

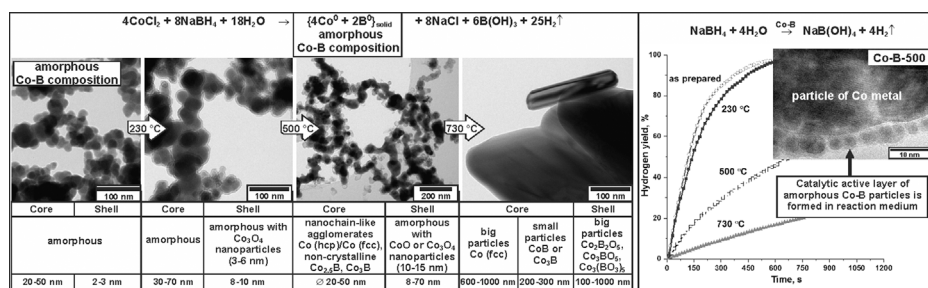


Research Paper

Amorphous ferromagnetic cobalt-boron composition reduced by sodium borohydride: Phase transformation at heat-treatment and its influence on the catalytic properties

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GRAPHICAL ABSTRACT



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ABSTRACT

The cobalt-boron composition by reduction of cobalt chloride in an aqueous solution of sodium borohydride is an amorphous ferromagnetic black powder consisting of spherical particles covered with a shell. Transformations of cobalt-boron composition upon its heat treatment from 20 to 1000 °C in an inert atmosphere have been studied by thermal analysis, magnetic susceptibility and HR TEM. On the basis of the obtained results the heating process was divided into five temperature intervals characterized by considerable changes in the structure of cobalt-boron composition. The end products of chemical and structural transformations are cobalt metal and cobalt borates – Co₂B₂O₅, Co₃BO₅, Co₃(BO₃)₂. In our study it was shown for the first time that the metallic phase with a face-centered cubic lattice forms from the amorphous core while the cobalt borates form as a result of transformation of an oxygen-containing shell under an inert atmosphere. The study of the effect of physicochemical properties of the calcined cobalt-boron composition on the rate of NaBH₄ hydrolysis has shown that it decreases with decline specific surface area of the sample and its phase composition determines the rate of formation of the catalytic active component in the reaction medium.

1. Introduction

Cobalt-boron (Co-B) compositions obtained by reduction of sodium borohydride have attracted much research interest because they are in

great demand as catalysts in the production of hydrogen from water by electrochemical splitting [1,2] or by photolysis [3] and as selective catalysts for liquid phase hydrogenation [4–6] and as anodes for alkaline secondary batteries [7]. Lately there has been intense research of

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the hydrolysis of boron-containing hydrides in the presence of cobalt-boron catalysts [8–10], including those modification by a supplemental metal or element for better activity and stability [11–17].

It was found that heat-treatment of Co-B compositions prepared by reduction of sodium borohydride has influence on their catalytic activity in sodium borohydride hydrolysis [18–21]. Thus, calcination temperatures below 300 °C had no substantial influence on the rate of NaBH₄ hydrolysis while at temperatures above 500 °C a drastic fall in activity was observed. The XRD data presented in different studies [22–26] failed to unambiguously indicate what chemical and structural changes determined the rate of NaBH₄ hydrolysis. According to Glavee et al. [27], Co-B composition formed upon addition of a solid sodium borohydride to a 0.01 M aqueous solution of cobalt chloride under aerobic conditions crystallized to metallic cobalt at 500 °C under argon. The heat-treatment of the same samples [28] led to formation of a cobalt boride phase with a structure of Co₂B at 500 °C in argon. And the more sodium borohydride was added to the cobalt salt solution the less was the intensity of reflections in the diffraction patterns of the calcined sample and the greater was their width. These changes indicate that the calcined sample became more amorphous when more hydride was added to the cobalt salt solution. But in [29] it was found that the lower was NaBH₄ concentration in the solution the more active were the particles of the Co-B composition forming from the cobalt chloride in the reaction medium. It was noted that the concentration of the NaBH₄ also had an influence on the phase composition of Co-B heat-treated at 650 °C under argon. Thus, in the case of Co-B composition formed in a 2 wt% aqueous NaBH₄ solution only metallic cobalt with a hexagonal lattice was formed. Thermal treatment of Co-B obtained in a 19 wt% aqueous NaBH₄ solution had led, along with the formation of metallic cobalt, also to crystallization of a cobalt pyroborate phase – Co₂B₂O₅. This is in contradiction with the results reported in [30] where the authors observed formation of other cobalt borates – Co₃(BO₃)₂ and Co(BO₂)₂ upon treatment at 500 °C in an inert nitrogen atmosphere. However, thermal treatment of the same sample at 400 °C in a flow of air led to the formation only of metallic cobalt: 68% of a hexagonal close-packed phase (hcp) and 32% of a face-centered cubic phase (fcc). The presence of metallic cobalt was also detected in Co@SiO₂ catalysts heat-treated in air at temperatures from 400 to 600 °C [31]. However, it was found [32] that Co-B composition heat-treated at 500 °C under continuous flow of air contained not only metallic cobalt but also cobalt borates whose crystallographic structure depended on the composition of the reaction medium. It was indicated that Co₂B₂O₅ was the final by-product of the thermal treatment of the sample obtained by addition of a 0.2 wt% aqueous solution of cobalt chloride to a 0.1 wt% NaBH₄ solution. In presence of oleic acid in a 0.2 wt% aqueous solution of cobalt chloride the crystallization of Co₃(BO₃)₂ was observed at 500 °C in a flow of air.

So, it can be inference that by now, there is no single opinion about the chemical and structural transformations occur in a Co-B composition at heat-treatment. First of all this is explained by the differing conditions of the synthesis and thermal treatment which determine both the phase composition of heat-treated Co-B samples and the NaBH₄ hydrolysis rate. This work was aimed firstly at studying the effect of heat-treatment (20–1000 °C) on the state of the Co-B composition forming as a result of reduction of cobalt chloride in aqueous NaBH₄ solution and secondly at revealing the dependence of the rate of sodium borohydride hydrolysis on the state of the Co-B composition after calcination.

2. Experimental

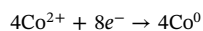
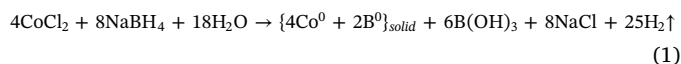
2.1. Materials

The commercial chemical reagents: sodium borohydride, NaBH₄ (CAS # 16940-66-2, Sigma-Aldrich) and cobalt (II) chloride hexahydrate, CoCl₂·6H₂O (CAS # 7791-13-1, Acros Organics) were used as

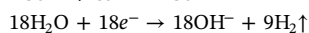
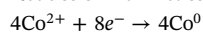
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2.2. Sample preparation

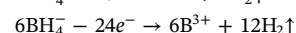
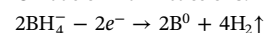
Solid Co-B composition («{4Co⁰ + 2B⁰}_{solid}» – in Eq. (1)) was prepared by reduction of cobalt chloride in an aqueous NaBH₄ solution at ambient temperature:



Reduction half-reactions:



Oxidation half-reactions:



NaBH₄ concentration in water is 0.12 M. The molar ratio of Co:NaBH₄ is 1:25. The produced solid Co-B composition was separated from the reaction medium, washed with distilled water and acetone and dried at 70 °C in a vacuum drying box for 4 h. Then the Co-B composition was heat-treated at 230, 500 and 730 °C for 4 h in a quartz reactor of a SNOL 0.2/1250 oven at an argon flow of 25 mL/min. To prevent sample oxidation, after heating the reactor was cooled down in a flow of argon ambient temperature and then evacuated after which it was placed into a glove box and all the manipulations with the sample were performed under argon. The cobalt-boron compositions are denoted as Co-B-T, where T indicates the calcination temperatures of the samples.

2.3. Sample characterization

The chemical analysis (contents of cobalt and boron in the samples) was performed by atomic-emission spectroscopy with inductively-coupled plasma on an Optima 4300 DV instrument (Germany).

The high-temperature diffraction studies under a vacuum were performed on a D8 (Bruker Germany) diffractometer with a CuKα radiation in a high-temperature Anton Paar (Austria) chamber. The diffractometer was equipped with a Gobel (Bruker, Germany) mirror forming a parallel X-ray beam. The studies under a vacuum were performed at a residual pressure of 5·10⁻⁶ bar. The diffraction patterns were recorded in the of angles from 15° to 70° range with 0.05° increments and a counting time of 5–20 s per point. The heating rate was 10 °C/min. The crystallite size was calculated by the Scherrer formula from the (111) reflection for Co metal. In these calculations, the physical line broadening characteristic of the Bruker diffractometer (0.07°) was subtracted from the observed line width. The calculation error was 10%. The quantities the crystalline phases in the samples were determined using the PCW program.

Thermal analysis was performed on a STA 449C Jupiter instrument in a flow of argon (10 mL/min) at temperatures from 20 to 1000 °C and the heating rate of 10 °C/min, sample mass of 130 mg.

The high-resolution transmission electron microscopy (HR TEM) study of the catalysts was carried out on a (JEM-2010, Japan) instrument with a lattice resolution of 1.4 Å and an accelerating voltage of 200 kV. The periodic images of the lattice structures were analyzed by digital Fourier transformation. To construct the particle size distribution diagrams, the diameters of at least 300 particles were determined.

The magnetic characterization was performed using a vibrating sample magnetometer (VSM-7407, Lake Shore) in a field of 10 kOe in an argon atmosphere. The samples were first heated to 1030 °C at a rate of 2 K/min, and then cooled to room temperature. The hysteresis loops before heating, after heating and after cooling were recorded in an applied magnetic field between –5 kOe and +5 kOe.

2.4. Hydrogen generation experiments

Sodium borohydride hydrolysis (2) was carried out at 40 °C in a

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