C}$  (exothermic process). Hot pulp was filtrated and washed with hot water until sulfate ions were removed [2]. The precipitate was dried in the thermostat at  $105^\circ\text{C}$  until the uniform substance was obtained. Content of boron (14.7%) in the mixture was determined by volumetric method and cobalt (44.0%) was determined by spectroscopic method (Perkin Elmer, B3150050). The results showed that we synthesized compound contains  $\text{CoO}\cdot\text{B}_2\text{O}_3$  ( $\text{CoB}_2\text{O}_4$ ). The reaction of synthesis can be written as:



Synthesized  $\text{CoO}\cdot\text{B}_2\text{O}_3$  was identified by thermographic and X-ray analysis.

Thermogravimetric method of analysis of synthesized  $\text{CoO}\cdot\text{B}_2\text{O}_3$  was performed on derivatograph Q-1500 D with rate of heating  $10^\circ\text{C}/\text{min}$ . On TG and DTG curves at  $350^\circ\text{C}$ , it can be observed the loss of mass caused by evaporation of adsorbed and bounded water. On DTA curve, in the range of  $350^\circ\text{C}$  -  $600^\circ\text{C}$ , exoeffects with two maximums at temperatures of  $420^\circ\text{C}$  and  $500^\circ\text{C}$  were observed. This phenomenon can be explained by overlay of exoeffect of oxidation of  $\text{CoO}$  by oxygen to  $\text{Co}_3\text{O}_4$  on endothermic effect of partial conversion of solid solution (Figure 1).

X-ray investigation of synthesized sample annealed at  $350^\circ\text{C}$  in a muffle furnace for 2 hours was performed on "DRON-3M" diffractometer by  $\text{CuK}_\alpha$ -irradiation in monochromatic conditions in the interval of reflection angle  $2\theta = 20^\circ$  -

65°. Phase content of studied samples was determined by comparison of experimental set of interplanar distances and relative intensity of diffraction maxima with directory of ASTM. Based on X-ray data the main phase of the sample, annealed at 350°C is  $\text{CoO}\cdot\text{B}_2\text{O}_3$  (2.88 Å, 2.44 Å, 2.08 Å, 2.03 Å, 1.75 Å, 1.65 Å, 1.56 Å, 1.43 Å). In the sample annealed at 600°C, peaks of new phase of  $\text{Co}_3\text{B}_2\text{O}_6$  were detected together with the main phase peaks of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  (3.99 Å, 3.49 Å, 2.69 Å, 2.50 Å, 2.25 Å, 2.09 Å, 1.74 Å, 1.67 Å, 1.53 Å). Identification of  $\text{Co}_3\text{O}_4$  (Figure 1, curve DTA, 350°C - 600°C), is complicated due to similarity with X-ray picture of  $\text{CoO}\cdot\text{B}_2\text{O}_3$ .

Surface morphology of synthesized sample (photo 1) was studied by scanning electron microscopy (SEM) with different magnification ( $\times 1000$ ,  $\times 10,000$  and  $\times 27,000$ ) (Figure 2).

After catalytic decomposition of  $\text{NaH}_2\text{PO}_2$  hydrogen was generated in a glass reactor placed in a thermostat and provided with condenser and sealed nozzle

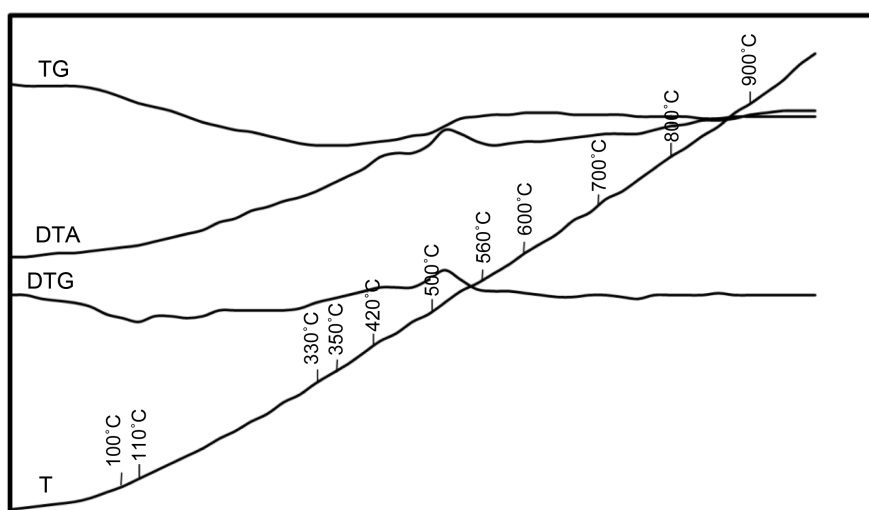


Figure 1. Derivatogram of synthesized sample of  $\text{CoO}\cdot\text{B}_2\text{O}_3$ .

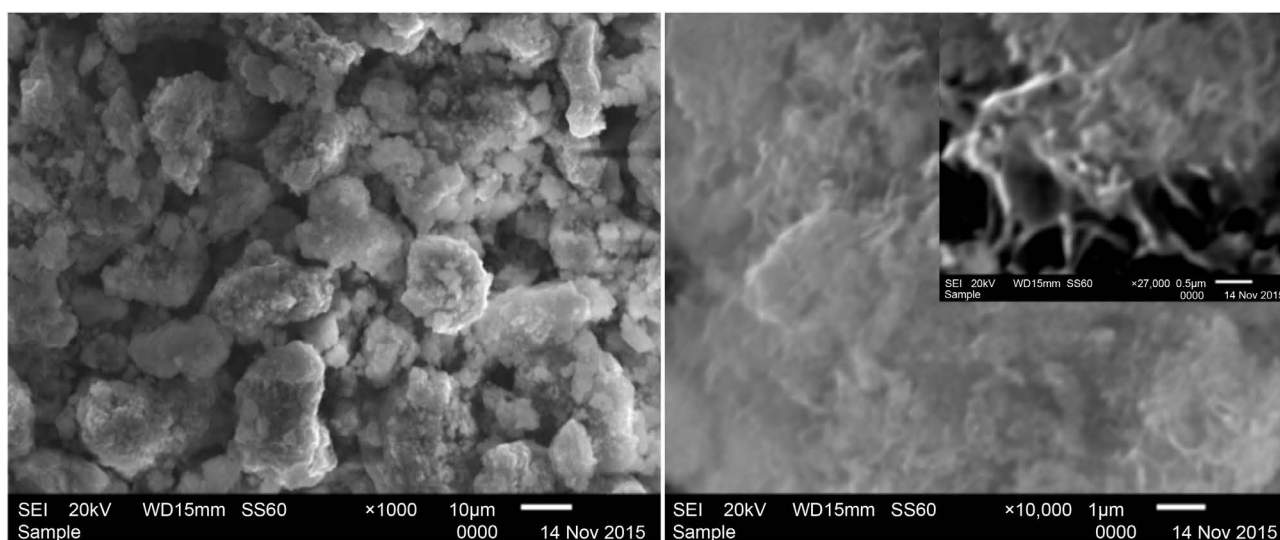


Figure 2. Surface of synthesized sample of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  annealed at 350°C.

with gas outlet tube connected to the burette (Figure 3). The amount of evolved hydrogen was calculated by the equation:

$$V_0 = (P_{\text{atm}} - P_{\text{H}_2\text{O}}) 273 \left( \frac{V}{760(273+t)} \right) \quad (3)$$

$V_0$ —volume of hydrogen at normal temperature and pressure (NTP) (ml);  
 $V$ —volume of evolved hydrogen (ml) under experimental conditions;  $P_{\text{H}_2\text{O}}$   
 —pressure of water vapor (mmHg);  $t$ —ambient temperature ( $^{\circ}\text{C}$ ).

Specific rate of hydrogen evolution  $W$  ( $\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ ) in the range of temperatures  $20^{\circ}\text{C}$  -  $80^{\circ}\text{C}$  is determined by equation:

$$W = Vt^{-1}m^{-1} \quad (4)$$

$V$  is volume of hydrogen generated at room temperature (ml);  $t$ —time of reaction (min);  $m$ —mass of catalyst (g).

Based on the method discussed, hydrogen will be obtained on site in fuel cell and problems with storage and transportation of hydrogen will be avoided.

### 3. Results and Discussions

Hydrolysis of  $\text{NaH}_2\text{PO}_2$  is performed in solution of  $2\text{ M NaH}_2\text{PO}_2 + 2\text{ M NaOH}$  in presence of  $0.1\text{ g}$  of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst (dried at temperature  $105^{\circ}\text{C}$ ) until the full evolution of hydrogen.. With increase of temperature of solution, rate of hydrogen evolution is significantly increased: in  $60\text{ min}$  at  $30^{\circ}\text{C}$ ,  $620\text{ ml}$  of hydrogen was evolved, while at  $80^{\circ}\text{C}$  the same volume of hydrogen was evolved in  $4\text{ min}$ . The rate of generation of hydrogen increased almost  $20\text{ times}$  (Figure 4).

Catalytic activity of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  was determined in a process of hydrolysis of  $\text{NaH}_2\text{PO}_2$  (solution temperature  $30^{\circ}\text{C}$ ) in presence of catalysts annealed at  $105^{\circ}\text{C}$ ,  $280^{\circ}\text{C}$ ,  $350^{\circ}\text{C}$  and  $480^{\circ}\text{C}$ . Efficiency of hydrogen evolution reached  $95\%$  on a catalyst annealed at  $280^{\circ}\text{C}$ . Generation of hydrogen on a catalyst annealed at  $350^{\circ}\text{C}$  was finished in  $25\text{ min}$  and the efficiency was  $78\%$ . The same time ( $25$

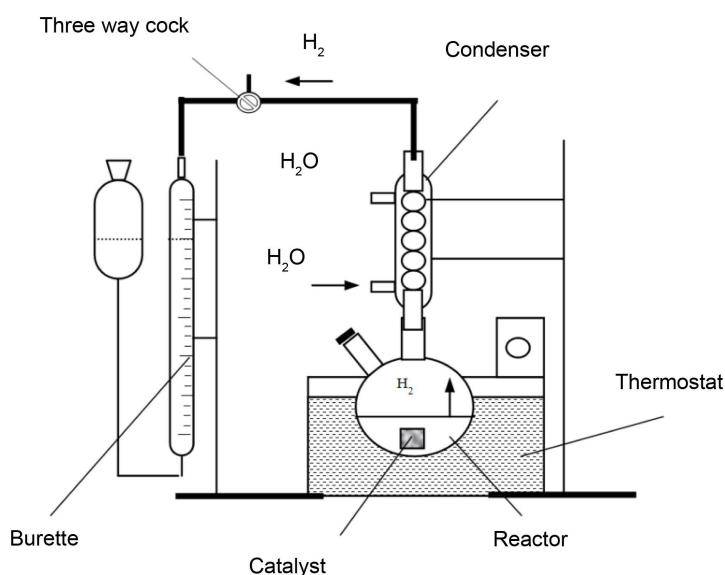
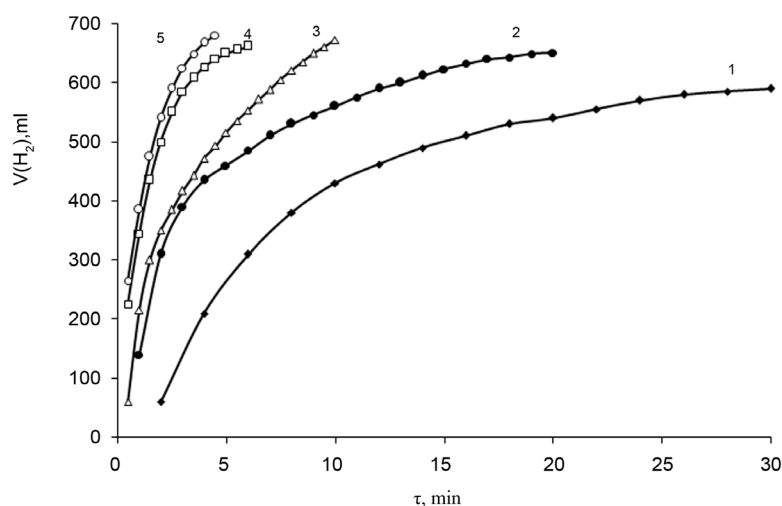


Figure 3. Scheme of a set up for catalytic decomposition of  $\text{NaH}_2\text{PO}_2$ .

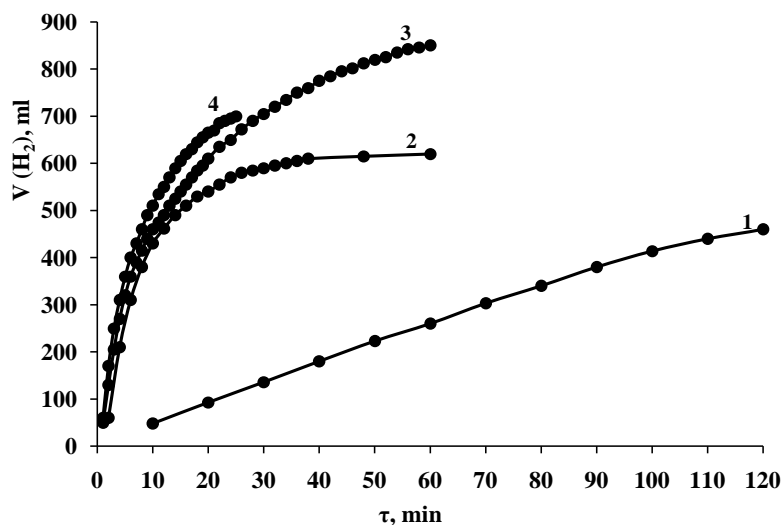
min) was necessary to generate hydrogen with 74% at a catalyst annealed at 280 °C (Figure 5).

Figure 6 and Figure 7 show results of experiments conducted with catalysts annealed at 280 °C and 350 °C and with rest of conditions as above. The change of temperature of solution from 30 °C to 80 °C accelerated generation of hydrogen about 22 times (from 14 mL/min to 315 mL/min) in the first case (catalyst annealed at 280 °C) and 16 times (from 24 mL/min to 390 mL/min) in the second case (catalyst annealed at 280 °C).

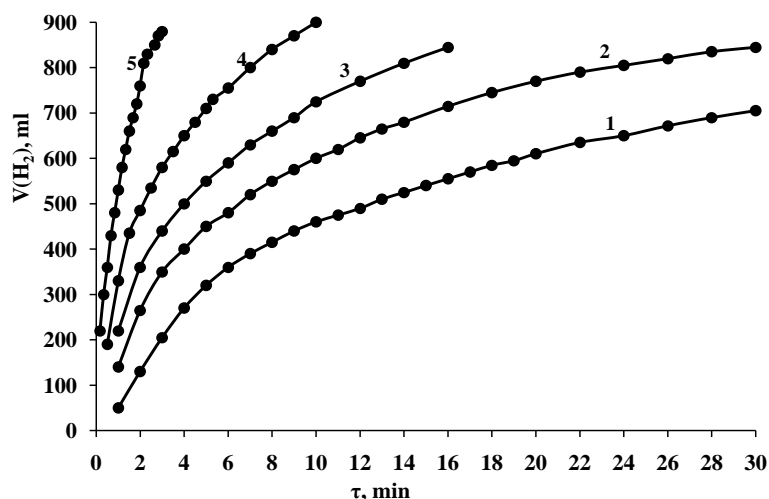
Reactions rate constants, energy of activation and temperature coefficients of reforming rates of sodium hypophosphate reforming rates on  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst



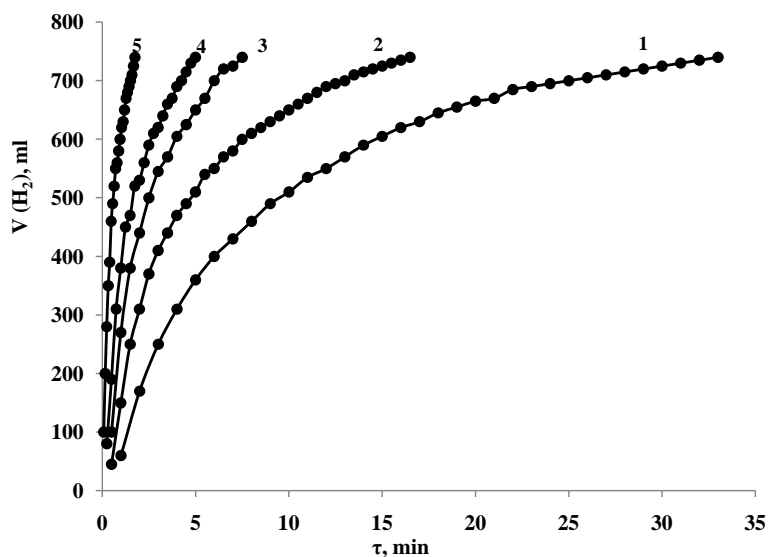
**Figure 4.** Dependence of volume of generated hydrogen during the process of  $\text{NaH}_2\text{PO}_2$  hydrolysis with presence of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst at solution temperature (solution volume 20 mL; solution composition—2 M  $\text{NaH}_2\text{PO}_2$  + 2 M  $\text{NaOH}$ ; mass of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst—0.1 g): 1—30 °C; 2—40 °C; 3—50 °C; 4—60 °C; 5—80 °C.



**Figure 5.** Dependence of volume of generated hydrogen during the process of  $\text{NaH}_2\text{PO}_2$  hydrolysis in presence of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  annealed at different temperatures (solution volume—20 mL; solution composition 2 M  $\text{NaH}_2\text{PO}_2$  + 2 M  $\text{NaOH}$ ; mass of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst—0.1 g; solution temperature 30 °C): 1—480 °C; 2—105 °C; 3—280 °C; 4—350 °C.



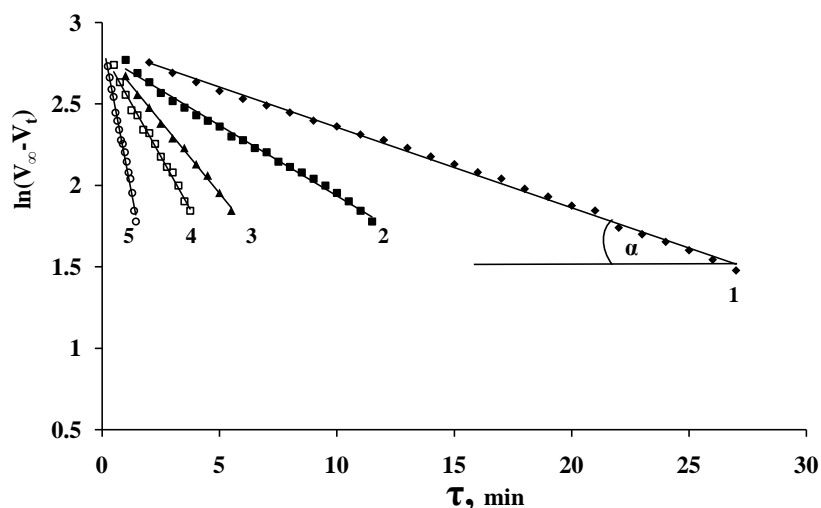
**Figure 6.** Dependence of volume of generated hydrogen during the process of  $\text{NaH}_2\text{PO}_2$  hydrolysis in presence of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  at solution temperature (solution volume—20 mL; solution composition 2 M  $\text{NaH}_2\text{PO}_2$  + 2 M  $\text{NaOH}$ ; mass of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst annealed at  $280^\circ\text{C}$ —0.1 g): 1— $30^\circ\text{C}$ ; 2— $40^\circ\text{C}$ ; 3— $50^\circ\text{C}$ ; 4— $60^\circ\text{C}$ ; 5— $80^\circ\text{C}$ .



**Figure 7.** Dependence of volume of generated hydrogen during the process of  $\text{NaH}_2\text{PO}_2$  hydrolysis in presence of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  at solution temperature (solution volume—20 mL; solution composition 2 M  $\text{NaH}_2\text{PO}_2$  + 2 M  $\text{NaOH}$ ; mass of  $\text{CoO}\cdot\text{B}_2\text{O}_3$  catalyst annealed at  $350^\circ\text{C}$ —0.1 g): 1— $30^\circ\text{C}$ ; 2— $40^\circ\text{C}$ ; 3— $50^\circ\text{C}$ ; 4— $60^\circ\text{C}$ ; 5— $80^\circ\text{C}$ .

annealed at  $350^\circ\text{C}$  were determined. Using data of five parallel experiments we built the plot showing dependence of natural log of difference of hydrogen volumes on time  $\ln(b_\infty - b_t) - \tau$ , where  $b_\infty$ —hydrogen volume at a normal temperature and pressure (NTP) (ml), allocated until the full decomposition of  $\text{NaH}_2\text{PO}_2$ ,  $b_t$ —hydrogen volume (ml) (NTP), generated in time point  $\tau$  (**Figure 8**). Straight lines not crossing the origin of coordinate axes were obtained. Tangent of slope angle of the straight line to an axis of time is equal to a reaction rate constant:

$$K = \text{tg } \alpha \tag{5}$$



**Figure 8.** Dependence of logarithm of the difference of the volumes hydrogen on time at different temperatures of solution: 1—30 °C; 2—40 °C; 3—50 °C; 4—60 °C; 5—80 °C (solution volume 20 ml, solution composition 2 M NaH<sub>2</sub>PO<sub>2</sub> + 2 M NaOH; mass of CoO·B<sub>2</sub>O<sub>3</sub> catalyst —0.1 g).

At each temperature,  $k^{30^\circ} = 8.53 \times 10^{-4} \text{ s}^{-1}$ ;  $k^{40^\circ} = 1.62 \times 10^{-4} \text{ s}^{-1}$ ;  $k^{50^\circ} = 3.06 \times 10^{-3} \text{ s}^{-1}$ ;  $k^{60^\circ} = 5.06 \times 10^{-3} \text{ s}^{-1}$ ;  $k^{80^\circ} = 1.39 \times 10^{-2} \text{ s}^{-1}$  were calculated.

Using Equations (6) and (7) and rate constants calculated at two temperatures, temperature coefficient and activation energy of chemical reaction were calculated as  $\gamma = 0.917$ ;  $E_A = 49.59 \text{ kJ}\cdot\text{mol}^{-1}$ .

$$\gamma = \frac{T_2 - T_1}{T_1 T_2} \sqrt[k_2 - k_1] \quad (6)$$

$$E_A = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1} \quad (7)$$

$\gamma$ —temperature coefficient of rate of chemical reaction;  $k_1$  and  $k_2$  rate constants at  $T_1$  and  $T_2$ , respectively;  $R$ —universal gas constant;  $E_A$  energy of activation.

#### 4. Conclusions

Catalyst CoO·B<sub>2</sub>O<sub>3</sub> is synthesized and identified by chemical and X-ray analysis. Thermal stability of the sample is estimated and temperature of conversion is determined.

Synthesized compound CoO·B<sub>2</sub>O<sub>3</sub> was used as a catalyst during reforming of sodium hypophosphate. Samples annealed at 280 °C - 350 °C demonstrated best catalytic activity. Reforming of NaH<sub>2</sub>PO<sub>2</sub> was conducted in a solution of 2 M (NaH<sub>2</sub>PO<sub>2</sub> + NaOH) at range of temperatures 30 °C - 80 °C; rate constants  $k^{30^\circ} = 8.53 \times 10^{-4} \text{ s}^{-1}$ ;  $k^{40^\circ} = 1.62 \times 10^{-4} \text{ s}^{-1}$ ;  $k^{50^\circ} = 3.06 \times 10^{-3} \text{ s}^{-1}$ ;  $k^{60^\circ} = 5.06 \times 10^{-3} \text{ s}^{-1}$ ;  $k^{80^\circ} = 1.39 \times 10^{-2} \text{ s}^{-1}$ , temperature coefficient  $\gamma = 0.917$  and activation energy  $E_A = 49.59 \text{ kJ}\cdot\text{mol}^{-1}$  are calculated.

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## References

- [1] Mesyac, G. and Prokhorov, M. (2004) Vodorodnaiyajenergetika I toplivnyejelementy. *Journal Vestnik RAN*, **74**, 579-597.  
[http://vivovoco.astronet.ru/VV/JOURNAL/VRAN/2004/04\\_07/HYDRO.HTM](http://vivovoco.astronet.ru/VV/JOURNAL/VRAN/2004/04_07/HYDRO.HTM)
- [2] Nikoleishvili, P., Tsurtsumia, G., Kveselava, V., Gorelishvili, G., Kurtanidze, R., Sharabidze, D. and Dzanashvili, D. (2015) Using Hydrogen Obtained by Reforming of NaBH<sub>4</sub> on Modified Cobalt Catalyst in Hydrogen-Oxygen Fuel Cell. *Russian Journal of Electrochemistry*, **51**, 665-671.
- [3] Stiegel, G.J. and Ramezan, M. (2006) Hydrogen from Coal Gasification: An Economical Pathway to a Sustainable Energy Future. *International Journal of Coal Geology*, **65**, 173-190. <http://www.elsevier.com/locate/ijcoalgeo>
- [4] Baschuk, J.J. and Li, X. (2001) Carbon Monoxide Poisoning of Proton Exchange Membrane Fuel Cells. *International Journal of Energy Research*, **25**, 695-713.  
<https://doi.org/10.1002/er.713>
- [5] Schlapbach, L. (2002) Hydrogen as a Fuel and Its Storage for Mobility and Transport. *MRS Bulletin*, **27**, 675-679. <https://doi.org/10.1557/mrs2002.220>
- [6] Pena-Alonso, R., Sicurelli, A., Callone, E., Carturan, G. and Raj, R. (2007) A Picoscale Catalyst for Hydrogen Generation from NaBH<sub>4</sub> for Fuel Cells. *Journal of Power Sources*, **165**, 315-323. <https://doi.org/10.1016/j.jpowsour.2006.12.043>
- [7] Lee, J., Kong, K.Y., Jung, C.R., Cho, E., Yoon, S.P., Han, J., Lee, T.-G. and Nam, S.W. (2007) A Structured Co-B Catalyst for Hydrogen Extraction from NaBH<sub>4</sub> Solution. *Catalysis Today*, **120**, 305-310. <https://doi.org/10.1016/j.cattod.2006.09.019>
- [8] Dunn, S. (2002) Hydrogen Futures: Toward a Sustainable Energy System. *International Journal of Hydrogen Energy*, **27**, 235-264.  
[https://doi.org/10.1016/S0360-3199\(01\)00131-8](https://doi.org/10.1016/S0360-3199(01)00131-8)
- [9] Dincer, I. (2002) Technical, Environmental and Exergetic Aspects of Hydrogen Energy Systems. *International Journal of Hydrogen Energy*, **27**, 265-285.  
[https://doi.org/10.1016/S0360-3199\(01\)00119-7](https://doi.org/10.1016/S0360-3199(01)00119-7)
- [10] Petrova, T. (2000) Khimicheskiepokritija. *Sorosovskiy Obozrevatelnyy Zhurnal*, **6**, 57-62.
- [11] Wu, C., Wu, F., Bai, Y., Yi, B. and Zhang, H. (2005) Cobalt Boride Catalysts for Hydrogen Generation from Alkaline NaBH<sub>4</sub> Solution. *Materials Letters*, **59**, 1748-1751.
- [12] Gang, W., Ning, L. and Song, D. (2004) Electrochemical Preparation and Characteristics of Ni-Co-LaNi<sub>5</sub> Composite Coatings as Electrode Materials for Hydrogen Evolution. *Materials Chemistry and Physics*, **83**, 307-314.  
<http://www.elsevier.com/locate/matchemphys>
- [13] Lupi, C. and DellEra, A. (2009) Nickel-Cobalt Electrodeposited Alloys for Hydrogen Evolution in Alkaline Media. *International Journal of Hydrogen Energy*, **34**, 2101-2106.
- [14] Hu, X., Brunschwig, B.S. and Peters, J.C. (2007) Electrocatalytic Hydrogen Evolution at Low Overpotentials by Cobalt Macrocyclic Glyoxime and Tetraimine Complexes. *Journal of the American Chemical Society*, **129**, 8988-8998.
- [15] Kuznecov, V., Kalinkina, A., Pshenichkina, T. and Balabaev, V. (2008) Electrocata-



lytic Properties of Cobalt-Molybdenum Alloy Deposits in the Hydrogen Evolution Reaction. *Russian Journal of Electrochemistry*, **44**, 1350-1358.

<https://doi.org/10.1134/S1023193508120070>

- [16] Dolgikh, O., Sockaija, N., Kravcov, I. and Slepova, O. (2007) Catalytic Activity of Nickel Alloy in the Hydrogen Evolution Reaction. *Vestnik VGU*, **1**, 33-38.



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