

Short Communication

Aqueous-alkaline NaBH₄ solutions: The influence of hydride decomposition on catalytic properties of Co₃O₄O.V. Netskina^{a,b,*}, O.V. Komova^a, S.A. Mukha^a, V.I. Simagina^a^a Laboratory of Hydride Investigation, Borevskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5, Novosibirsk 630090, Russia^b Novosibirsk State University, Pirogova Str. 2, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:

Received 20 April 2016

Received in revised form 6 July 2016

Accepted 7 July 2016

Available online 08 July 2016

Keywords:

Sodium borohydride

Hydrolysis

Reduction

Cobalt

Catalyst

ABSTRACT

The formation of the catalytically active phase of cobalt catalysts from Co₃O₄ has been studied in fresh aqueous-alkaline NaBH₄ solution and in solution after 1 year of storage. It was noted that the hydride concentration of the aged solution was reduced from 15 to 5.1 wt% while its pH increased from 11.5 to 12.9 with the formation of sodium borates. It was these changes in the solution composition that were responsible for the longer time of activation of the cobalt catalyst and its low activity for NaBH₄ hydrolysis as compared with the catalyst that was reduced in the fresh solution.

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1. Introduction

For an efficient operation of the proton exchange membrane fuel cell and the energy conversion devices based on hydrogen combustion the use of compact sources of high-pure hydrogen is necessary [1,2]. Now intense studies are under way to create hydrogen generators based on sodium borohydride (NaBH₄) hydrolysis [3,4]. Such generators use aqueous-alkaline solutions of sodium borohydride as a source of energy which do not freeze at temperatures to as low as –20 °C [5]. At any ambient temperature, high-pure hydrogen can be generated by feeding a solution of the hydride into a catalytic layer and the process proceeds without additional heating. When choosing a catalyst for hydrogen generators not only its activity but also its cost is to be taken into consideration and, therefore, among the studied catalytic systems based on Group VIII metals [6,7] the cobalt-containing catalysts are of much interest [8–11]. It has been shown [12,13] that after the addition of cobalt oxide to a NaBH₄ solution a hydrogen generation started after an induction period during which the active component was formed under the action of the hydride – a strong reducing agent [14,15]. The time of activation increased in the presence of sodium hydroxide [16] which is used to prevent sodium borohydride interaction with water during prolong storage. Nevertheless the non-catalytic hydrolysis of sodium borohydride does take place upon a prolong storage of an aqueous-alkaline solution of NaBH₄ [17,18]. A slowly proceeding interaction of the

hydride with water during the storage not only leads to a considerable decrease in the hydrogen content but also to a change in the composition of the solution. However, until now no information has been presented in the literature about the influence of changes in the composition of an aqueous-alkaline NaBH₄ solution on the *in situ* reduction of cobalt catalysts in the reaction medium.

In this work the formation of the active component of cobalt catalysts from Co₃O₄ in a fresh aqueous-alkaline NaBH₄ solution has been compared with this process in the hydride solution which was stored for 1 year (Table 1) under conditions approaching the real storage conditions of NaBH₄ solution as a source of hydrogen. The effect of the composition of reaction medium on the activity and stability of the cobalt catalysts was studied.

2. Experimental

2.1. Materials

Commercial chemical reagents: sodium borohydride, NaBH₄ (CAS 16940-66-2, Acros Organics, 98 wt%); cobalt oxide, Co₃O₄ (GOST 4467-79); sodium hydroxide, NaOH (GOST 4328-77) were used as received.

2.2. Hydrogen generation experiments and preparation of catalysts

Sodium borohydride hydrolysis was carried out at 40 °C in a temperature-controlled glass reactor with a magnetic stirrer at 800 rpm. At stirring rates higher than 200 rpm the influence of the external diffusion

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Table 1
Properties of aqueous-alkaline NaBH₄ solutions.

No	Composition of solution	Storage time	Extent of NaBH ₄ decomposition, wt%	NaBH ₄ content, wt%	H ₂ output, L/kg _{solution}	pH
1	15 wt% NaBH ₄ 5 wt% NaOH	Fresh	–	15	353.7	11.5
2	15 wt% NaBH ₄ 5 wt% NaOH	1 year ^a	66	5.1	120.3	12.9

^a – Stored at room temperature (23–25 °C).

processes was found to be negligible. 10 mL of an aqueous-alkaline solution of sodium borohydride was loaded into the reactor. A weighed amount of Co₃O₄ (0.025 g) was then added and the volume of the generated hydrogen gas was measured with a gas burette. Co₃O₄ was reduced *in situ* by the sodium borohydride in the reaction medium, whose composition was varied. **Co₃O₄-B-fresh** was obtained in a freshly prepared solution containing 15 wt% NaBH₄ and 5 wt% NaOH. **Co₃O₄-B-old** was obtained in a 15 wt% NaBH₄ and 5 wt% NaOH solution after a one-year storage. After the reaction was complete, the catalysts were separated from the reaction medium, washed with distilled water, dried at 40 °C for 4 h under argon and then studied by physical methods.

The long-term cyclic stability of catalysts was tested by repeating the above procedure of NaBH₄ hydrolysis. After the first portion of NaBH₄ solution (10 mL) was fully converted, the catalyst was separated from the solution and a new portion of NaBH₄ solution (10 mL) was added to the reactor. The hydride solution was the same that was used for the stage of catalyst reduction.

To obtain reliable data each experiment was repeated at least three times. Differences of the experimental values did not exceed ± 3%.

2.3. Physical measurements

The pH of fresh aqueous-alkaline NaBH₄ solutions and aqueous-alkaline NaBH₄ solution after a one-year storage was measured by an ANION-4100 m (Russia).

The ATR-IR spectra were obtained using an Agilent Cary 600 series spectrometer (Agilent Technologies, USA) equipped with a GladiATR accessory (PIKE Technologies) in the range from 4000 to 400 cm⁻¹ without pretreatment of the samples.

The phase analysis of the product of non-catalytic NaBH₄ hydrolysis was performed using a Bruker D8 Advance (Germany) diffractometer with a step 2θ = 0.05° and the time of accumulation of 2 s in each point, using a Lynxeye linear detector. Monochromatic CuK_α-radiation (λ = 1.5418 Å) was used.

The high-resolution transmission electron microscopy (HR TEM) study of the catalysts was carried out on a (JEM-2010, Japan)

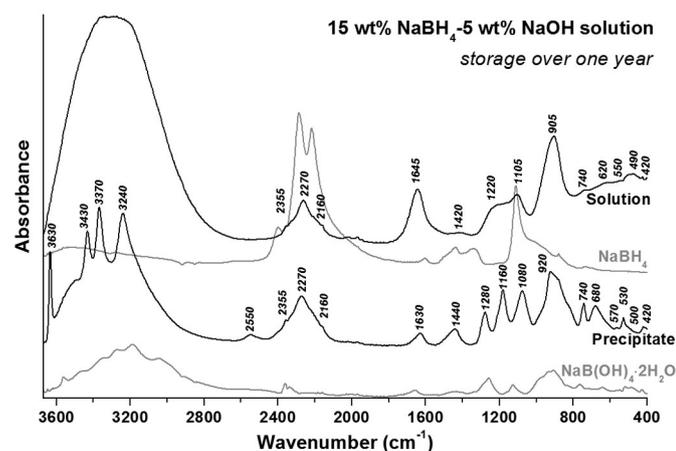


Fig. 1. IR spectra of the solution and the precipitate which formed after a one year storage of 15 wt% NaBH₄-5 wt% NaOH over one year.

instrument with a lattice resolution of 1.4 Å and accelerating voltage of 200 kV. The elemental analysis of the samples was carried out by energy dispersive X-ray microanalysis (EDX) on an EDAX Phoenix spectrometer equipped with a Si(Li) detector with an energy resolution of 130 eV and higher. The samples to be analyzed were applied to a holey carbon film fixed on a standard copper grid.

X-ray photoelectron spectra (XPS) were recorded on a SPECS (Germany) photoelectron spectrometer using a hemispherical PHOIBOS-150-MCD-9 analyzer and FOCUS-500 (Al K_α radiation, hν = 1486.74 eV, 150 W) monochromator. The binding energy (BE) scale was pre-calibrated using the positions of the peaks of Au4f_{7/2} (BE = 84.0 eV) and Cu2p_{3/2} (BE = 932.67 eV) core levels. The samples were placed onto a conducting double-sided copper scotch. The C 1s peak at 284.8 eV was used as internal standard. The survey spectra were taken at analyzer pass energy of 50 eV and the detailed spectra (B 1s, C 1s, O 1s Co 2p) were registered at 20 eV. Analysis of individual spectral regions allowed determination of the peaks, identification of the chemical state of elements and calculation of atomic concentration ratios of elements on the sample surface, which were corrected using corresponding atomic sensitivity factor.

3. Results and discussion

3.1. The effect of storage time of NaBH₄ solutions on their properties

In this work an aqueous-alkaline solution of sodium borohydride containing 15 wt% NaBH₄ and 5 wt% NaOH was used as the hydrogen source. It was established that during its storage for 1 year there took place a slow liberation of hydrogen and after one year hydride content was reduced from 15 to 5.1 wt % (Table 1). It was noted that pH of a solution increases from 11.5 to 12.9. According to IR spectroscopy data (Fig. 1) the non-catalytic hydrolysis NaBH₄ led to the formation of sodium borate which gradually accumulated in the solution and formed a precipitate (Fig. S1) as a result of its smaller solubility (28 g per 100 g water) as compared with the hydride (56 g per 100 g water). According to XRD (Fig. S2), the diffraction patterns of the precipitate showed reflections coinciding with those of hydrated sodium tetrahydroxyborate NaB(OH)₄·2H₂O (ICSD 72913).

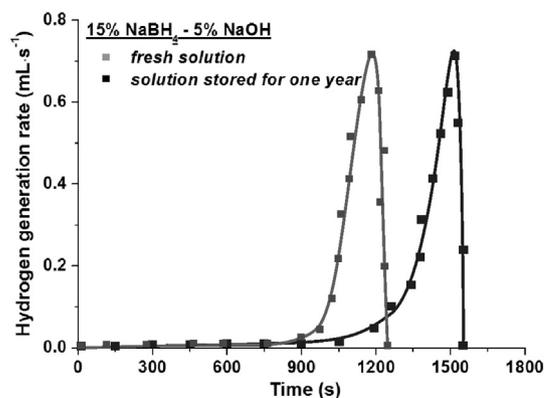


Fig. 2. Reduction of cobalt oxide in 15 wt% NaBH₄-5wt % NaOH solutions. Grey line and grey squares – fresh solutions. Black line and black squares – solutions stored for one year.

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