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Preparation and Characterization of Aluminosilicate Supports with a Synthesized Layer of Catalytic Filamentous Carbon: II. Synthesis of Carbon Nanofibers on a Supported Cobalt Catalyst

G. A. Kovalenko[a], N. A. Rudina[a], T. V. Chuenko[a], L. V. Perminova[a], T. G. Terent'eva[a], A. S. Rozanov[b], and S. N. Zagrebel'nyi[b]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*
E-mail: galina@catalysis.nsk.su

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Abstract—The synthesis of a layer of catalytic filamentous carbon (CFC) on a Co catalyst supported by homogeneous precipitation onto the surface of aluminosilicate supports (ceramic foam and vermiculite) was studied. The effects of CFC layer synthesis conditions (the catalyst concentration on a support, the pyrolysis temperature of a propane–butane mixture, and the composition of the gas mixture) on the specific surface areas of supports, the yield of carbon ((g C)/(g Co)), and the morphology of a surface CFC layer were examined. It was found that, in the case of ceramic foam, the concentration of cobalt hydroxide precipitated on the surface was lower by a factor of 15 and the yield of carbon was higher by a factor of 20–40 than those in vermiculite. The specific surface areas of supports, the yield of carbon, and the amount of synthesized carbon increased as the pyrolysis temperature of a propane–butane mixture was increased from 500 to 600°C. As found by scanning electron microscopy, the carbon content increased with pyrolysis temperature because of an increase in the length of carbon nanofibers. The properties (activity and stability) of biocatalysts prepared by the adsorption immobilization of a recombinant protein having glucose isomerase activity on CFC–Co-containing supports (ceramic foam and vermiculite) were studied.

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INTRODUCTION

It is well known that the catalytic synthesis of carbon nanofibers takes place in the course of hydrocarbon pyrolysis in the presence of a metal catalyst. In the majority of studies, Ni metal or a Ni–Cu alloy was used as such a catalyst [1, 2]; Co, Fe, and Fe–Co were used more rarely [3–5]. Studies devoted to the synthesis of a layer of catalytic filamentous carbon (CFC) several micrometers in thickness on the surface of macrostructured inorganic supports, such as a ceramic matrix [6] and glass fiber [7], are few in number. Only a few studies were devoted to the effects of pyrolysis conditions and the composition of a hydrocarbon-containing gas mixture on the kinetics of decomposition of the hydrocarbon (methane) and the synthesis of carbon nanofibers [5]. Zhang and Smith [5] found that the pyrolysis of methane on a supported Co catalyst in the presence of hydrogen or CO was accompanied by the synthesis of carbon nanofibers ~25 nm in diameter, whereas the diameter of a carbon fiber was 10 nm in the absence of hydrogen.

Previously, Kovalenko et al. [8–12] prepared macrostructured ceramic supports, on the surface of which a CFC layer was synthesized in the course of propane–butane pyrolysis on a supported Ni catalyst, and studied the adsorption properties of these materials with respect to enzymatically active substances (enzymes, cell membranes, and whole microorganisms).

It is well known that Co^{2+} ions are the activators of a glucose isomerase enzyme [13, 14]. Therefore, the introduction of this metal as a catalyst constituent is of interest for the synthesis of supports for the immobilization of this enzyme and the preparation of biocatalysts for a practically important process of the production of glucose–fructose syrups.

The aim of this work was to study the synthesis of a CFC layer on a Co catalyst supported on the surface of ceramic foam or vermiculite, in particular, to study the effect of CFC layer synthesis conditions (the cobalt concentration on a support, the temperature of propane–butane pyrolysis, and the composition of the gas mixture) on the specific surface areas of supports, the yield of carbon ((g C)/(g Co)), and the morphology of the surface CFC layer; to examine the resulting CFC–Co-containing supports as adsorbents for the immobilization of a recombinant protein having glucose isomerase activity; and to study the properties (activity and stability) of the immobilized enzyme in the fructose isomerization reaction.

EXPERIMENTAL

Ceramic foam (Powder Metallurgy Research Institute, Minsk, Belarus) having a cellular three-dimensional macrostructure with an average cell size of ~2 mm and ~70% open porosity was used as a starting support. The specific surface area of the ceramic foam was 0.5 m^2/g. Vermiculite, a lamellar natural mineral with the trade name S-VERAD AGRO foamed vermiculite (OOO IPP Artaliya, St. Petersburg, Russia), was also used in this study. This vermiculite is intended for agricultural use as a natural sorbent and active mineral additive for plant growth, as well as a water-retaining component of soil. This support was used as granules (2–3 mm) with a packed density of ~0.1 g/cm^3. The specific surface area of vermiculite was 9 m^2/g.

The supported Co catalyst was prepared by homogeneous precipitation. For this purpose, a starting support was placed in a glass vessel with a solution of cobalt nitrate (0.01–0.05 mol/l) and urea (0.1 mol/l), and this vessel was heated in a water bath to 85 ± 1°C and kept for 3 h at the specified temperature. The ratio of the support weight (g) to the solution volume (ml) was 1 : ~5 or 1 : ~25 for ceramic foam or vermiculite, respectively. Then, the support with supported cobalt (catalyst for pyrolysis) was washed with distilled water and dried under an IR lamp for 4–6 h. The dried catalysts were cooled and kept in a desiccator. The concentration of supported nickel (wt %) was determined by atomic absorption spectrometry on an ASSIN instrument with a flame-ionization detector.

The synthesis of CFC on the supported Co catalyst was performed by the pyrolysis of a propane–butane mixture at 500–600°C. A fixed-bed reactor was used for this purpose. The catalyst bed was formed using a packing material of stainless steel gauze, which was placed in a horizontally arranged quartz tube reactor 200 mm in length and 30 mm in diameter. The products of pyrolysis (coke deposits) were mechanically removed from the above packing material at regular intervals. The geometric surface area of steel gauze was ~0.1 cm^2. Up to 20 g of the catalyst with a total surface area of ~2–20 m^2 was placed in the reactor. The temperature of the furnace in which the reactor was placed, was controlled using a PROTERM-100 microprocessor temperature regulator. The flow rates of gases were adjusted with a fine-adjustment regulator in a gas supply unit and measured with a foam flow meter. The catalyst in the system was additionally dried at 85°C in a flow of nitrogen (flow rate of 12 l/h) for 30 min. Then, the flow of nitrogen was replaced with a flow of gas mixtures of various compositions, the temperature was increased to 500–600°C at a rate of 10 K/min, and the process of pyrolysis was performed as follows: procedure 1, the pyrolysis of a propane–butane mixture (flow rate of 24 l/h) for 1 h; procedure 2, the pyrolysis of a hydrogen/(propane–butane) gas mixture (1 : 8, by volume) for 1 h. The two-stage synthesis of CFC (procedure 3) involved a step of the prereduction of cobalt hydroxide with hydrogen at 500–600°C for 0.5 h followed by the pyrolysis of a propane–butane mixture at the specified temperature for 0.5 h. The amount of carbon (wt %) synthesized on the surface was determined gravimetrically from either (1) an increase in the catalyst weight, which was measured before and after pyrolysis, or (2) a decrease in the weight of an adsorbent (with a CFC layer) upon annealing in an atmosphere of oxygen at 800°C for 3 h. In the calculations of carbon contents, the hygroscopicity of the starting support, which was determined from weight loss after heating to constant weight (200°C; 4 h), was taken into consideration and the weight loss of the starting support under conditions of pyrolysis (600°C; 1 h) and annealing (800°C; 3 h) was also determined. The experimental error was 1–2%. As found experimentally, the hydroscopicity of vermiculite was 13.2% and the weight loss of vermiculite upon annealing was 19.2%.

The process productivity of the synthesis of CFC was characterized by the yield of carbon (Y), which is equal to the weight (g) of synthesized carbon per gram of cobalt metal catalyst ((g C)/(g Co)).

Metal ions were washed out from the CFC-containing vermiculite in accordance with the following procedure: A weighed portion (1 g) of the support and 20 ml of a 0.02 M phosphate buffer solution (pH 7.8) were placed in a thermostat at 60°C. After 6 h, the buffer solution was replaced and the washing procedure was repeated. The concentration (μg/ml) of ions in the solution was determined by atomic absorption spectrometry.

The specific surface areas (S_{BET}, m^2/g) of supports were determined using the thermal desorption of argon on a SORBI-M instrument (ZAO Meta, Russia). The electron-microscopic studies of the morphology of cobalt hydroxide supported on the surface and the synthesized CFC layer were performed with the use of JSM 6460 LV (Japan) and LEO 1430 (Germany) instruments.

Recombinant protein having glucose isomerase activity isolated from the *E. coli* strain BL21 DE3 was used for adsorption immobilization. In this protein, a modified glucose isomerase gene was cloned into an expressing plasmid. The given protein contained an additionally introduced terminal hexahistidine tag sequence (His_6). For the separation and purification of His_6-glucose isomerase, the biomass of *E. coli* BL21 DE3 was ultrasonically disintegrated and the supernatant liquid containing His_6-glucose isomerase was separated by centrifugation. Then, affinity chromatography on Co^{2+}-containing TALON Sepharose (BD Biosciences Clontech) was performed. The adsorption of

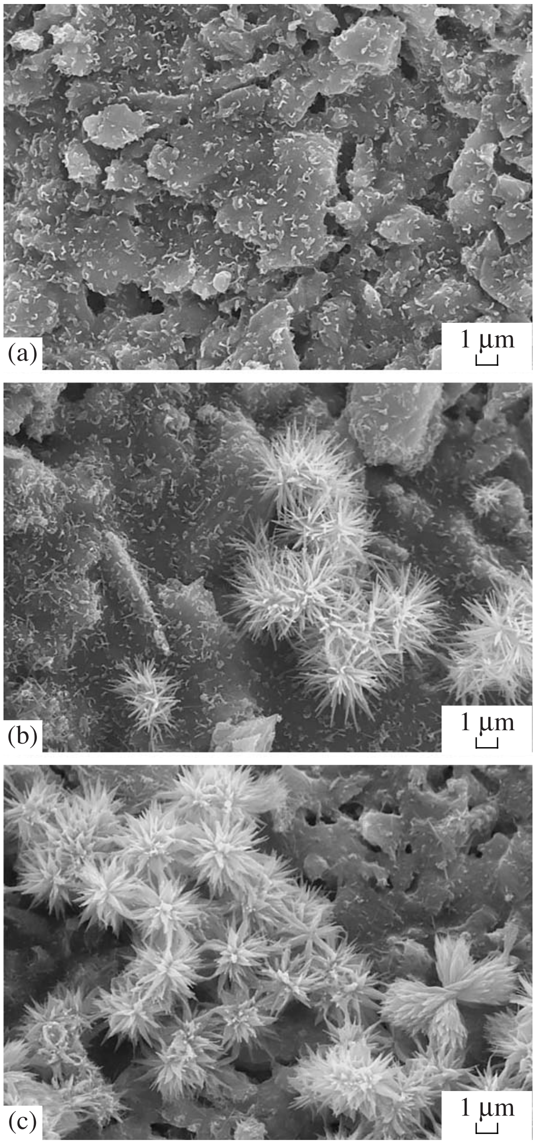

Fig. 1. Electron micrographs of the surface of ceramic foam with supported cobalt hydroxide: (a) 0.08, (b) 0.14, and (c) 0.37% Co.

recombinant His_6-glucose isomerase and the preparation of heterogeneous biocatalysts were performed under conditions described previously [8, 9]. The glucose isomerase activity was measured under the following conditions: 50°C; 0.02 M phosphate buffer solution, pH 7.8; 1 mM Co^{2+}; 5 mM Mg^{2+}; 0.5 M fructose. With the use of Co-containing supports, cobalt ions were not added to the reaction medium. The activity of heterogeneous biocatalysts was determined in a column flow reactor with the circulation of a substrate solution through the biocatalyst bed at a flow rate of 35 ml/min. The specific glucose isomerase activity in solution was 0.55 μmol min^{-1} (mg protein)$^{-1}$. The activity of immobilized His_6-glucose isomerase was expressed in (μmol glucose) min^{-1} (g heterogeneous biocatalyst)$^{-1}$.

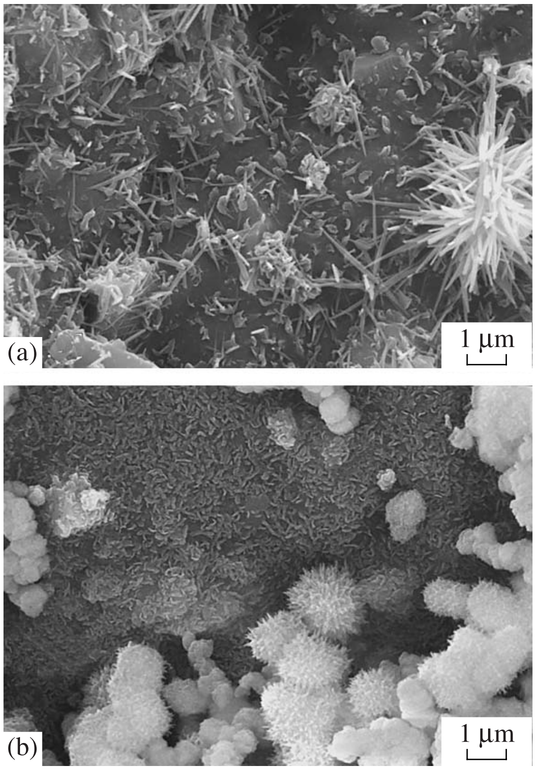

Fig. 2. Electron micrographs of the surface of ceramic foam with supported (a) cobalt hydroxide (0.14%) or (b) cobalt hydroxide (0.12%) and nickel hydroxide (0.21%).

The stability was determined on keeping in a buffer solution at 10–15°C measuring the residual activity at regular intervals and comparing it with the activity of the freshly prepared catalyst. The half-inactivation time ($t_{1/2}$) of the biocatalyst, during which the initial activity decreased by a factor of 2, was taken as a measure of stability.

RESULTS AND DISCUSSION

Formation of Cobalt Catalysts on Ceramic Foam and Vermiculite Surfaces

We found that the amount of cobalt supported on the surface of ceramic foam or vermiculite was a linear function of the initial concentration of cobalt nitrate in solution in homogeneous precipitation. In this case, the concentration of supported cobalt (wt %) on ceramic foam was lower by one order of magnitude than that on vermiculite. On the other hand, the surface concentration of supported cobalt (on a 1 m^2 basis) on vermiculite was higher than that on ceramic foam by a factor of 20; these surface concentrations were equal to 0.58 and 0.03 (mmol Co)/m^2, respectively. The formation of individual flaked particles on the surface of ceramic foam at low cobalt concentrations can be observed in electron micrographs (Fig. 1a). Then, bulky structures as needle crystals were observed along with individual

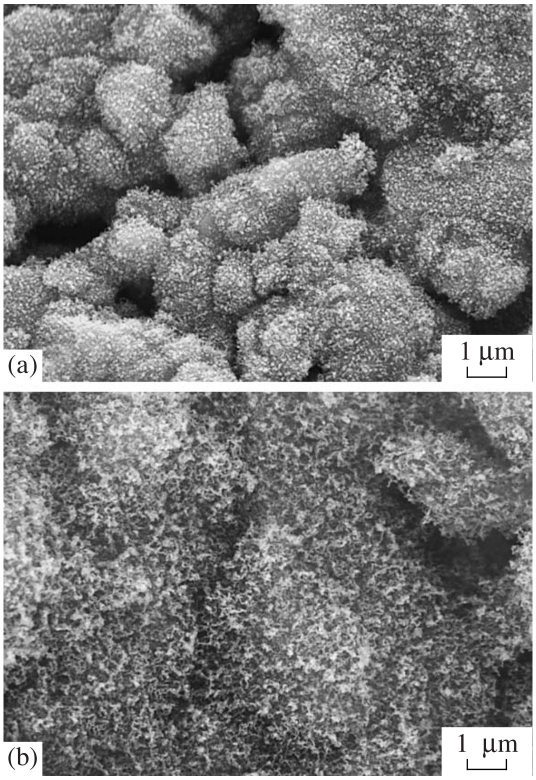

Fig. 3. Electron micrographs of the surface of ceramic foam with a CFC layer synthesized in accordance with procedures (a) 1 and (b) 2 on a supported Co catalyst (0.08%).

particles of cobalt hydroxides as the concentration of cobalt nitrate was increased (Figs. 1b, 1c). Analogous coarse crystalline formations of cobalt hydroxide on the surface of vermiculite were distributed very nonuniformly; they mainly occurred near the end faces of lamellar vermiculite structures. A nonuniform pink color, which is characteristic of cobalt hydroxides, was also observed visually in vermiculite granules.

The formation of a Co catalyst in the presence of nickel nitrate was studied using the simultaneous combined homogeneous precipitation of two metals. In the precipitation of Co^{2+} onto ceramic foam in the presence of Ni^{2+}, the concentration of cobalt was lower than that of nickel by a factor of ~2, whereas the concentrations of cobalt and nickel supported on vermiculite were practically equal. Based on a comparison of these data and data obtained under conditions of the separate precipitation of Co^{2+} and Ni^{2+} nitrates, we can conclude that the compounds of cobalt and nickel were independently distributed over ceramic foam; the concentration of supported cobalt was practically independent of the presence of Ni^{2+}. Electron micrographs exhibited some differences: for example, it is likely that smaller flaked particles (Fig. 2a) of nickel hydroxide and coarse needle formations of cobalt hydroxide (Fig. 2b) were formed in the combined precipitation of Co^{2+} and Ni^{2+} on support surfaces. Under conditions of precipitation on vermiculite in the absence of nickel from solution, the concentration of supported cobalt increased (by a factor of ≥1.5); this suggests that the hydroxides of these metals are deposited at the same sites, namely, the end faces of lamellar structures.

Synthesis of a CFC Layer

Previously [15], we found that, with the use of ceramic foam, the characteristics of the resulting adsorbents (the amount of CFC synthesized, the yield of carbon, and the specific surface areas of supports) were practically independent of the procedure used for the synthesis of carbon nanofibers on a supported Ni catalyst; the average yield of carbon was 34 (g C)/(g Ni). In this work, we found that, unlike the Ni catalyst, the yield of carbon on the Co catalyst supported on ceramic foam was ~6 (g C)/(g Co) (Table 1). In electron micrographs, it can be seen that shorter fibers were formed in the pyrolysis of a propane–butane mixture in accordance with procedure 1 (Fig. 3a), as compared with fibers synthesized in accordance with procedures 2 and 3 (Fig. 3b). In this case, the amount of carbon synthesized in accordance with procedure 1 was very low. Procedure 2 (the pyrolysis of a hydrogen–propane–butane mixture) was chosen for the subsequent synthe-

Table 1. Effect of synthesis procedures on the characteristics of a CFC layer on a Co catalyst supported on ceramic foam at 600°C

CFC synthesis procedure*	Cobalt content, %	Carbon content, %	Y, (g C)/(g Co)	S_{BET}, m^2/g
1	0.08	0.46	5.8	5
2	0.08	3.10	38.8	15
	0.14	4.50	32.1	15
	0.37	7.10	19.1	15
3	0.07	2.24	32.0	12

* 1, pyrolysis of a propane–butane mixture (with no hydrogen); 2, pyrolysis of a hydrogen–propane–butane mixture; 3, two-stage procedure with the prereduction of cobalt hydroxide.

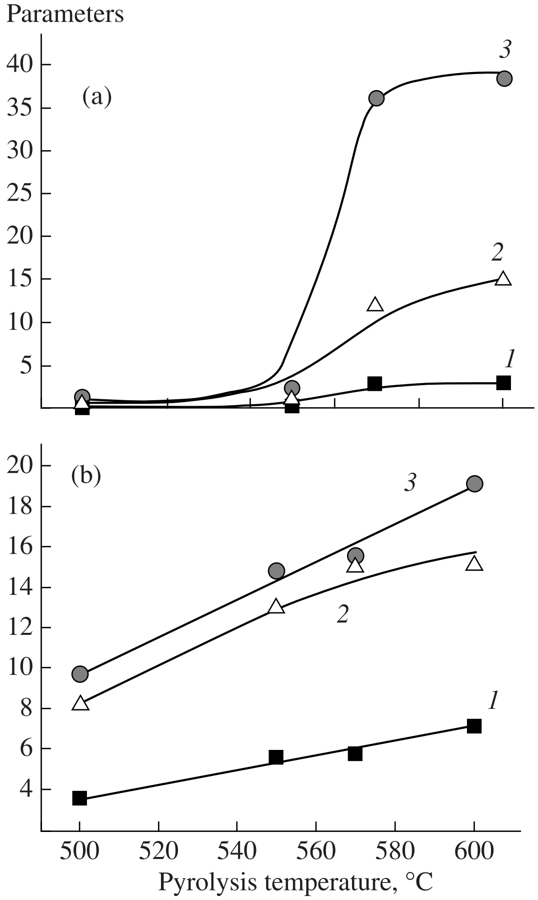

Fig. 4. Effect of the temperature of pyrolysis of a hydrogen–propane–butane mixture (procedure 2) on a (a) 0.08% or (b) 0.37% Co catalyst supported on ceramic foam upon the following characteristics of the supports: (*1*) carbon content (%), (*2*) specific surface area (m^2/g), and (*3*) yield of carbon ((g C)/(g Co)).

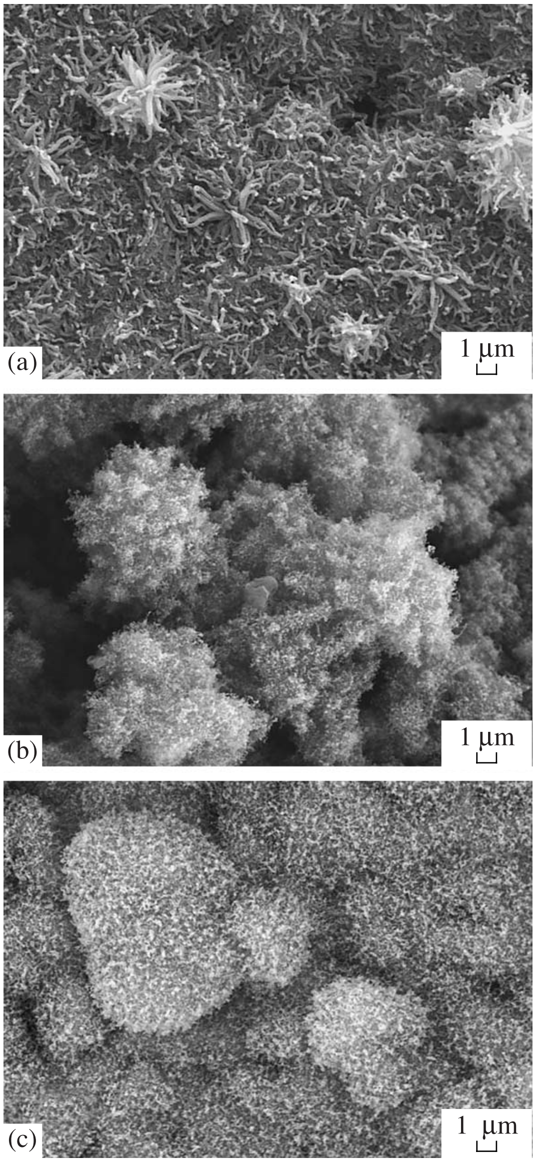

Fig. 5. Electron micrographs of the surface of a CFC layer synthesized on ceramic foam with a supported Co catalyst (0.14%) depending on pyrolysis temperature: (a) 500°C (0.48% CFC), (b) 550°C (0.52% CFC), and (c) 600°C (4.5% CFC).

sis of a CFC layer. This procedure allowed us to synthesize a comparatively high weight amount of carbon, which was uniformly distributed over the surface as relatively long carbon nanofibers.

We studied the effect of the temperature of pyrolysis of a hydrogen–propane–butane mixture (procedure 2) on the characteristics of the resulting adsorbents. As the pyrolysis temperature was increased, the amount of CFC synthesized, the yield of carbon, and the specific surface area of ceramic foam increased (Fig. 4). If the concentration of cobalt on the surface of ceramic foam was low, a dramatic increase in the above parameters was observed at a temperature higher than 550°C (Fig. 4a). If the concentration of cobalt on the surface of ceramic foam was relatively high, an almost linear increase in the parameters with temperature was observed (Fig. 4b). The electron microscopic studies demonstrated that, at a pyrolysis temperature of 500°C, the synthesis of CFC on a Co catalyst occurred with an insignificant intensity at several active sites of the Co catalyst with the formation of very short carbon nanofibers deposited (Fig. 5a) to resemble the shape of crystalline cobalt hydroxide formations. As the pyrolysis temperature was increased, longer carbon nanofibers were synthesized; these fibers shielded the shape of cobalt hydroxide crystallites (Figs. 5b, 5c). The subsequent synthesis of a CFC layer on the supported Co catalyst was performed using the pyrolysis of a hydrogen–propane–butane mixture (procedure 2) at 600°C. We also found experimentally that the pyrolysis of a hydrogen–propane–butane mixture at 500–600°C almost did not occur in the absence of a supported Co catalyst from ceramic foam and vermiculite; the maximum

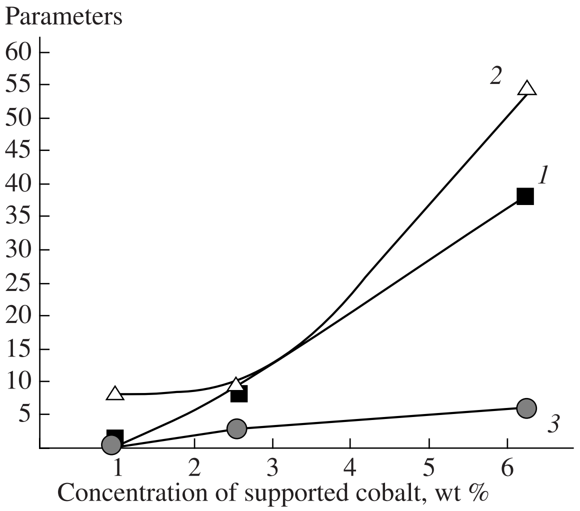

Fig. 6. Support characteristics as functions of the concentration of a Co catalyst supported on vermiculite: (*1*) carbon content (%), (*2*) specific surface area (m^2/g), and (*3*) yield of carbon ((g C)/(g Co)).

amount of pyrocarbon formed on vermiculite was 0.6%.

We studied the effect of Co concentration on the synthesis of CFC under the conditions described above. In Table 1, it can be seen that the amount of synthesized CFC increased with the Co content of ceramic foam, whereas the yield of carbon decreased (by a factor of 2). It is likely that coarser Co-catalyst particles exhibited a comparatively lower specific catalytic activity or they were blocked and deactivated in the course of pyrolysis.

All of the tested characteristics of vermiculite were essentially different from those observed in ceramic foam; this was likely due to the chemical composition of the former natural mineral, which contained Al, Mg, Fe, and Ca. All of the characteristics, including the specific surface area, the amount of synthesized CFC, and the yield of carbon, dramatically increased with the cobalt content (Fig. 6). The electron micrographs indicate that carbon nanofibers on the surface of vermiculite were nonuniformly synthesized (Fig. 7) mainly on the end faces of lamellar vermiculite structures in accordance with the surface distribution of a Co catalyst (Fig. 7b).

We found that the characteristics of CFC-containing adsorbents depend on the composition of the supported metal catalyst. It can be seen in Table 2 that the synthesis of CFC on ceramic foam at a low temperature (550°C) mainly occurred on a Ni catalyst. The synthesis of CFC on vermiculite at 550°C also occurred with the participation of a supported Ni catalyst. As can be seen in electron micrographs, carbon nanofibers were nonuniformly distributed (Fig. 8), whereas carbon nanofibers were not synthesized on a Co catalyst under these conditions on the surface of vermiculite.

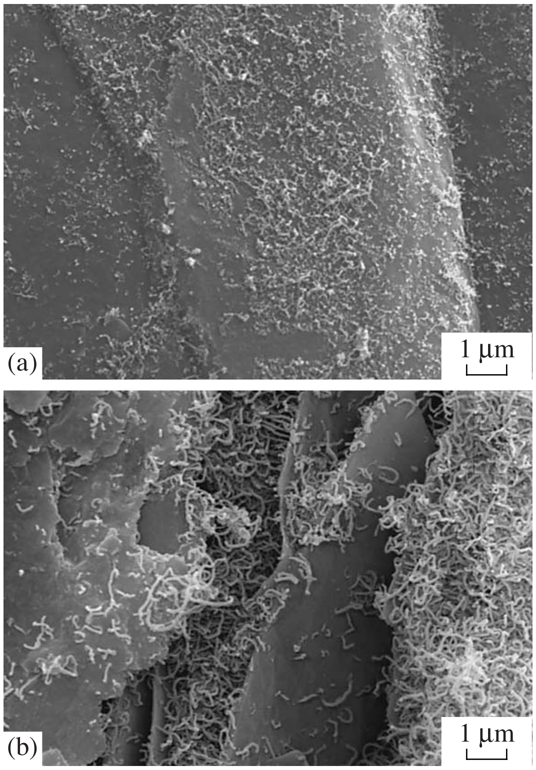

Fig. 7. Electron micrographs of the surface of vermiculite: (a) with a CFC layer (8.1%) synthesized on 2.54% Co and (b) with a CFC layer (38.2%) synthesized on 6.23% Co by the pyrolysis of a hydrogen–propane–butane mixture (procedure 2) at 600°C.

Adsorption of Glucose Isomerase

The adsorbents obtained in this study were used for the first time for the immobilization of the recombinant protein His_6-glucose isomerase in order to prepare a biocatalyst for the production of glucose–fructose syrups, which are used in the food industry as natural sweeteners. It is well known that Co^{2+} and Mg^{2+} ions are enzyme activators; they also considerably increase the stability of the enzyme, whereas Ni^{2+}, Ca^{2+}, and Pb^{2+} ions partially and Cu^{2+} ions fully inhibit the enzyme [13, 14]. We studied the washout of Co and Ni from CFC-containing vermiculite and found that the concentrations of these ions in a buffer solution with pH 7.8 did not depend on the supported catalyst content and equaled 1–6 μmol/l for Co^{2+} and Ni^{2+} ions. Magnesium (30–60 μmol/l), calcium (40–50 μmol/l), iron (1–2 μmol/l), and aluminum (2–4 μmol/l) were also detected in a contact buffer solution with pH 7.8. Evidently, the concentrations of these metals in the near-surface layer were higher by an order of magnitude. A study of the properties of the prepared biocatalysts demonstrated that His_6-glucose isomerase retained no more than 10% activity of the enzyme in solution upon adsorption on the test carbon-containing supports. This suggests a considerable deformation of the protein molecule or the shielding of its active site.

We found that the His$_6$-glucose isomerase adsorbed on CFC synthesized on a Co catalyst supported on vermiculite was characterized by a comparatively high activity and stability even in the absence of Co ions from the reaction medium. This was likely due to the high Co content of the support (Table 3). On the other hand, His$_6$-glucose isomerase adsorbed on a CFC layer synthesized on a Co catalyst supported on ceramic foam was characterized by a comparatively low activity, and it was fully deactivated after storage in a buffer solution at 10–15°C for a week (Table 3). Comparative studies demonstrated that a biocatalyst prepared by the immobilization of His$_6$-glucose isomerase in a CFC layer synthesized on a Ni catalyst supported on glass foam also exhibited low enzymatic activity and stability; this was likely due to the washout of nickel ions (Table 3). A biocatalyst prepared by the adsorption of His$_6$-glucose isomerase on the mesoporous carbon support Sibunit, which did not contain metal ions (Table 3), exhibited maximum activity and stability, and the given ions were added to the reaction medium in optimum concentrations of 1 mmol/l for Co^{2+} and 5 mmol/l for Mg^{2+}.

Thus, in this work, as a result of the synthesis of a CFC layer on a supported Co catalyst, adsorbents for the immobilization of Co-dependent enzymes, including glucose isomerase, were prepared.

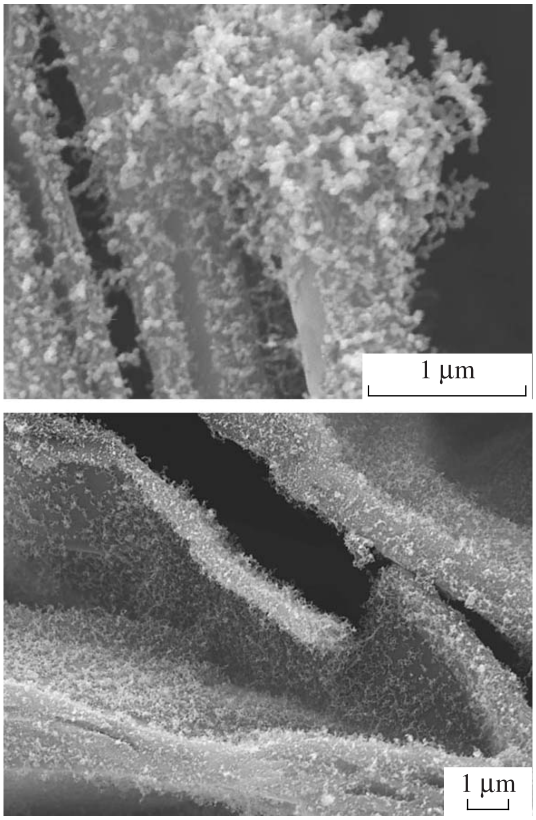

Fig. 8. Electron micrographs of the surface of vermiculite with a CFC layer synthesized on a bimetallic catalyst (0.59% Co and 0.64% Ni) by the pyrolysis of a hydrogen–propane–butane mixture at 550°C.

Table 2. Effect of the composition of a metal catalyst supported on ceramic foam upon the synthesis of CFC in the pyrolysis of a hydrogen–propane–butane mixture at 550°C

Catalyst composition		Carbon content, %	Y, (g C)/(g M)	S_{BET}, m^2/g
cobalt content, %	nickel content, %			
0.14	0	0.52	3.7	4
0.12	0.21	14.00	42.3	41
0	0.18	7.17	39.8	23

Table 3. Recombinant protein adsorption on carbon-containing supports and the biocatalytic properties of immobilized His$_6$-glucose isomerase

Support			Adsorption, mg/g	Activity*, μmol min^{-1} (g biocatalyst)$^{-1}$	$t_{1/2}$, day
parent matrix	catalyst content, %	carbon content, %			
Vermiculite	6.23 Co	38.20	10.2	0.50	22
Ceramic foam	0.37 Co	7.57	6.7	0.19	7
Glass foam	0.29 Ni	13.60	11.7	0.20	10
Sibunit	–	99.80	22.2	0.50	50

Notes: Adsorption conditions: 18–22°C; 0.02 M phosphate buffer solution, pH 7.8; initial protein concentration in solution, ~2 mg/ml; adsorption time, 20 h.

Conditions of the determination of activity: 50°C; 0.02 M phosphate buffer solution, pH 7.8; 0.5 M fructose; 5 mM Mg^{2+} for ceramic foam and vermiculite; 1 mM Co^{2+}, 5 mM Mg^{2+} for glass foam and Sibunit.

Biocatalyst storage conditions: 10–15°C; 0.02 M phosphate buffer solution, pH 7.8.

* Initial activity of freshly prepared biocatalyst.

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