



Cobalt oxide catalyst for hydrolysis of sodium borohydride and ammonia borane

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ABSTRACT

The catalytic properties of Co_3O_4 in NaBH_4 and NH_3BH_3 hydrolysis have been studied. Experiments were carried out at 20–40 °C using 0.12 M hydride solution. According to magnetic susceptibility measurements, FTIR, XRD, and TEM studies, Co_3O_4 is reduced to the ferromagnetic catalytically active Co_2B phase under the action of the NaBH_4 hydrolysis reaction medium. A correlation was found between the content of the cobalt boride phase formed *in situ* and catalyst activity. The reduction of Co_3O_4 in NH_3BH_3 proceeds at slower rate than in NaBH_4 . The addition to a solution of NH_3BH_3 of even a small amount of NaBH_4 increases considerably the reduction rate of Co_3O_4 . Using a Co_3O_4 -based precursor instead of the widely used CoCl_2 leads to the formation of a stable catalytically active phase of cobalt boride.

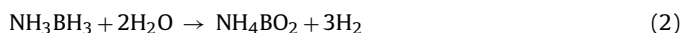
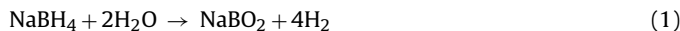
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1. Introduction

Today's hydrogen storage is one of the most important problems in hydrogen economy. Many studies to find effective storage materials have been performed but none has reached a level that is acceptable for practical applications. Among the various materials that have been intensively studied, the complex hydrides such as NaBH_4 , LiBH_4 , NaAlH_4 , $\text{Mg}(\text{BH}_4)_2$, NH_3BH_3 are attractive hydrogen storage materials [1]. These compounds currently have no competitors in terms of hydrogen content. Sodium borohydride (NaBH_4) has attracted attention since the late 1990's because of its high content of hydrogen of as high as 10.7 wt.%, high stability of its alkali solutions, non-toxicity and fire-safety [2–4]. In addition, this hydride is the least expensive and commercially available. It is one of the best candidates to be used in portable devices [5]. In the last years ammonia borane (NH_3BH_3) was beginning to be seriously considered as a potential source of hydrogen [6–10]. Unlike most hydrides, this compound contains 19.6 wt.% of hydrogen and has a high stability in solid state and aqueous solutions at ambient temperatures and does not require special storage conditions [11].

NaBH_4 and NH_3BH_3 both liberate hydrogen upon hydrolysis at ambient temperature only in the presence of suitable catalysts as

shown in (1) and (2), respectively:



Today, most of the published papers about the NaBH_4 and NH_3BH_3 hydrolysis deal with improvement of catalytic materials. Different acids and metal-based systems have been studied as catalysts for these hydrolysis processes [3,11]. The catalysts containing noble metals Pt, Rh, Ru (supported or not) have shown the best performance [2,12–14]. However the high cost of these catalysts has initiated studies into the development of catalytic systems not requiring noble metals. The most promising among them are the cobalt-based catalysts such as Co nanoparticles [15–17], Au@Co core-shell nanoparticles [18], cobalt salts [19–22], cobalt oxides [23–25], Cu/ Co_3O_4 [26], cobalt borides [27–33], Co–P [34,35], supported Co-containing catalysts [36–40], etc.

Recently, the high catalytic activity of Co_3O_4 and LiCoO_2 in NaBH_4 hydrolysis was reported in [23–25]. It was suggested that in a NaBH_4 water solution these oxides can be reduced to an active cobalt boride phase. Reduction of water-soluble cobalt salts in aqueous NaBH_4 solutions is a well-known process [3,41–45]. However, the investigation of the active phase formed from cobalt oxides under the action of hydride solutions has been started only recently. The composition and the rate of formation of the amorphous cobalt-containing active phase and their effect on hydrogen generation rate are not well studied. In addition to this, the efficiency of cobalt oxides in NH_3BH_3 hydrolysis has been not

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Table 1
Initial composition of hydride solutions used in catalytic hydrolysis reaction.

No.	Initial composition of hydride solutions ($V=10$ ml)	The molar ratio of $\text{NaBH}_4\cdot\text{NH}_3\text{BH}_3$ (ω)
1	1.2 mmol NaBH_4	–
2	1.2 mmol NH_3BH_3	–
3	1.2 mmol NH_3BH_3 + 0.072 mmol NaBH_4	0.06
4	1.2 mmol NH_3BH_3 + 0.144 mmol NaBH_4	0.12
5	1.2 mmol NH_3BH_3 + 0.288 mmol NaBH_4	0.24
6	1.2 mmol NH_3BH_3 + 0.48 mmol NaBH_4	0.4

discussed in the literature. This data is important for understanding the catalytic action mechanism of Co-based catalysts formed during hydrolysis.

In this paper Co_3O_4 as catalyst of NaBH_4 and NH_3BH_3 hydrolysis has been investigated. The catalytic activity of the active phase formed *in situ* from Co_3O_4 has been compared with that of the phase formed from CoCl_2 which is traditionally used in hydrolysis of hydrides under study. The state of cobalt oxide during its contact with the hydride reaction medium has been studied by several physical methods (FTIR, magnetic susceptibility measurements, XRD, TEM).

2. Experimental

2.1. Catalysts used

Commercially available Co_3O_4 powder (GOST 4467-79) was used as catalysts for NaBH_4 and NH_3BH_3 hydrolysis. Co_3O_4 has specific surface area of $16\text{ m}^2/\text{g}$. For a comparative study, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (GOST 4525-77) was also used to prepare cobalt boride active phase *in situ* under the action of NaBH_4 reaction medium as described later.

2.2. Hydrogen generation experiments

Hydrogen generation experiments were carried out at 40°C (or 20°C) in a glass temperature-controlled internal mixing reactor equipped with a magnetic stirrer at an 800 rpm stirring rate. A freshly prepared aqueous solution ($V=10$ ml) of NaBH_4 (Acros Organics, 98%) or NH_3BH_3 (JSC "AVIABOR", 99%) or of a mixture of them was placed into the reactor. The content of hydrides in 10 ml of distilled water is shown in Table 1. The catalyst (0.0117 g) was added and the volume of generated hydrogen was measured with a gas burette.

Several catalytic samples were taken during NaBH_4 hydrolysis and analyzed by FTIR, XRD, TEM, and magnetic susceptibility studies. In this case, the hydrolysis process was performed at 20°C . The initial amount of Co_3O_4 was 0.0117 g. The initial reaction medium contained the standard amount of aqueous NaBH_4 (1.2 mmol in 10 ml). The process was stopped at different stages of NaBH_4 hydrolysis: at the beginning of the reaction (at the end of the induction period) at a 5% (Sample B), 50% (Sample C), and 100% (Sample D) of NaBH_4 conversion. The solid catalysts were taken from the reaction medium by a magnet, rapidly washed with acetone, and dried at 80°C for 3 h under vacuum and then studied. The list of catalyst samples taken for analysis is presented in Table 2. Fig. 1 shows the reaction times and the generated volumes of H_2 at which the catalytic samples were taken from the reaction medium.

A comparative study of the activity and stability of Co_3O_4 - and CoCl_2 -based catalysts formed *in situ* under the action of NaBH_4 was carried out for NaBH_4 and NH_3BH_3 hydrolysis. For this study a cat-

Table 2
Catalytic samples taken during NaBH_4 hydrolysis at 20°C .

Catalytic sample	Description ^a
A	Co_3O_4 before reaction
B	Solid sample was taken from the reactor at the end of the induction period when the NaBH_4 conversion achieved 5%
C	Solid sample was taken from the reactor in the middle of reaction when achieved NaBH_4 conversion was 50%
D	Solid sample was taken from the reactor at the end of reaction when NaBH_4 conversion achieved 100%

^a See Fig. 1.

alyst suspension was preliminary obtained in the catalytic reactor during NaBH_4 hydrolysis of the standard amount of aqueous NaBH_4 (1.2 mmol in 10 ml) at 40°C . The started weight of Co_3O_4 (or CoCl_2) was 0.0117 g. After the complete hydrolysis of NaBH_4 , the catalyst sample was separated from the reaction mixture by a magnet, washed with distilled water in air and then the hydride (1.2 mmol, NaBH_4 or NH_3BH_3) dissolved in 10 ml of distilled water was added. Before the addition of the next portion of hydride solution the procedure of catalyst water treatment was repeated. Catalyst samples prepared from Co_3O_4 and CoCl_2 were denoted as *Catalyst 1* and *Catalyst 2*, respectively.

2.3. Catalyst characterization

The bulk concentration of Co and B in the samples of catalysts was determined using inductively coupled plasma atomic emission spectrometry on an Optima 4300 DV instrument.

The room temperature XRD studies were carried out under vacuum (5×10^{-6} bar) on a Bruker D8 diffractometer (Germany) with an Anton Paar high temperature vacuum sample chamber (Austria). The diffractometer was equipped with a Gobel mirror (Bruker, Germany) that formed a parallel X-ray beam. The $\text{CuK}\alpha$ radiation was used. The crystallite size of Co_3O_4 spinel was estimated by the broadening of XRD peak (3 1 1) by using Scherrer's equation.

High-resolution transmission electron microscopy (HRTEM) studies were carried out using a JEM-2010 instrument with a lattice resolution of 1.4 \AA and an accelerating voltage of 200 kV. The samples were fixed on "holey" carbon films supported by copper grids and investigated with an electron microscope.

The 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.

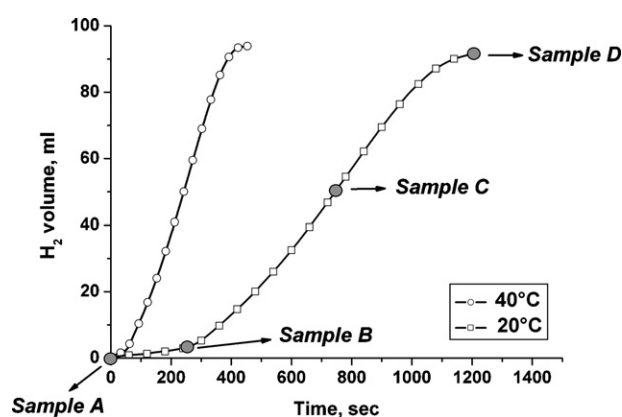


Fig. 1. Effect of reaction temperature on the volume of H_2 generated from NaBH_4 solution (1.2 mmol in 10 ml) over Co_3O_4 , where Sample A was Co_3O_4 before reaction, Samples B, C, and D were taken from NaBH_4 hydrolysis at the conversions of 5%, 50%, and 100%, respectively (Table 2). The catalyst weight was 0.0117 g.

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