



Cobalt boride catalysts for small-scale energy application



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ABSTRACT

The objects of investigation were cobalt boride catalysts for a one-step production of hydrogen from NaBH₄. Cobalt oxides prepared by calcination of cobalt salts at 500 °C were used as precursors of the catalyst active phase. It was shown that the nature of the cobalt oxide precursor has a substantial influence on the rate of formation of active component in the reaction medium of sodium borohydride and, hence, on its activity in NaBH₄ hydrolysis. The length of the activation period and catalytic activity do not correlate with the dispersion and the specific surface area of the synthesized Co₃O₄ samples but depend on their inhomogeneity and the defect structure of the oxide due to the distribution of cobalt ions in the crystal lattice. The more defects are present in Co₃O₄ the faster the rate of its reduction and, hence, the higher its catalytic activity in NaBH₄ hydrolysis.

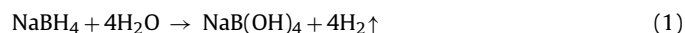
On the basis of active oxide prepared from cobalt chloride, solid state NaBH₄ pellets have been prepared. For the first time, NaBH₄ pellets were used as a source of H₂ source for a thermo-electrical energy conversion device based on combustion technologies.

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1. Introduction

The use of the state-of-the-art mobile devices is not possible without reliable charging devices, including their operation under field conditions. The problem is especially important in the developing countries where they have no developed power energy transmission networks. The absence of stationary energy supplies in non-electrified regions stimulates development of autonomous energy-generation-systems. In spite of considerable progress in this direction fuel-cell based energy sources still remain expensive. An alternative method for power energy generation which has actively been developed during the past decade consists in thermoelectric and thermo-photoelectric conversion of the heat and the thermal radiation released as a result of fuel combustion in microchambers [1]. The relatively low cost of the components and materials involved, the absence of stringent requirements for the gas purity, the environmental friendliness and safety of this method make it attractive for use in small-scale autonomous energy sources. Both fuel cells and combustion-based devices

require systems for hydrogen storage and hydrogen generation. Sodium borohydride is an attractive hydrogen storage material (with a high hydrogen capacity) for small-scale autonomous energy sources [2,3]. Unlike most of the other hydrides, NaBH₄ is not dangerous in storage and slowly reacts with water, with the latter serving as an additional source of hydrogen.



Complete release of hydrogen is possible only in the presence of catalysts which help to obtain hydrogen of a high purity at ambient temperatures without additional heating [4]. Cobalt boride forming in the reaction medium provides a cheap and efficient catalyst for sodium borohydride hydrolysis [5–7]. Different compounds of cobalt have been studied for use as catalyst precursors in NaBH₄ hydrolysis. Cobalt oxides have been found to be an efficient catalyst for this application [8]. Unlike the salts of cobalt, cobalt oxides are gradually reduced by sodium borohydride which ensures a high rate of H₂ gas generation even in repeated durability tests in a batch reactor [9].

In this work cobalt oxide has been used as a catalytic additive in solid-state NaBH₄ pellets. The pellets were then tested as a source of hydrogen for thermo-electrical energy conversion device based on combustion technologies. The physicochemical

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properties of different samples of Co_3O_4 and their activity in sodium borohydride hydrolysis have been studied. The importance of these studies has been emphasized by Demirci and Miele [10] who believe that systematic studies of the effect of the nature of precursors on the catalytic activity of cobalt catalysts are essential, especially for finding the mechanism of sodium borohydride hydrolysis on cobalt catalysts.

2. Experimental

2.1. Material

Commercial chemical reagents sodium borohydride, NaBH_4 (Acros Organics, 98 wt.%); cobalt (II) chloride hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (GOST 4525-77); commercial cobalt (II, III) oxide, Co_3O_4 (GOST 4467-79); cobalt (II) nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (GOST 4528-78); cobalt (II) acetate tetrahydrate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (GOST 5861-79); sodium hydroxide, NaOH (GOST 4328-77); acetone (GOST 2603-79) were used as received.

Commercial Co_3O_4 was prepared by calcining cobalt hydroxide at 900°C . Chemical analysis showed it to contain: Co – 81.4 wt.%; Ni – 0.12 wt.%; Fe, Cu, Zn < 0.01 wt.% (of each metal); Ca – 0.03 wt.%; N, S, K, Na < 0.05 wt.% (of each element).

2.2. Cobalt oxide preparation

Three types of cobalt oxide catalysts were prepared: (I) $\text{Co}_3\text{O}_4\text{-Cl}$ prepared by calcination of cobalt chloride; (II) $\text{Co}_3\text{O}_4\text{-C}$ prepared by calcination of cobalt acetate; (III) $\text{Co}_3\text{O}_4\text{-N}$ prepared by calcination cobalt nitrate. All salts were calcinated at 500°C in the air for 4 h.

2.3. Pellet preparation

Weighed amounts of mixtures of NaBH_4 and cobalt oxide catalysts were mixed by a mortar grinder (PULVERISETTE 2, Germany) and pressed into pellets using a manual tablet press machine (TDP-0, China).

2.4. Sample characterization

The bulk concentration of Co in the studied samples and the impurities in the commercial Co_3O_4 were determined by inductively coupled plasma atomic emission spectrometry using an Optima 4300 DV instrument. The relative error of determination was $\pm 5\%$.

The chlorine content was determined by X-ray fluorescence analysis on a VRA-30 instrument with a Cr anode of the X-ray tube. The relative error of determination was $\pm 2\%$.

The specific surface area of cobalt oxides was measured by thermal desorption of argon. The relative error of determination was $\pm 3\%$.

The phase analysis of cobalt oxide was performed using an URD-63 (Seifert-FPM, Germany) diffractometer with a $\text{Cu K}\alpha$ radiation. The crystallite size was calculated using the Scherrer formula. The particle sizes (coherent scattering region-CSR) were calculated by the Scherrer formula for Co_3O_4 using – (3 1 1) reflection. The computation error of CSR is 10%.

FTIR spectra of the samples were recorded in air at room temperature on a Bomem MB-102 Fourier spectrometer. For the analysis, the samples were pressed with CsI.

Near-IR spectra of the powdered samples were recorded in air at room temperature on NIR Interspec 2010.

Diffuse reflectance electronic spectra were recorded in air at room temperature on a Specord M-40 spectrophotometer (Carl Zeiss Jena) equipped with a standard diffuse reflectance attachment.

Raman spectra were recorded with a FT-Raman RFS 100/S BRUKER spectrometer (Germany) in the region $100\text{--}3600\text{cm}^{-1}$. The 1064 nm line of Nd-YAG laser was used for the spectral excitation.

The high-resolution transmission electron microscopy (HR TEM) studies of the catalysts were carried out using a JEM-2010 (JEOL, Japan) instrument with a lattice resolution of 1.4Å and an accelerating voltage of 200 kV. The periodic images of the lattice structures were analyzed by digital Fourier transformation. The local elemental analysis was performed by the EDX method on an Energy-dispersive X-ray Phoenix Spectrometer equipped with a Si (Li) detector with an energy resolution of at least 130 eV or higher. The samples were fixed on “holey” carbon films supported on copper grids and examined with an electron microscope.

Magnetic measurements were performed by the Faraday method in fields (H) from 1 to 10 kOe. Measurements in the temperature interval from 300 to 900 K were carried out under a vacuum of 10 to 4 mm Hg. To prevent sample interaction with the atmosphere, the powder under study was wrapped into Parafilm.

The temperature-programmed reduction of catalysts was carried out in a flow reactor placed into a gradient-free often with forced ventilation. The rate of heating from room temperature to 600°C was $10^\circ\text{C}/\text{min}$ (β). To ensure an even heat exchange in the catalyst layer, a 0.4–0.7 mm fraction of quartz glass was added to the catalyst sample. The studies were performed on the catalyst fraction with a granular size of 0.25–0.5 mm. The feed rate of the hydrogen-containing gas (10 vol% H_2/Ar) was 40 mL/min. Changes in the content of hydrogen in the reaction medium was determined with a catarometer.

2.5. Hydrogen generation experiments

Catalytic hydrolysis of NaBH_4 was performed in two ways.

With NaBH_4 solution: a weighed amount of NaBH_4 (0.0465 g) was placed into the reactor and dissolved in 10 mL of distilled water. A weighed amount of the catalyst (0.0117 g) was added to NaBH_4 solution. Hydrogen generation experiments were carried out at 40°C in a temperature-controlled glass reactor equipped with a magnetic stirrer at 800 rpm stirring rate.

With solid-state NaBH_4 pellet: A solid-state NaBH_4 pellet (0.0465 g of NaBH_4 with the catalyst) was placed into the batch reactor (Fig. 1) and then 10 mL of distilled water was added. Hydrogen generation experiments were carried out at 20°C .

The volume of the produced hydrogen gas was measured with a 100 mL gas burette with a resolution of 0.2 mL. The data obtained were corrected to N.T.P. based on three repeated experiments under the same conditions. The experimental uncertainty was less than 5%.

2.6. The energy-converter based on hydrogen combustion

The principal scheme of the energy-converter includes thermo-electric (TE) modules producing electricity due to temperature difference between the solid heated by diffusion microflame and the solid with rather low temperature close to the room one is shown in Fig. 2. Diffusion flame stabilized on the capillary end 1 heats copper semispherical dome 2. The Plates 3 provide natural cooling of one of the working sides of thermo-electric modules 4, set over the dome perimeter 2. The system serves to use five series-connected thermoelements. In the system the small-scaled thermoelectric modules of TB grade produced by “KrioTherm” company (St. Petersburg) with the dimensions $3\text{ mm} \times 3\text{ mm}$ were used.

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