Catalysis Today 138 (2008) 260–265

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

$LiCoO_2$-based catalysts for generation of hydrogen gas from sodium borohydride solutions

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ARTICLE INFO

Article history:
Available online 15 August 2008

Keywords:
Sodium borohydride
Hydrogen generation
Lithium cobalt oxide
Cobalt boride

ABSTRACT

The catalytic performance of lithium cobaltite, $LiCoO_2$, in sodium borohydride hydrolysis has been studied and compared with catalytic properties of Co_3O_4, $CoCl_2$ and $Co(NO_3)_2$. Activation times and observed H_2 generation rates were found dependent on the chemical nature and dispersion of the catalysts, as well as on the reaction temperature. The magnetic susceptibility method was used to demonstrate that all studied cobalt compounds, including cobalt oxides and soluble salts, are being reduced under catalytic conditions to form catalytically active cobalt boride phases. Impregnating $LiCoO_2$ with Pt and Rh chlorides increases only the initial catalytic activity, which then quickly declines during cyclic stability tests and in just a few cycles approaches that of the starting $LiCoO_2$ material.

1. Introduction

Development and wider adaptability of portable fuel cells requires highly efficient and safe technologies for generation and storage of hydrogen gas. One of the most promising methods for hydrogen gas generation involves catalytic hydrolysis of $NaBH_4$ [1,2]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$

The presence of catalysts not only accelerates $NaBH_4$ hydrolysis but also prevents formation of undesirable side products, i.e. volatile hydrides. Hydrogen gas obtained via catalytic hydrolysis is saturated only with water vapor and can be fed directly to an anode space of the fuel cell without additional purification or wetting.

Catalysts containing platinum group metals (Pt, Rh, Ru) have shown the best performance in $NaBH_4$ hydrolysis [2–5]. However the high cost of such catalysts has initiated studies into development of catalytic systems not requiring precious metals. The most promising among them are several cobalt-based catalysts, including cobalt metal [6], Raney Co, Raney $Co_{50}Ni_{50}$ and cobalt salts [7], cobalt borides [8,9], cobalt oxide and lithium cobaltite [10]. It has been suggested that cobalt salts and oxides (Co_3O_4, $LiCoO_2$) are being reduced in the $NaBH_4$ reaction mixture to form catalytically active cobalt boride phases [7,10,11].

Investigations of Co_xB catalysts in $NaBH_4$ hydrolysis have started relatively recently and there are still remaining certain questions requiring additional detailed studies. For example, the important problem of cyclic stability has not been studied for these catalysts in detail. At the same time, the ideal operation of a portable hydrogen generator combined with the fuel cell assumes that the catalytic $NaBH_4$ hydrolysis can be paused depending on the end-user requirements. It is also necessary to study the stability of cobalt oxide compounds modified with platinum group metals, since high activity of $Pt/LiCoO_2$ and $Pt–Ru/LiCoO_2$ has been reported [2,10,12–14]. Furthermore, it is not clear how different are the catalytic properties of cobalt boride phases formed under catalytic conditions from different starting cobalt compounds, cobalt salts and oxides. The composition and properties of cobalt borides formed *in situ* during $NaBH_4$ hydrolysis have not yet been sufficiently studied.

In this paper we report on how catalytic properties of $LiCoO_2$ in $NaBH_4$ hydrolysis depend on the reaction temperature, dispersion, and modification with Pt or Rh. The catalytic activity of lithium cobaltite has been compared with catalytic properties of $CoCl_2$, $Co(NO_3)_2$ and Co_3O_4. Also reported are the results of cyclic stability performance tests. Nature of lithium cobaltite after contact with the $NaBH_4$ reaction medium has been studied by several physical methods.

2. Experimental

2.1. Preparation of catalysts

Two cobalt salts, $CoCl_2 \cdot 6H_2O$ (>98 wt.% GOST 4525-77) and $Co(NO_3)_2 \cdot 6H_2O$ (>97 wt.% GOST 4528-78), examined in this

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doi:10.1016/j.cattod.2008.06.030

Table 1
Lattice parameters and specific surface area of studied $LiCoO_2$ samples

Sample	$a = b$ ($\pm$0.00003) (Å)[a]	c($\pm$0.0002) (Å)[a]	c/a[a]	S_{BET} (m^2/g)
$LiCoO_2$-1	2.8168	14.056	4.990	2.5
$LiCoO_2$-2	2.8148	14.049	4.991	1.6
$LiCoO_2$-3[b]	2.8150	14.055	4.993	3.4

[a] Lattice parameters according to XRD.
[b] Prepared via mechanical activation.

work as catalysts for sodium borohydride hydrolysis were used as supplied without any additional treatment or purification. Cobalt oxide, Co_3O_4, was prepared from cobalt nitrate by heating in air at 500 °C for 4 h. The resulting product was analyzed by XRD and confirmed to be a pure Co_3O_4 phase (JCPDS: 42-1467). The specific surface area of thus-synthesised cobalt oxide was 7.6 m^2/g.

Three lithium cobaltite samples were tested in $NaBH_4$ hydrolysis (Table 1). $LiCoO_2$-1 sample was a commercially available $LiCoO_2$ powder (Novosibirsk Chemical Concentrate Plant). $LiCoO_2$-2 and $LiCoO_2$-3 samples were prepared from Li_2CO_3 (>99 wt.% TU 6-09-3728-83) and Co_3O_4 (Co-71-74 wt.% GOST 4467-79). To prepare $LiCoO_2$-3, the Li_2CO_3 and Co_3O_4 mixture was additionally subjected to a mechanical activation (MA) treatment. Mechanical activation was carried out for 3 min using a planetary mechanical activator APF with jars and balls made of steel. Activated and non-activated mixtures were then annealed at 700 °C for 8 h in air [15]. According to XRD analysis all three $LiCoO_2$ samples were composed of a single crystalline phase corresponding to the high-temperature modification HT-$LiCoO_2$ (Table 1). HT-$LiCoO_2$ has an ideal layered α-$NaFeO_2$ structure ($R\bar{3}m$ space group) with ABCABC oxygen packing, with cobalt and lithium ions ordered in the octahedral positions of different (1 1 1) planes [15]. The ratio of the lattice parameters "c/a" was found equal to 4.99 in all three samples.

Pt- and Rh-containing catalysts were prepared by impregnation using aqueous solutions of $RhCl_3$ and H_2PtCl_6 (Aurat). After impregnation catalyst samples were dried in air at 110–130 °C for 2 h. The metal content was 1 wt.%.

2.2. Characterization of catalysts

High-resolution transmission electron microscopy (HRTEM) studies were carried out using a JEM-2010 instrument with lattice resolution of 1.4 Å and accelerating voltage of 200 kV. Periodic images of lattice structures were analyzed using Digital Fourier Transformation. Local elemental analysis was performed using an EDX method on an Energy-dispersive X-ray Phoenix Spectrometer equipped with the Si (Li) detector with energy resolution better than 130 eV. Analyzed samples were fixed on "holey" carbon films supported by copper grids and investigated with an electron microscope. SEM studies were performed using a LEO 1430 scanning electron microscope. The average particle sizes of $LiCoO_2$ samples was obtained by counting about 100 particles. X-ray diffraction analysis of $LiCoO_2$ and Co_3O_4 samples was performed using URD-63 and DRON-3.0 diffractometers with Cu Kα radiation. The specific surface areas (S_{BET}) of $LiCoO_2$ and Co_3O_4 samples were determined by a thermal argon desorption technique. Bulk concentrations of Co, Li and B were determined using inductively coupled plasma atomic emission spectrometry on an Optima 4300 DV instrument. The analysis was performed after dissolving $LiCoO_2$ samples in an acidic mixture. The magnetic susceptibility was measured in the temperature range of 300–1200 K by a Faraday method in magnetic fields of 2, 5 and 10 kOe.

2.3. Hydrogen generation experiments

Hydrogen generation was carried out at 20–40 °C in a glass temperature-controlled internal mixing reactor equipped with a magnetic stirrer at the stirring rate of 800 rpm. Dry $NaBH_4$ (Acros Organics, 98%) was stored in a desiccator in order to minimize possible interaction with water vapor present in air. Handling of $NaBH_4$ during tests, e.g. weighing, was done in air. 0.0465 g of $NaBH_4$ was placed into the reactor and dissolved in 10 ml of distilled water. A weighed amount of the catalyst was then added and the volume of generated hydrogen measured using a gas burette. In all cases the hydrogen yield was 90–93% of theoretical. An estimated decrease in hydrogen generation due to reduction of $Co^{2+,3+}$ was less then than 2%.

The hydrogen generation rate (W^{50}) was calculated as $W^{50} = V/(t \times m)$, where V is a volume of hydrogen produced (ml); t is the 50% conversion time (s); m is the catalyst mass (g). When necessary, the catalyst was separated from the reaction medium, washed with distilled water, dried at 110 °C for 2 h in air and further studied with an array of physical methods.

Long-term cyclic stability of catalysts was tested by repeating the hydrolysis reaction as described above. After the complete conversion of one $NaBH_4$ portion (0.0465 g dissolved in 10 ml of distilled water), the catalyst was separated from the reaction mixture and washed with distilled water in air. Subsequently, this catalyst was used in hydrolysis of the next portion of $NaBH_4$.

3. Results and discussion

3.1. Investigation of $NaBH_4$ catalytic hydrolysis

The kinetics of hydrogen release during sodium borohydride hydrolysis using $LiCoO_2$-1, $CoCl_2$, $Co(NO_3)_2$ and Co_3O_4 catalysts are compared in Fig. 1a. One can see that the catalytic activity decreases as $LiCoO_2 > Co_3O_4 > CoCl_2 > Co(NO_3)_2$.

Reduction of cobalt salts in aqueous $NaBH_4$ solutions is known to be a fast and vigorous process even at room temperature [8,11,16]:

$$2Co^{2+} + 2BH_4^- + 2H_2O \rightarrow Co_2B\downarrow + HBO_2 + 2H^+ + 4.5H_2\uparrow \quad (2)$$

$$6Co^{2+} + 5BH_4^- + 6H_2O \rightarrow 2Co_3B\downarrow + 3HBO_2 + 7H^+ + 11H_2\uparrow \quad (3)$$

In our case we have also observed instantaneous formation of a black cobalt boride (Co_xB) precipitate when either cobalt nitrate or cobalt chloride was used. This process was characterized by a very high initial hydrogen generation rate (Fig. 1b). The following sharp decrease in activity of these catalysts is apparently related to aggregation of cobalt boride particles.

A different trend was observed for the hydrogen generation kinetics when using $LiCoO_2$ and Co_3O_4 catalysts, with the former being more active. During the first 10–30 s the hydrogen evolution over these samples was insignificant (Fig. 1a and b). This was followed by a substantial increase in the hydrogen production (Fig. 1b). The time delay required for activation of these catalytic systems was attributed to a period of time

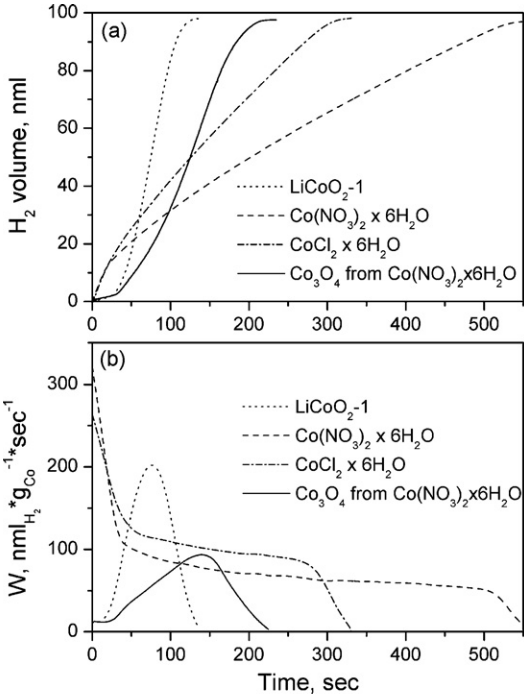

Fig. 1. (a) The volume of generated hydrogen (ml) and (b) the hydrogen generation rate normalized to 1 g of cobalt metal, as a function of time for different catalytic systems. The reaction was performed at 40 °C with 0.0117 g of catalyst in all cases.

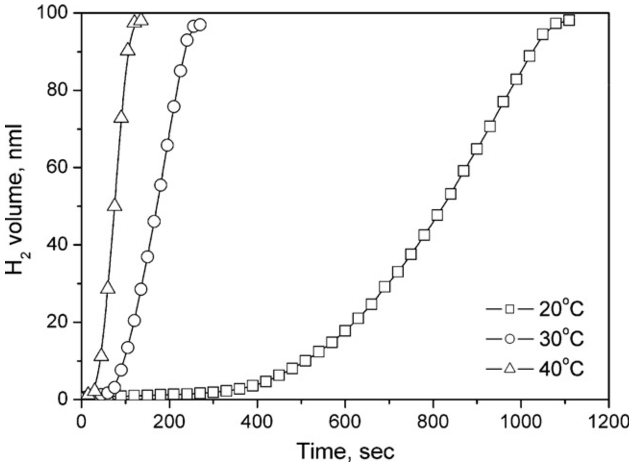

Fig. 2. The volume of generated H_2 at different temperatures as a function of time for $LiCoO_2$-1. The catalyst weight was 0.0117 g.

necessary to reduce insoluble cobalt oxide compounds by the sodium borohydride solution to form active cobalt boride [10]. Note, that decreasing the temperature from 40 to 20 °C leads to both the hydrogen generation rate decrease and to significant lengthening of the induction period from 10–15 to 400 s (Fig. 2).

To study the effect of $LiCoO_2$ dispersion on its catalytic properties we prepared lithium cobaltite samples by a traditional ceramic method, $LiCoO_2$-2 (Fig. 3a), and by using mechanical activation, $LiCoO_2$-3 (Fig. 3b). According to SEM data, the average size of particles in the $LiCoO_2$-2 sample was 1.2 μm (Fig. 3a). When mechanical activation was used in $LiCoO_2$-3, the average particle size was reduced by about three times (Fig. 3b). This result is further confirmed by the surface area measurements (Table 1). The data presented in Fig. 4 show that finely dispersed $LiCoO_2$-3 is more active then $LiCoO_2$-2 prepared without mechanical activa-

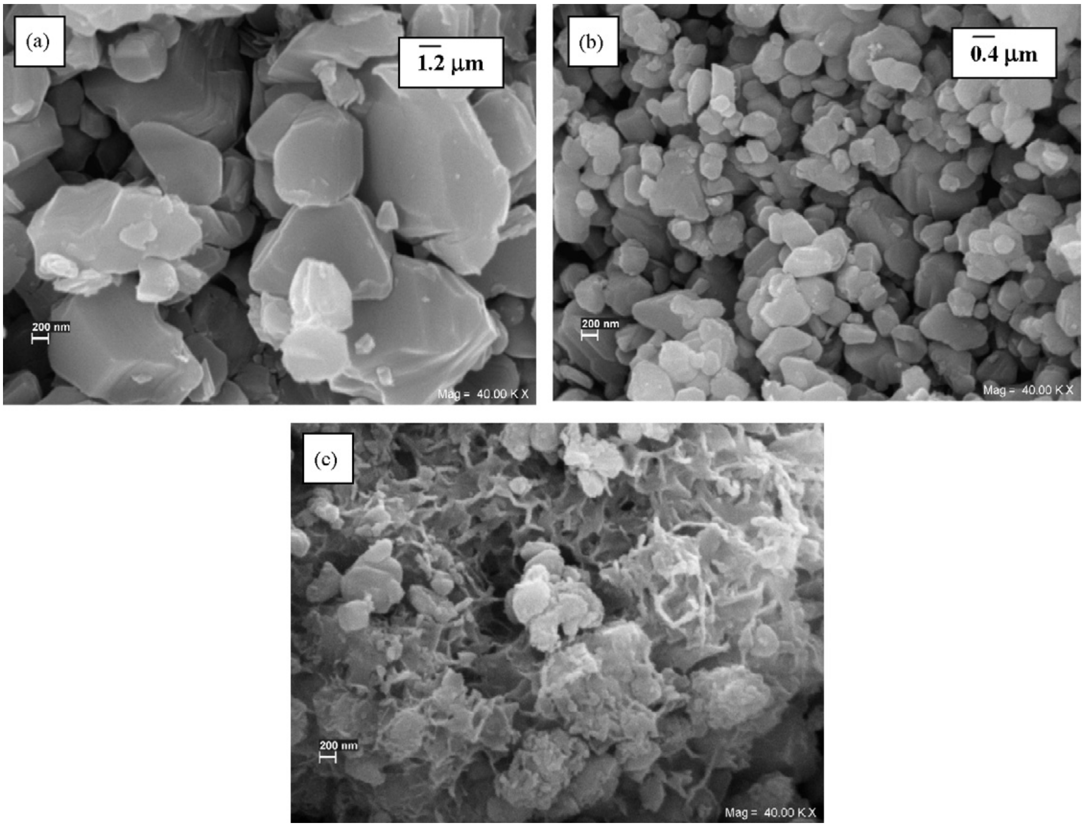

Fig. 3. SEM images of (a) $LiCoO_2$-2 prepared by a ceramic method and $LiCoO_2$-3 prepared by mechanical activation (b) before and (c) after testing in $NaBH_4$ hydrolysis.

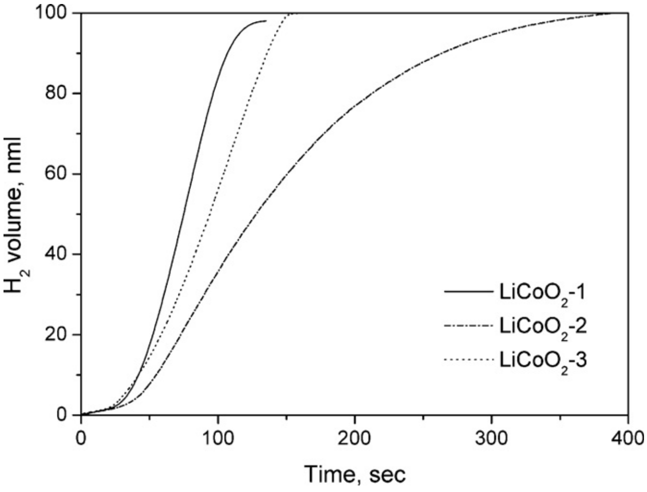

Fig. 4. The volume of generated H_2 as a function of time for different $LiCoO_2$ samples. The reaction was performed at 40 °C with 0.0117 g of catalyst in all cases.

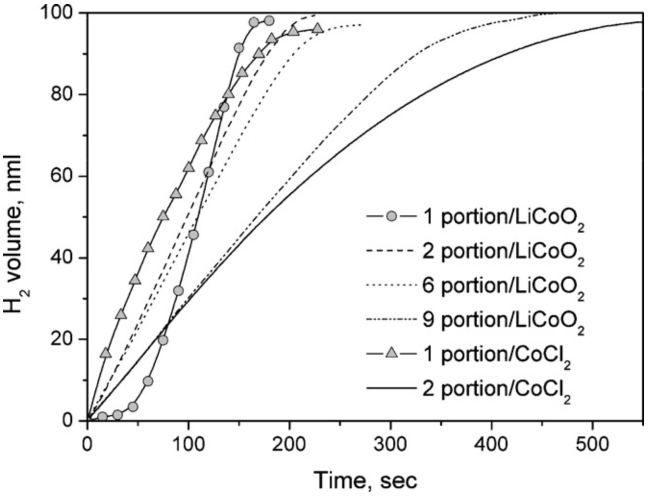

Fig. 5. The volume of generated H_2 as a function of time at 40 °C for Co_xB formed from $LiCoO_2$-3 and $CoCl_2$ during cyclic stability tests. The weight of cobalt metal in both cases was 0.0070 g.

tion. Also, the dependence of generated hydrogen volume on time for $LiCoO_2$-2 was characterized by the longest activation period.

The results of cyclic stability tests performed for cobalt borides formed from $LiCoO_2$-3 and $CoCl_2$ are compared in Fig. 5. Starting with the second cycle the activation period disappears for $LiCoO_2$. At the same time, an even sharper decrease in the catalytic activity is observed for Co_xB formed from cobalt chloride. The loss of activity in the latter case is most likely caused by continuing aggregation of cobalt boride particles, or their instability in the presence of air [11].

Reduction of the lithium cobaltite phase during $NaBH_4$ hydrolysis is apparently gradual. Previously, using XRD, FTIR and DRS, we have shown that the crystal structure of lithium cobaltite is partially destroyed after the first cycle of $NaBH_4$ hydrolysis [15]. Present chemical analysis data also reveal distinct changes in the $LiCoO_2$ composition under action of the $NaBH_4$ reaction media (Table 2). According to SEM (Fig. 3c) and TEM (Fig. 6), the reduction process starts at the catalyst surface. A flake-like morphology of amorphous cobalt boride similar to shown in Fig. 3c has been previously described in [17]. TEM data indicate that under the reaction conditions, the surface of $LiCoO_2$-3 is gradually reduced to form finely dispersed Co-containing nanoparticles. A glass-like layer also observed in these samples most likely consists of boron oxide or lithium boron oxide (Fig. 6).

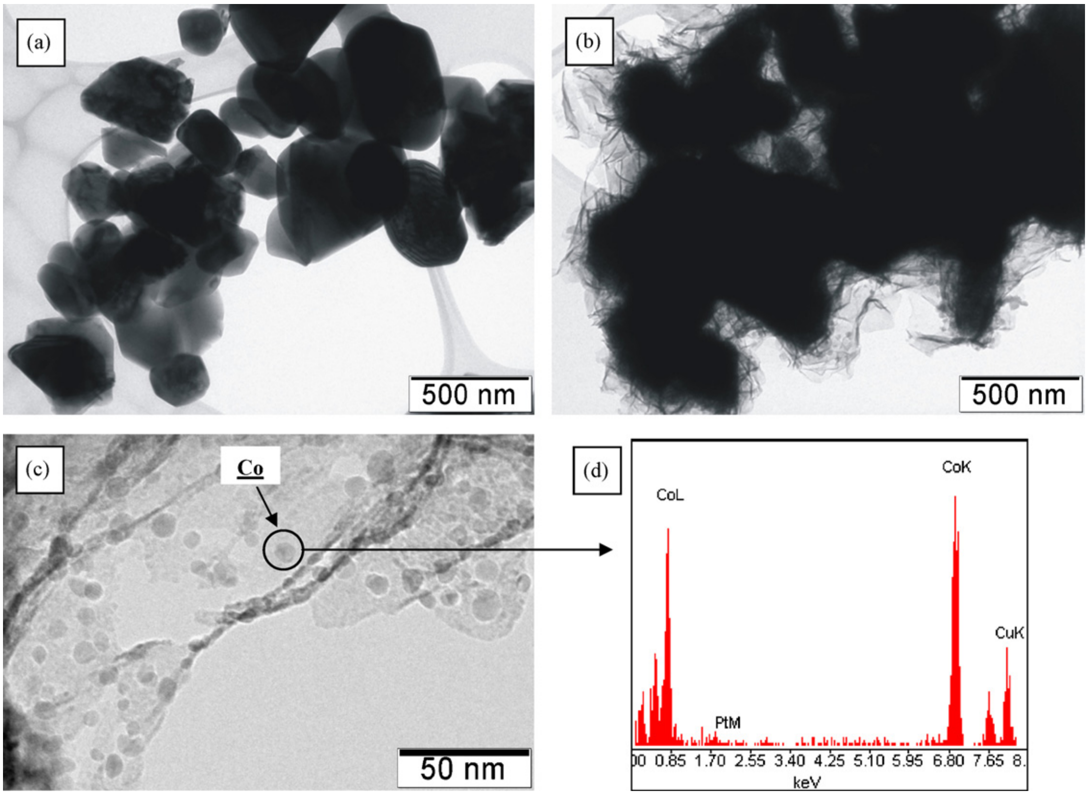

Fig. 6. TEM images of $LiCoO_2$-3 (a) before, and (b and c) after testing in $NaBH_4$ hydrolysis at 40 °C. (d) EDX analysis of the catalyst particle highlighted in the image (c).

Table 2
Chemical analysis of $LiCoO_2$-3 before and after the catalytic reaction

Sample	Element content (wt.%)		
	Co	Li	B
Before	58.25	7.55	–
After	62.26	3.66	1.40

According to the catalytic activity data presented in Fig. 7, additional deposition of precious metals (Pt, Rh) increases the initial hydrogen generation rate in agreement with the previously reported literature data on high activity of $Pt/LiCoO_2$ and $Pt–Ru/LiCoO_2$ systems [2,10,12–14]. However, during the cyclic stability tests the catalyst activity quickly declines, and starting with the forth cycle the hydrogen generation rate is now comparable to that of starting $LiCoO_2$. This effect is most likely caused by degradation of the surface of lithium cobaltite particles (Figs. 3c and 6). Thus, the impregnation of lithium

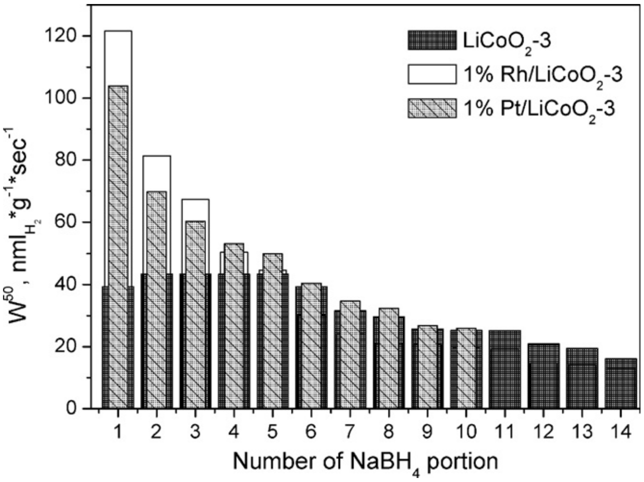

Fig. 7. Cyclic stability tests for $LiCoO_2$-3 and modified 1%$Rh/LiCoO_2$-3 and 1%$Pt/LiCoO_2$-3 catalysts at 40 °C. The catalyst weight was 0.0117 g.

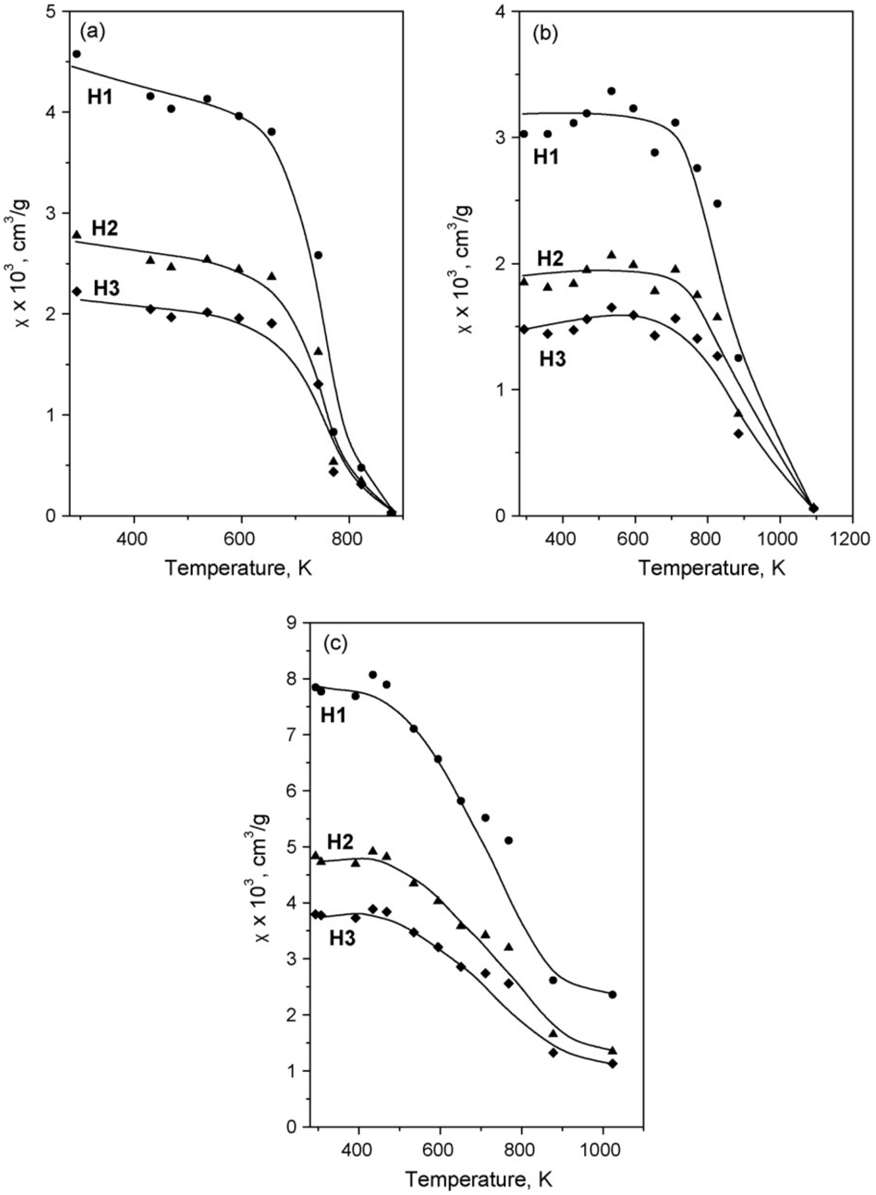

Fig. 8. The temperature dependence of the magnetic susceptibility for (a) $CoCl_2$, (b) Co_3O_4 and (c) $LiCoO_2$-2 reduced in the sodium borohydride hydrolysis reaction.

cobaltite with either Rh or Pt chlorides is not beneficial, since the active component in these catalysts is formed *in situ* in the $NaBH_4$ reaction medium.

3.2. Magnetic properties of cobalt boride catalysts

Cobalt boride samples, Co_xB ($x = 1–3$), prepared by reaction of cobalt-containing salts with sodium borohydride in aqueous and ethanol solutions are perhaps the most studied today. At the same time, cobalt borides formed from insoluble cobalt oxides reacting with $NaBH_4$ have been studied only scarcely. Both, the composition and the structure of cobalt borides have been shown to primarily depend on the catalyst preparation conditions [11]. Earlier, XDR and XPS were used to investigate phases formed from $LiCoO_2$ and Co_3O_4 upon reaction with $NaBH_4$ [10]. It was shown that after drying the reduced oxides were X-ray amorphous. The investigation of binding energy values by XPS showed that the electron density was partially donated from boron to cobalt similar to the case of Co_xB formed from soluble salts. This observation supported the idea that similar cobalt borides could also form during reduction of cobalt oxides [10,17,18].

It is difficult to study the composition of borides formed immediately after interaction of cobalt compounds with $NaBH_4$ because they are amorphous to X-rays and their crystallization starts during calcination in inert atmosphere [9,11,17]. However, Co_xB and cobalt metal differ considerably by their magnetic characteristics. Therefore, they can be distinguished and studied by magnetic methods. In accordance with the literature data [18], CoB is a diamagnetic phase, whereas Co_3B, Co_2B and Co are ferromagnetic materials with the following ordering temperatures: Co_3B, 747 K; Co_2B, 429 K; Co, 1403 K. The magnetic susceptibilities of $LiCoO_2$, $CoCl_2$ and Co_3O_4 are also well described in the literature. In the temperature range in question all three phases do not possess magnetic order. $CoCl_2$ [19,20] and Co_3O_4 [21] can be ordered antiferromagnetically. However, their Neel points are low, and at $T > 100$ K both phases behave as typical paramagnetic materials. As for $LiCoO_2$, here the magnetic susceptibility does not depend on the temperature because Co^{3+} is in the low-spin state with the magnetic moment equal to zero [22].

To identify cobalt boride phases which can possibly form during reduction of $LiCoO_2$, $CoCl_2$ and Co_3O_4 with $NaBH_4$ we have performed a series of magnetic susceptibility measurements as follows. The measurements were carried out with the samples dried in air in the temperature range of 300–1200 K with three values of the external magnetic field: H1 = 2 kOe, H2 = 5 kOe, H3 = 10 kOe. The obtained temperature dependences are summarized in Fig. 8. These results indicate that the paramagnetic phases of $LiCoO_2$, $CoCl_2$ and Co_3O_4 transform upon reduction into ferromagnetic phases. The field dependence of the magnetic susceptibility is the first evidence of the ferromagnetic state in the reduced phases. It disappears only after magnetic disordering when the temperature exceeds the Curie point (T_c). The Curie temperature found for all reduced samples studied falls in the range of 600–800 K. Therefore, it is now possible to suggest that the result of reduction of Co_3O_4 and $LiCoO_2$ with $NaBH_4$ is most likely the same Co_3B phase that is formed upon reduction of cobalt chloride. The formation of this phase can be attributed to instability of Co_2B when dried [11].

4. Conclusions

We have studied the catalytic performance of lithium cobaltite, $LiCoO_2$, and several other Co-containing compounds, Co_3O_4, $CoCl_2$ and $Co(NO_3)_2$, in the sodium borohydride hydrolysis reaction. The following conclusions can be made based on our observations:

1. $LiCoO_2$ is reduced by sodium borohydride to form the catalytically active cobalt boride phase. According to the magnetic susceptibility data, a similar cobalt boride phase (Co_3B) is also formed during reduction of $CoCl_2$ and Co_3O_4 in $NaBH_4$ followed by drying in air.
2. Reduction of $LiCoO_2$ and Co_3O_4 is much slower than that of soluble cobalt salts.
3. Lowering the reaction temperature leads to a significant decrease in the $LiCoO_2$ reduction rate.
4. Significantly higher hydrogen generation rates and shorter reduction times are typical for $LiCoO_2$ with higher dispersion.
5. Cyclic stability tests indicate that the $LiCoO_2$ activity gradually decreases but not as fast as in the case of water-soluble cobalt salts.
6. Impregnation of $LiCoO_2$ with Pt and Rh chlorides increases only the initial activity of the catalyst. During the cyclic stability tests the activity of such systems quickly declines and approaches that of starting $LiCoO_2$.

Acknowledgements

We are grateful to N.V. Kosova for preparation of $LiCoO_2$ samples and fruitful discussions. We also thank S.V. Tsybulya, L.S. Dovlitova, T. Yu. Volozhanina and A.M. Ozerova for assistance in the investigation of the catalysts.

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