

LiCoO₂-Supported Catalysts for Hydrogen Generation from Sodium Borohydride Solution

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Abstract

Effect of LiCoO₂ support prepared by traditional ceramic and mechanochemical route on the activity of Rh and Pt catalysts in the reaction of NaBH₄ hydrolysis was studied and compared with traditional supports, such as γ -Al₂O₃, TiO₂ (anatase) and carbon (sibunit). Catalysts supported on LiCoO₂ prepared using mechanical activation were found to have the highest catalytic activity. However, the endurance tests of 1 % Rh–LiCoO₂ и 1 % Pt–LiCoO₂ catalysts showed their gradual degradation. To understand the reason of this phenomenon, the interaction of LiCoO₂ with NaBH₄ solution was studied by XRD, FTIR, DRS and TEM.

INTRODUCTION

The development of fuel cells and their wide application are impossible without developing highly efficient and safe technologies for obtaining pure hydrogen and its storage. According to many researchers [1–4], catalytic hydrolysis of NaBH₄ is a promising method for hydrogen synthesis for use in portable fuel cells.

Different catalytic systems have been suggested for the NaBH₄ hydrolysis reaction. In recent publications, one can find information on the use of ruthenium catalysts supported on anion-exchange resins (A-26, IRA-400) [2, 5, 6], platinum group metals on various supports [3, 4, 7], cobalt borides [8, 9], nickel boride [10] and finely dispersed metallic nickel and cobalt [11, 12] in this reaction. In the last few years, several publications on the use of catalysts containing platinum group metals supported on LiCoO₂ appeared in the literature [3, 13–15]. LiCoO₂ is well known cathode material for lithium ion batteries, widely produced by different companies. However, the authors used

commercially produced LiCoO₂ missing the description of preparation method and of characteristics of as-used LiCoO₂. In addition, there is no information on the stability of this catalytic system under endurance tests.

In the present paper, LiCoO₂ supports were prepared by two methods: traditional ceramic and using preliminary mechanical activation (MA) of reagent mixture. Their effect on the activity of Pt and Rh catalysts in the NaBH₄ hydrolysis was studied and compared with traditional supports, such as γ -Al₂O₃, TiO₂ (anatase) and carbon (sibunit). The stability of LiCoO₂ in the NaBH₄ solution was also investigated.

EXPERIMENTAL

Catalyst preparation

Aqueous solutions of RhCl₃ (Aurat) and H₂PtCl₆ (Aurat) were used for the catalyst preparation. Water was added to the weighted support sample and stirred for 5 min using a mag-

TABLE 1
Specific surface area of LiCoO₂ samples

Sample	Annealing temperature, °C	S_{BET} , m ² /g
LiCoO ₂ -1	700	1.6
LiCoO ₂ -2*	700	3.4
LiCoO ₂ -3	800	0.7
LiCoO ₂ -4*	800	2.4

*Synthesis included the MA stage.

netic stirrer. Then, the RhCl₃ or H₂PtCl₆ solution of desired concentration was added, and the resulting suspension was stirred for 15 min at room temperature. Afterwards, the sample was heated to 80 °C and dried under continuous stirring. After impregnation, the catalysts were dried in air at 110–130 °C for 2 h. The metal content was 1 mass %.

To prepare LiCoO₂, Li₂CO₃ and Co₃O₄ were used as reagents. MA was carried out using a planetary mechanical activator APF with steel jars and balls. The time of MA was 3 min. The activated and non-activated mixtures were annealed at 700 and 800 °C for 8 h in air. The main synthesis parameters and the values of surface area for LiCoO₂ samples are presented in Table 1.

The effect of as-prepared LiCoO₂ supports on the activity of Pt and Rh catalysts in the NaBH₄ hydrolysis was compared with traditional supports, such as carbon (Sibunit) [16] with $S_{\text{BET}} = 530$ m²/g and grain size 0.08–0.1 mm; γ -Al₂O₃ (Katalizator Co.) with $S_{\text{BET}} = 170$ m²/g and grain size smaller than 0.04 mm; and TiO₂ (Sigma-Aldrich) with $S_{\text{BET}} = 243$ m²/g.

LiCoO₂ and catalyst characterization

The crystal and local structure of as-prepared LiCoO₂ samples was analyzed by XRD and FTIR spectroscopy. Powder diffraction patterns were recorded using DRON-3.0 diffractometer with CuK _{α} irradiation. FTIR spectra were registered in the 200–4000 cm⁻¹ wavelength range using a Bomem MB-102 Bruker FTIR spectrometer at room temperature. The samples were diluted with Cs¹ and pelletized. Specific surface area of the LiCoO₂ samples was determined using thermal adsorption of argon.

The interaction of LiCoO₂ with NaBH₄ solution was studied by XRD, FTIR and DRS spectroscopy. The DRS spectra were recorded at room temperature in air using a Specord M-40 spectrometer (Carl Zeiss Jena) with a standard diffuse reflectance attachment in the wavelength range 45 000–11 000 cm⁻¹ and an Interspec 2010 Fourier Transform spectrometer (Spectrolab Co.) with a diffuse reflectance attachment in the wavelength range 10 000–3500 cm⁻¹. Particle morphology of LiCoO₂ before and after treatment with NaBH₄ was studied using high resolution transmission electron microscopy (HRTEM). Electron micrographs were obtained with JEM-2010 instrument with lattice resolution 1.4 Å and accelerating voltage 200 kV. Periodic images of lattice structures were analyzed using digital Fourier transformation. Local elemental analysis was performed with EDX method on Energy-Dispersive X-ray Phoenix Spectrometer equipped with Si (Li) detector with energy resolution not worse than 130 eV. Samples were fixed on “holey” carbon films supported on copper grids and investigated with the electron microscope.

Hydrogen generation

The hydrogen generation reaction was carried out at 40 °C in a glass temperature-controlled internal mixing reactor equipped with a magnetic stirrer at the 800 rpm stirring rate. The volume of generated hydrogen was measured using a 100-ml gas burette.

Weighted amount of NaBH₄ (0.0465 g; Acros Organics, 98 %) was placed into the reactor and dissolved in 10 ml of distilled water. The catalyst was added in desired metal-to-hydride molar ratio equal to 1 : 2000. Then, the reactor was sealed with an outlet tube connected to volumetric burette.

The hydrogen generation rate (W^{50}) was calculated using the following equation:

$$W^{50} = v_{\text{H}_2} t_{1/2}^{-1} m_{\text{Me}}^{-1} \quad (1)$$

where W^{50} is a reaction rate, ml_{H₂}/(g_{cat} s); v_{H_2} is a volume of hydrogen produced during time $t_{1/2}$, ml; $t_{1/2}$ is a half-reaction time, s; m_{Me} is a catalyst mass, g.

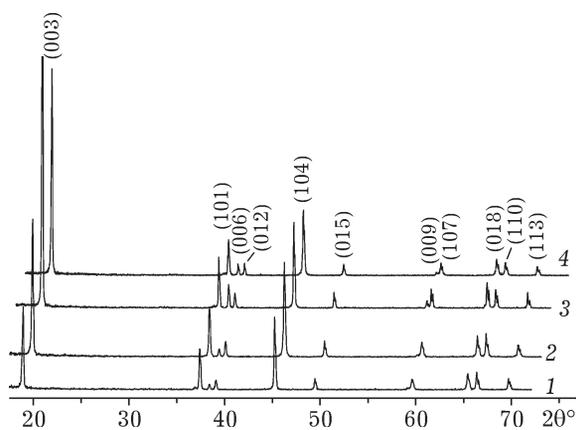


Fig. 1. X-ray diffraction patterns of as-prepared LiCoO₂ samples (see Table 1): 1 - LiCoO₂-1, 2 - LiCoO₂-2, 3 - LiCoO₂-3, 4 - LiCoO₂-4.

The catalyst endurance tests were carried out at 40 °C. After conversion of the first portion of NaBH₄ (0.0465 g dissolved in 10 ml of distilled water), the catalyst was separated from the reaction mixture and washed with distilled water. Then, the next portion of NaBH₄ was added.

RESULTS AND DISCUSSION

LiCoO₂ properties

Depending on the synthetic conditions, it is possible to prepare two different LiCoO₂ modifications: high-temperature (HT) and low-temperature (LT). HT-LiCoO₂ has an ideal layered α -NaFeO₂ structure (*R3m* space group) with ABCABC oxygen packing. Cobalt and lithium ions are ordered in the octahedral positions of different (111) planes. LT-LiCoO₂ has a spinel-like structure (*Fd3m* space group) where ~6 % of cobalt ions occupy the positions of lithium ions. According to the XRD data (Fig. 1), all as-prepared LiCoO₂ samples corresponded to high-temperature modification HT-LiCoO₂.

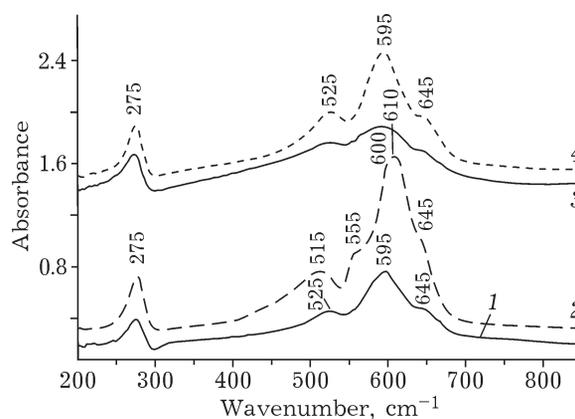


Fig. 2. FTIR spectra of as-prepared LiCoO₂ samples (see Table 1): 1 - LiCoO₂-1, 2 - LiCoO₂-2, 3 - LiCoO₂-3, 4 - LiCoO₂-4.

The splitting of the 006 and 012; 018 and 010 reflexes was observed in the diffraction patterns, whereas the ratio of the lattice parameters c/a was equal to 4.99 (Table 2). Both of these features are typical for HT-LiCoO₂. For LT-LiCoO₂, these reflexes do not split due to removal of the hexagonal distortion, and $c/a = 4.90$. However, the reflexes for samples prepared using MA are wider as compared with ceramic ones. This indicates that the average crystal size of their particles is smaller. This conclusion was confirmed by the surface area data (see Table 1). On the other hand, the intensity ratio of reflexes 003 and 104 was higher for the samples prepared without MA. This ratio grew with the annealing temperature (see Tables 1, 2). To our opinion, this growth reflects an increased textural orientation of the samples. Meanwhile, no significant change of the lattice parameters was observed (see Table 2).

Figure 2 shows FTIR spectra of as-prepared LiCoO₂. For all the samples, the absorption bands at 640, 600, 555, 515 and 275 cm⁻¹ are observed. Their positions and intensity ratios are characteristic of HT-LiCoO₂ and close to liter-

TABLE 2

Lattice parameters of synthesized LiCoO₂ samples according to the XRD data

Sample	$a \pm 0.00003$, nm	$c \pm 0.0002$, nm	c/a	I_{003}/I_{104}
LiCoO ₂ -1	0.28148	1.4049	4.991	1.43
LiCoO ₂ -2	0.28150	1.4055	4.993	1.12
LiCoO ₂ -3	0.28151	1.4045	4.989	4.88
LiCoO ₂ -4	0.28149	1.4045	4.990	3.13

ature data [17]. The first four bands correspond to vibrations of the CoO_6 octahedrons, whereas the band at 276 cm^{-1} is related to vibrations of the LiO_6 octahedrons. It should be noted that the intensity of the absorption bands of MA samples (LiCoO_2 -2 and LiCoO_2 -4 in Table 1) is higher than those of ceramic samples (LiCoO_2 -1 and LiCoO_2 -3 in Table 1). To our opinion, this is a result of different amount of delocalized electrons in the systems [18].

NaBH_4 hydrolysis

The catalyst loaded into the reactor consists of rhodium or platinum chloride supported on lithium cobalt oxide. After its contact with the first portion of NaBH_4 , the supported rhodium and platinum compounds are quickly reduced to the corresponding metals forming the active component of the catalyst.

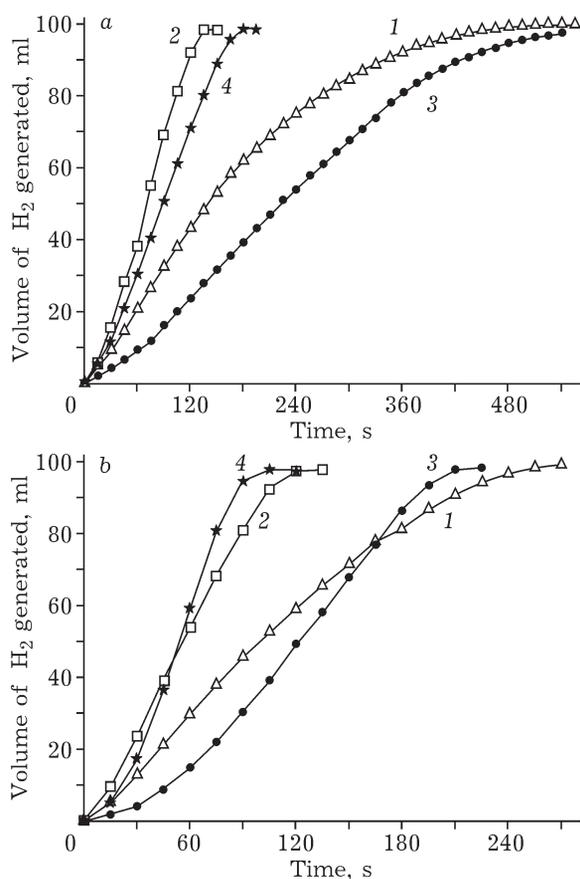


Fig. 3. Cumulative hydrogen generation rate at 40 °C on 1% Rh/LiCoO₂ (a) and 1% Pt/LiCoO₂ (b) catalysts supported on different LiCoO₂ supports (see Table 1): 1 – LiCoO₂-1, 2 – LiCoO₂-2, 3 – LiCoO₂-3, 4 – LiCoO₂-4.

The investigation of Rh and Pt catalysts supported on as-prepared HT-LiCoO₂ samples in the NaBH_4 hydrolysis reaction (Fig. 3, a, b) showed that the synthetic conditions significantly influence the activity of the catalysts. The catalysts supported on fine LiCoO₂ samples prepared using the MA stage were the most active. For 1% Rh/LiCoO₂ catalysts, a decrease of the LiCoO₂ annealing temperature from 800 to 700 °C resulted in a significant increase in hydrogen generation rate (see Fig. 3, a). On the other hand, the effect of the LiCoO₂ annealing temperature on the activity of 1% Pt/LiCoO₂ catalysts was different (see Fig. 3, b): for the LiCoO₂ supports prepared at higher temperature, the type of the hydrogen generation curve changes for samples prepared with and without the MA stage and the longer activation stage is observed. Note that the hydrogen generation rate increases with the growth of specific surface area of initial LiCoO₂.

The activity of catalysts supported on as-prepared LiCoO₂-2 was compared with others based on traditional supports, such as $\gamma\text{-Al}_2\text{O}_3$, TiO₂ (anatase) and carbon (sibunit) (Fig. 4). Despite the lower surface area of LiCoO₂ support as compared with the other supports (see above), the 1% Rh/LiCoO₂-2 and the 1% Pt/LiCoO₂-2 catalysts were characterized by significantly higher hydrogen generation rates.

The results of the endurance tests of the 1% Rh/LiCoO₂-2 and 1% Pt/LiCoO₂-2 catalysts are presented in Fig. 5, a, b. One can see

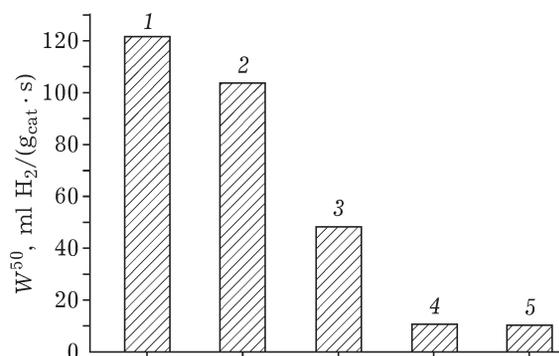


Fig. 4. Cumulative hydrogen generation rate at 40 °C on 1% Pt/LiCoO₂ (a) and 1% Pt/LiCoO₂ catalysts supported on different LiCoO₂ supports (see Table 1): 1 – 1% Rh/LiCoO₂-2, 2 – 1% Pt/LiCoO₂-2, 3 – 1% Rh/TiO₂, 4 – 1% Rh/Sibunit, 5 – 1% Rh/Al₂O₃.

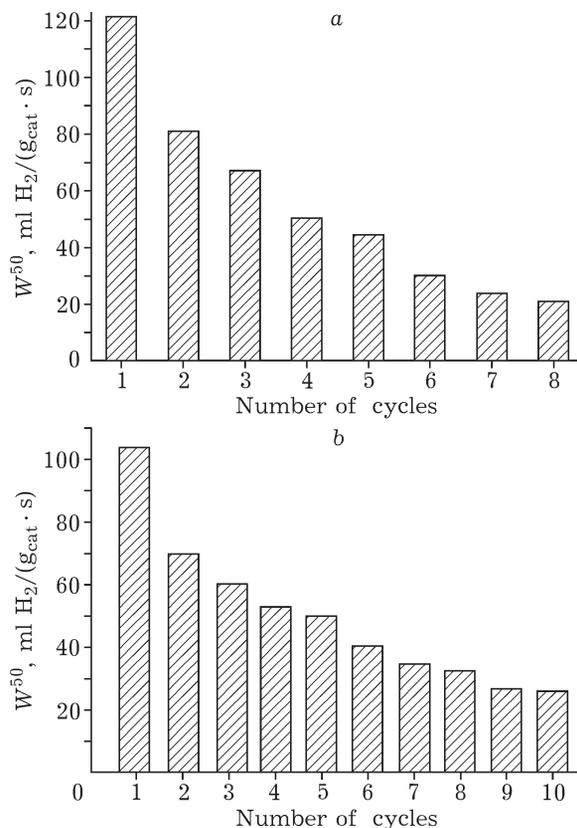


Fig. 5. Endurance tests for H₂ generation rate for 1% Rh/LiCoO₂-2 (a) and 1% Pt/LiCoO₂-2 (b) at 40 °C.

that after addition a new NaBH₄ portion, the activity of the catalysts gradually decreases.

Figure 6 presents hydrogen generation rate for the 1% Rh/LiCoO₂-2 catalyst as a function of time for 1–8 cycles. The 1st cycle is characterized by sharp generation of hydrogen. During the other cycles, hydrogen generation rate dramatically decreased and became much more uniform, however, the total amount of generated hydrogen remains constant. The similar results were obtained for the 1% Pt/LiCoO₂-2 catalyst.

To understand the reasons of degradation of the LiCoO₂-supported catalyst activity, we carried out an XRD, FTIR, DRS and TEM investigation of lithium cobalt oxide support after its treatment with NaBH₄ solution.

According to XRD, the intensity of reflexes of LiCoO₂-2 treated with 1.2 M solution of NaBH₄ at 40 °C is reduced more than twice. However, the lattice parameters remain unchanged. Figure 7 presents the FTIR spectra of LiCoO₂-2 before (curve 1) and after (curve 2)

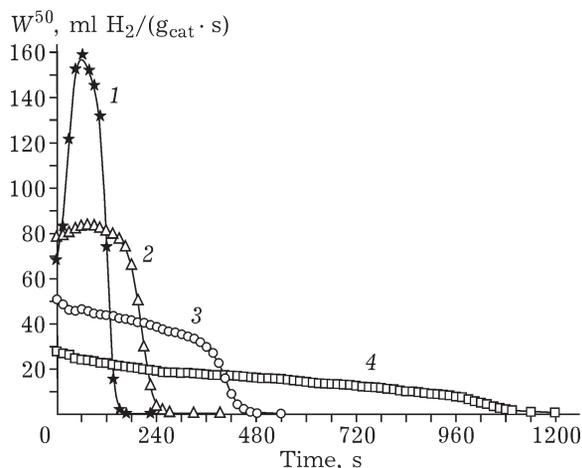


Fig. 6. Hydrogen generation rate for 1% Rh/LiCoO₂-2 catalyst as a function of time: 1–4 – cycle 1, 2, 5, 8, respectively.

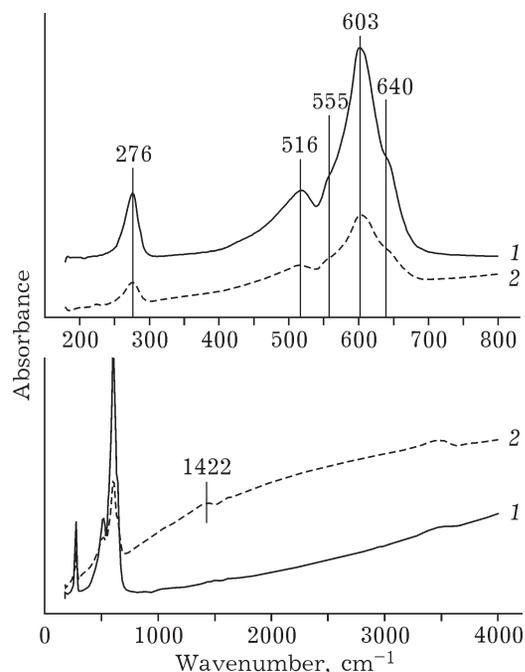


Fig. 7. FTIR spectra of LiCoO₂-2 (see Table 1) before (1) and after (2) treatment with 1.2 M NaBH₄ solution at 40 °C.

its treatment with NaBH₄. It shows that the sample treatment does not noticeably affect the positions of the LiCoO₂ absorption bands or their intensity ratios. The low-intensity band at 1422 cm⁻¹ can be attributed to vibrations of carbonates. Thus, the most part of the LiCoO₂ sample retains its structure. On the other hand, the drop of the intensity of the IR absorption bands and the appearance of significant background absorption are observed.

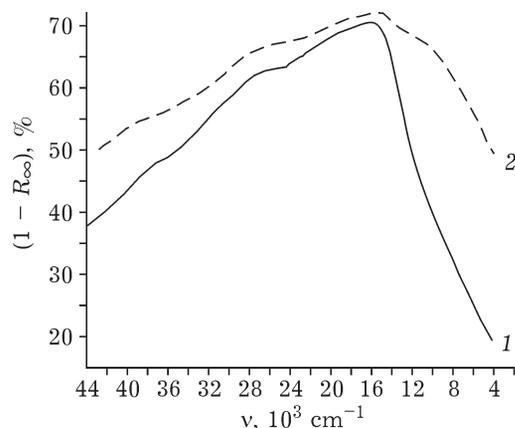


Fig. 8. DRS spectra of LiCoO₂-2 (see Table 1) before (1) and after (2) treatment with 1.2 M NaBH₄ solution at 40 °C.

Some changes are also observed in the DRS electronic spectrum of treated LiCoO₂-2 (Fig. 8). Substantial additional absorption, most significant in the near-IR region, appears after reaction (curve 2). Such absorption is typical for metals and metal-like compounds. We suppose that partial LiCoO₂ reduction occurs on the surface

of the particles with the formation of CoB_x nanoparticles. Cobalt borides of variable composition CoB_x are known to be formed after Co²⁺ reaction with BH₄⁻ in aqueous solutions. Their conductivity is close to that of metallic cobalt [19–22].

According to TEM (Fig. 9), the surface of LiCoO₂ particles drastically changes after treatment. The formation of Co particles and glass-like layer, most probably, consisting of lithium boron oxide, are clearly observed. One can suppose that this layer is the reason of catalyst degradation after prolonged cycling because of worsening contacts of metallic catalytic particles with support. However, additional studies are required to prove this hypothesis.

CONCLUSION

It is shown that the catalysts supported on LiCoO₂ prepared using mechanical activation have the highest catalytic activity in the NaBH₄

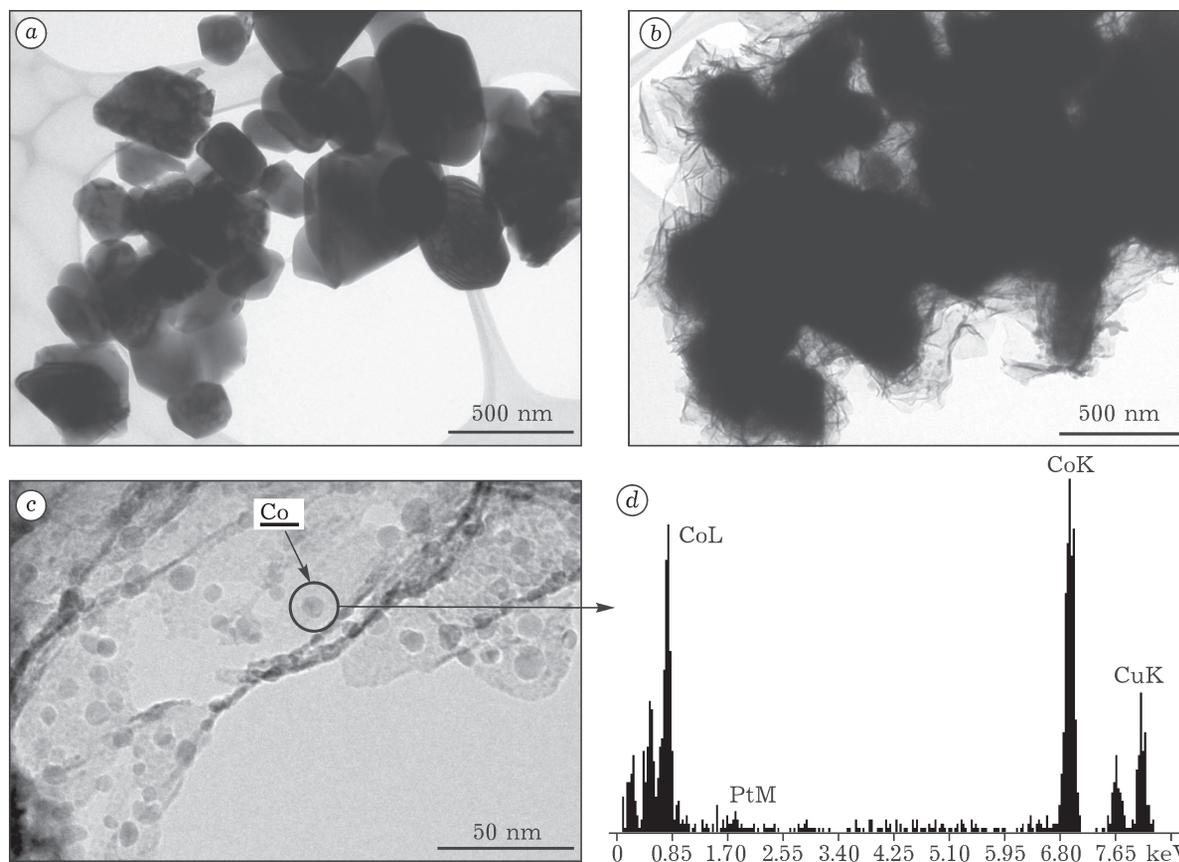


Fig. 9. TEM images of LiCoO₂-2 (see Table 1) before (a) and after (b, c) treatment with 1.2 M NaBH₄ solution at 40 °C; d – EDX analysis of particle shown in image c.

hydrolysis as compared with catalysts supported on ceramic LiCoO₂ and other traditional supports (γ -Al₂O₃, anatase, carbon material). The endurance tests of the catalysts supported on MA-LiCoO₂ showed that their activity gradually decreases with each new portion of converted substrate. This was associated with partial surface interaction of LiCoO₂ particles with a NaBH₄ solution leading to the formation of glass-like lithium boron oxide layer.

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