

Cobalt Nanowires as a Catalyst for Ethylene Hydrogenation

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Abstract—In this work, we demonstrate the effect of increasing the catalytic activity of the surface of cobalt in the ethylene hydrogenation reaction. The way to increase the activity of the surface is to increase its area by creating an array (set) of nanoscale nanowire columns on it. The nanowire arrays are studied by scanning electron microscopy before and after catalytic experiments. An estimated calculation of the increase in the surface area is carried out. It is shown that in the presence of an array of nanowires on the surface, its effective area increases tenfold. The proposed method makes it possible to use relatively cheap cobalt for catalysis. It is also important and convenient for practical use that the catalytic activity manifests itself at a rather low temperature, about 200°C. It is shown that when such a surface is used, the catalytic effect (conversion) increases to 20%. It is found that the magnitude of the effect depends on the geometrical parameters of the nanowires. The greatest effect is observed for nanowires with a diameter of 100 nm. It is also shown that the effect depends on their length, increasing with increasing length. Calculations of the increase in the area for structures with different diameters and lengths of nanowires are carried out. Their stability during catalysis is studied.

Keywords: nanowires, matrix synthesis, extended surface, catalysis, catalytic activity, ethylene hydrogenation, electron microscopy, elemental analysis

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INTRODUCTION

The problem of searching for new catalysts has existed for a long time, however, to date it has not lost its relevance [1]. A common way to increase the catalytic activity is to increase the surface area. It is known that “structuring” of the surface makes it possible to increase its area tenfold. The latter, in some cases, makes it possible to enhance the catalytic effect and successfully use cheap materials with a relatively low catalytic capacity. One way to increase the surface area is to form on it an array of one-dimensional threads: nanowires (NWs), i.e., the creation of a particular nanomaterial [2–4]. Such NWs can be obtained in various ways, including the method of matrix (template) synthesis. The essence of the method is that the pores in a specially prepared matrix (template) are filled with the required substance [5–7]. In this work, we use the most common variant of the process: filling pores in a polymer track membrane with a metal (cobalt) by galvanic deposition [8–10]. The resulting structures have a set of special properties. For example, combinations of nanoscale diameter and a high aspect ratio, together with the chosen material, make it possible to create magnets with unique properties [11]. Some possible applications are related to the special form of such structures. A small radius of rounding

of the ends of individual wires leads to a significant increase in the field strength, i.e., the pointed effect. The latter can be used to enhance the emission of electrons [12–14] or ions [15, 16] from the surface.

The result of creating an array of NWs on the surface is also an increase in the total surface area, leading to a number of effects. In [17, 18], an increase in the effect of surface cooling in the presence of a NW array on it was demonstrated. Another effect of increasing the surface area may be to increase the catalytic efficiency. Thus, earlier in our work [19], significant enhancement of the effect of carbon-monoxide oxidation on a copper surface was shown, the area of which was increased due to copper NWs grown on it (in the form of an array).

In this work, we study the possibility of catalytically accelerating the ethylene-hydrogenation reaction, which is widely used in organic chemistry [20, 21]. Ethylene hydrogenation is chosen as a model test reaction to study the catalytic activity of samples with nanowires. Typically, nickel, cobalt, and platinum metals act as hydrogenation catalysts. A large area of the available metal surface is usually achieved by depositing the metal on an inert support or by making a sponge metal. The fabrication of catalytically active metal nanowires on the substrate surface can be an

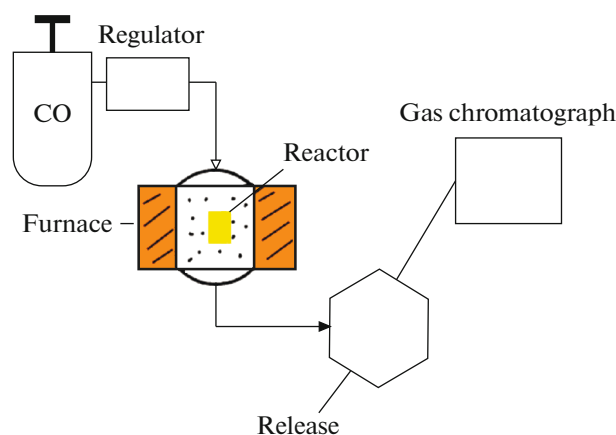


Fig. 1. Scheme of the installation for measuring conversion (with a chromatograph).

alternative method of catalyst preparation. A potential advantage of this method may be the preparation of a catalyst that can be easily removed from the reaction medium if hydrogenation is carried out in the liquid phase. Another advantage of these systems is the possibility of optimizing the catalyst by varying such parameters as the diameter and length of the nanowires, as well as the density of their arrangement on the substrate.

The use of catalytically active materials in the form of nanowires is described in publications [22–25]. For example, in [22], nickel nanowires were used to catalyze the ethanol-steam-reforming reaction. The authors of patent [23] suggested using nanowires of mixed metal oxides for the oxidative condensation of methane to ethylene. Nanowires based on cobalt oxide were used for the selective oxidation of CO in an excess of H₂ [24] and oxidative wastewater treatment [25].

The above ethylene-hydrogenation reaction can be accelerated on the cobalt surface. However, even upon heating, the catalytic activity of cobalt films is low. Since the surface area of the catalyst is one of the determining factors, it can be assumed that the use of a developed structure due to the creation of a NWs array will lead to a significant increase in conversion. This article is devoted to solving this issue.

EXPERIMENTAL

Matrix

Polymer track membranes based on a PET film 12 μm thick were used as a growth matrix (template). Four types of matrices with pores of different diameters were used: 30 nm (with a pore density of 9×10^9), 65 nm (with a pore density of 9×10^9), 100 nm (with a density of 1.2×10^9), (produced by the Joint Institute for Nuclear Research, Dubna). At the preliminary stage, the surface of these matrices was metallized with a layer of copper (successively by thermal spraying in

vacuum and galvanic deposition on the surface) to create an electrically conductive layer. The final thickness of the layer was up to 10 μm, and later this layer was the basis on which the NWs array was located.

NWs Electrodeposition

The main stage was the electrodeposition of cobalt into the pores of the track membrane, which was carried out in a galvanic cell. A solution of the following composition was used as an electrolyte: CoSO₄, 320 g/L; H₃BO₃, 40 g/L. An ELINS P-2X potentiostat galvanostat was used as the voltage source. Deposition was carried out at room temperature at a potential of 0.9 V. During the process, the time dependence of the current was recorded, which made it possible to control the filling of pores. (We note that surface metallization by the galvanic method at the preliminary stage was carried out from the same solution using an INSTEC 4 source).

After receiving the samples, a number of analyses were carried out. It should be noted that only in the case of X-ray diffraction analysis did we study NWs located in the polymer matrix (i.e., the latter was not removed). For other experiments (microscopy and investigation of the catalytic activity) it was necessary to remove the growth matrix, which was carried out in a concentrated alkali solution (6N, temperature 60°C). As a result, arrays of free NWs from cobalt were obtained, which were located on a common growth base (made of copper).

Electron-Microscopy Studies

The studies were carried out using a JCM-6000plus (JEOL) scanning-electron microscope in the secondary-electron mode at an accelerating voltage of 15 kV. The microscope was equipped with an energy-dispersive attachment for elemental analysis.

Measurement of Catalytic Conversion

The study was carried out by measuring the concentration of ethylene in the gas mixture after the reaction. The installation contains a tubular quartz reactor with a diameter of 6 mm, a gas supply and exhaust system, a gas-flow regulator, and a programmable furnace. The installation diagram is shown in Fig. 1.

The composition of the initial gas mixture was C₂H₄(2%)–N₂(10%)–N₂. The flow rate was 20 mL/min. The samples of copper films (flat pieces) with cobalt nanowires 9 × 6 mm in size were loaded into the reactor. These samples were placed vertically in the reactor tube without deforming the film. The width of a film sample of 6 mm corresponds to the inner diameter of the tube; therefore, the film was located along the central axis, and the gas mixture flowed around it from both sides. Two control samples were also prepared: a

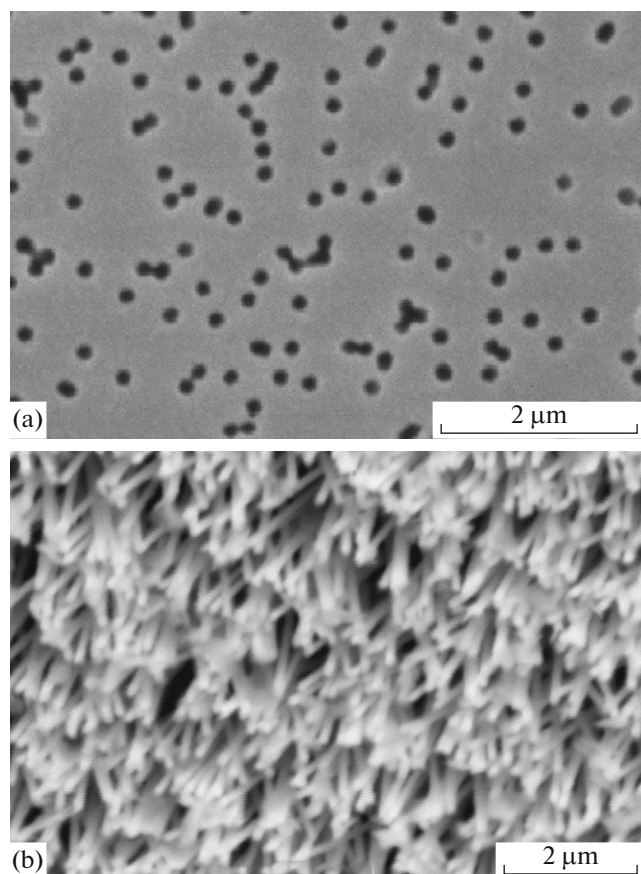


Fig. 2. SEM images: (a) surface of the initial track membrane with a pore diameter of 100 nm; (b) images of the NWs array (on a common base).

cobalt film with a size of 9×6 mm and a copper film (without nanowires) of the same size. After the reaction, part of the gas mixture was sampled using a loop for chromatographic analysis on a Khromatek-2000 chromatograph. The samples were heated gradually in the temperature range 150–300°C. The composition of the gas was determined 5 min after the temperature was established.

RESULTS

SEM was carried out both for certification of the initial membranes and for studying the NWs array on the substrate. The results obtained (images of the surface of the track membranes and grown NWs arrays) are shown in Figs. 2a and 2b, respectively.

Analysis of the obtained images of the matrix surface makes it possible to determine the diameter of the matrix pores, which correspond to those declared by the manufacturer. The images of the NWs array make it possible to estimate the diameter and length of the NWs in the array. It can be seen that the NWs diameter corresponds rather well to the pore diameter of the

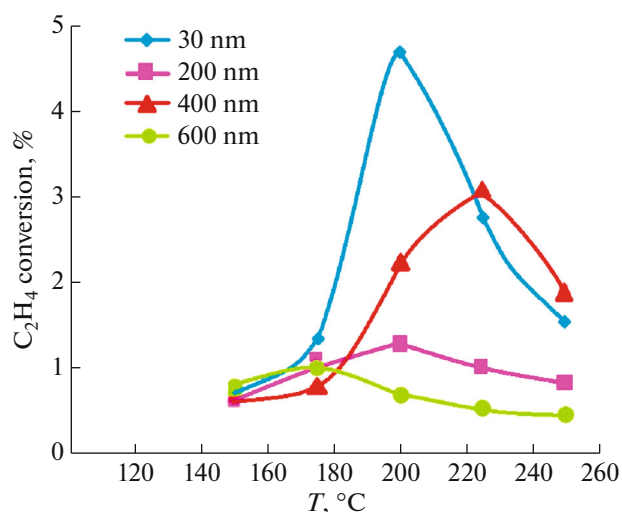


Fig. 3. Dependence of conversion on temperature for NWs samples with different diameters.

growth matrix. The length is determined by the time of growth and is approximately proportional to it.

Conversion measurements were carried out on the setup and in the modes described above. The obtained dependences of conversion on the NWs diameter (for the studied samples with diameters of 30, 200, 400, and 600 nm) are shown in Fig. 3.

It can be seen that for the studied samples, the conversion depends on the temperature; it has the greatest value at temperatures of 200–230°C. It can also be seen that the conversion value increases with decreasing NWs diameter. However, the highest yield was obtained for samples not with the smallest diameter, but with a diameter of 100 nm (see below). The results for these samples are shown separately in Fig. 4a, where the data for the cobalt film are also shown for comparison.

The data of Figs. 3 and 4 allow us to conclude that the use of a sample with an array of cobalt NWs gives a noticeably higher conversion compared to the Co film. The maximum conversion (up to 20%) is observed for NWs samples with a diameter of 100 nm at relatively low temperatures: 225°C. It can be noted that the control sample made of a flat copper film did not show catalytic activity.

The stability of samples during catalysis is their most important parameter. To study it, the dependence of the catalytic activity on time was measured. The results, i.e., the dependence of the conversion on time, are shown in Fig. 4b. It can be seen that the conversion value decreases, but these changes are small.

The NWs array during catalysis was studied by SEM. An example of images of the samples after the catalytic experiment is shown in Fig. 5.

Comparing the electron-microscopy images of the NWs arrays before and after the reaction, it can be seen that there are no significant changes in the NWs. The

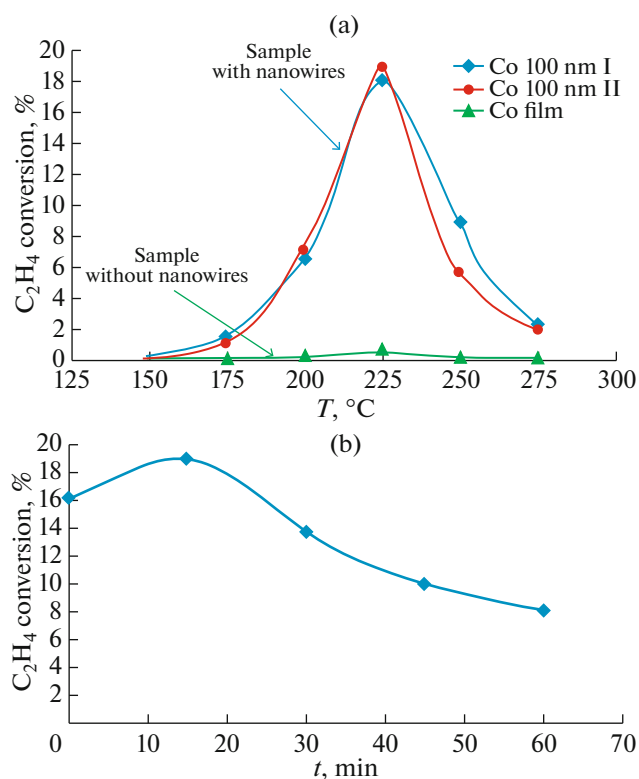


Fig. 4. Catalytic activity of the cobalt NWs and Co film (a); time dependence of catalytic activity at $T = 225^{\circ}\text{C}$ (b).

latter (as well as the plot of the dependence of the activity on time) proves the sufficient stability of the NWs during this process.

At the same time, the elemental analysis carried out after the catalysis experiment (Fig. 5c) showed the appearance of a certain amount of carbon (probably on the surface of the NWs). Data on the total elemental composition before and after catalysis are given in Table 1. We note that since the relative values are calculated, the appearance of carbon leads to a relative decrease in the amount of other elements, in particular, cobalt. In the future, it is necessary to identify the causes of the appearance of carbon and the degree of its influence on sample degradation.

In this work, we also studied the effect of the NWs length on the catalytic activity of the array. Using the method described above, on the basis of a matrix with a pore diameter of 100 nm, samples of arrays with different lengths of NWs of 2, 4, 6, and 8 μm were obtained. The curves of the dependence of the conversion value on temperature for samples with different lengths are shown in Fig. 5a.

Analyzing the graph, we can conclude that an increase in length leads to an increase in catalytic activity. Based on these data, the dependence of the ethylene conversion value was determined (at the same temperature 175°C and the same holder area) on

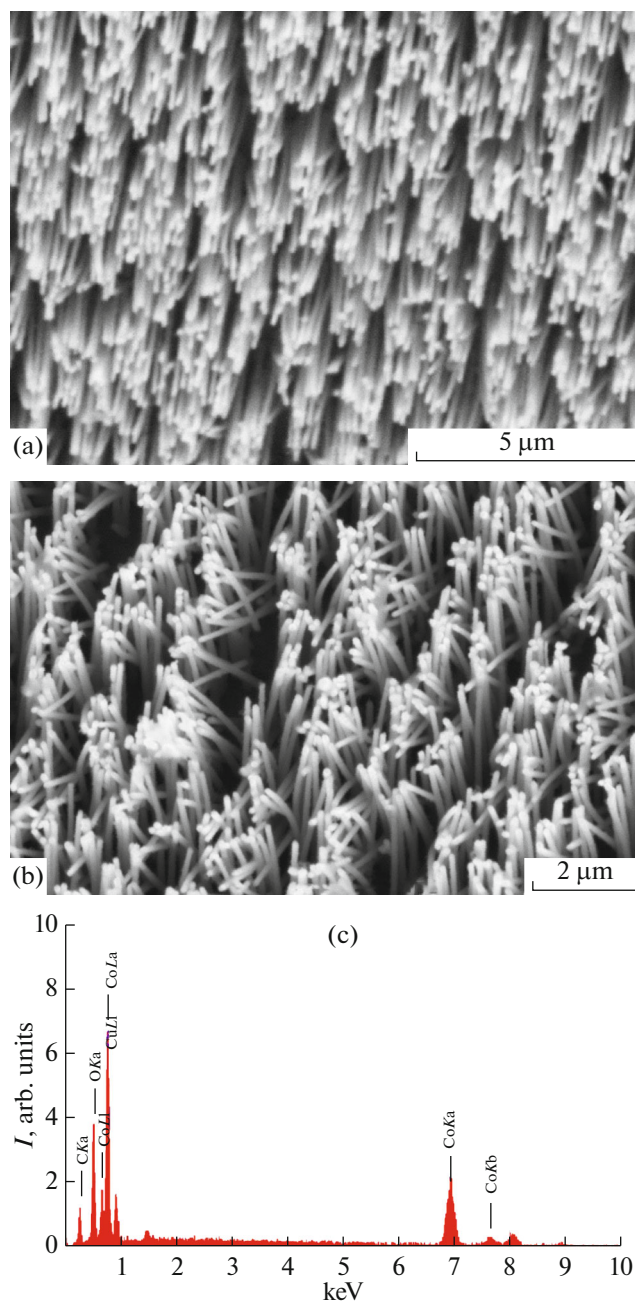


Fig. 5. SEM image of a NWs array (100 nm in diameter): (a) before conversion; (b) after conversion; and (c) elemental analysis after conversion.

the length of the cobalt NWs (the graph is shown in Fig. 6b).

A general analysis of the results obtained allows us to conclude that an increase in the surface area (due to a decrease in the NWs diameter or an increase in length) generally leads to an increase in catalytic activity.

The calculation of the surface area increase in the NWs array is given below. By the example of an NWs

Table 1. Sample composition (at %)

Element	Initial	After catalysis
C	4.9	35.3
O	3.3	38.9
Co	91.8	25.8

array sample with a density of 1.2×10^9 pores per 1 cm^2 and a NWs height of $10 \text{ }\mu\text{m}$.

$$\text{Increase in area} = \frac{S_{\text{all NWs}} + S_{\text{sample}}}{S_{\text{sample}}},$$

$$S_{\text{all NWs}} = N_{\text{NWs}} S_{\text{NWs}},$$

$$S_{\text{NWs}} = H\pi D.$$

Respectively,

$$\text{Increase in area} = \frac{H\pi D N_{\text{NWs}} S_{\text{sample}}}{S_{\text{sample}}},$$

where

$S_{\text{all NWs}}$ is the surface area of all NWs;

S_{sample} is the sample area;

S_{NWs} is the surface area of a single NWs;

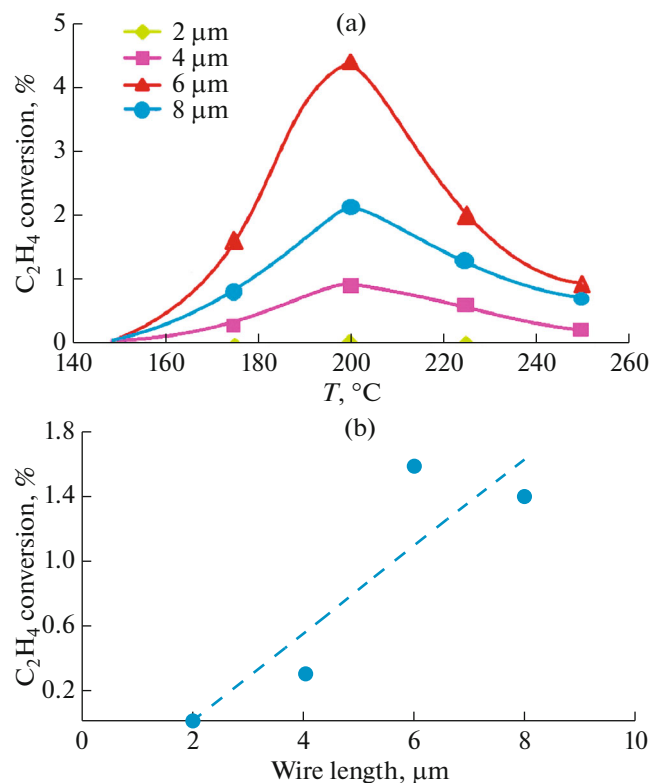


Fig. 6. Ethylene conversion dependence for samples of cobalt NWs arrays with different lengths at different temperatures (a). The dependence of the ethylene conversion at a temperature of 175°C on the length of the NWs (b).

N_{NWs} is the number of NWs per 1 cm^2 ;

H is the height of the NWs;

D is the NWs diameter.

Example: we calculate the increase for a sample with a nanowire diameter of 100 nm , an area of 1 cm^2 , a nanowire length of 10^4 nm , and a NWs density $1.2 \times 10^9 \text{ pcs/cm}^2$.

$$\begin{aligned} \text{Increase in area} &= \frac{10^{-5} \pi \times 10^{-7} \times 1.2 \times 10^9 + 10^{-4}}{10^{-4}} \\ &= 38.68 \text{ times.} \end{aligned}$$

The above estimate shows a significant (tens of times) increase in the surface area in the presence of a NWs array on it. It is also easy to see that the increase is proportional to the length of the NWs. A similar calculation for NWs with a smaller diameter (at which the surface density of NWs increases accordingly) also leads to an increase in the total surface. Thus, the obtained dependences of the activity on the geometrical parameters can be easily explained by the increase in the total surface area, which is achieved when using a NWs array.

The existing deviations from this dependence for NWs with a small diameter of 65 and 30 nm and for NWs with a length of $8 \text{ }\mu\text{m}$ (the longest ones) can also be easily explained based on the analysis of SEM images: a noticeable slope is observed in these samples, leading to the adhesion of NWs to each other. It can be assumed that the latter leads to a decrease in the effective area of their total surface. It can be assumed that the shape of NWs can also play a certain role (for example, the radius of curvature of their tips). It is planned to study these issues in the future.

CONCLUSIONS

It has been shown that an array of cobalt NWs exhibits catalytic activity in the ethylene-hydrogenation reaction. The highest conversion of 20% is observed in NWs with a diameter of 100 nm at a temperature of 225°C . The relatively low value of this temperature makes the use of cobalt NWs especially attractive.

In the process of catalysis, some decrease in activity is observed, which is associated with the formation of carbon on the surface. The catalytic activity increases with an increase in the area of NWs in the array with an increase in their length and a decrease in their diameter (with a corresponding increase in the amount of NWs). Violations of this dependence for NWs of maximum length or minimum diameter can be explained by the observed adhesion of NWs.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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