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

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Abstract—The synthesis of catalytic filamentous carbon (CFC) on a Ni catalyst supported by homogeneous precipitation onto the surface of aluminosilicate ceramic supports (honeycomb monoliths, ceramic foam, glass foam, and haydite) was studied. The effects of CFC 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, and the morphology of a surface CFC layer were examined. As found by scanning electron microscopy, the uniformity of distribution and the size of carbon nanofibers synthesized depended on the conditions of their synthesis. The resulting CFC-containing supports were tested as adsorbents for the immobilization of enzymatically active substances (individual enzymes, cell membranes, and microorganisms) in order to prepare highly stable heterogeneous catalysts for biotechnology and biocatalysis.

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INTRODUCTION

Supports based on catalytic filamentous carbon (CFC) are of considerable current scientific and practical interest. This is likely due to the fact that these supports are similar to exotic fullerenes and carbon nanofibers in chemical properties [1–3]. Previously, the formation of CFC on catalysts for hydrocarbon conversion, for example, in the Fischer–Tropsch process, was considered as a very undesirable side process, which results in the degradation of a catalyst and reactor walls [1]. Mesoporous supports based on CFC with a specific surface area of ≥200 m^2/g are currently under intensive study as adsorbents, materials for gas storage (for hydrogen and methane), and supports for immobilized catalysts (Table 1) [1, 4–13].

In previous publications [14–17] devoted to the synthesis of CFC on Ni catalysts, it was found that the size of supported nickel metal particles (Ni^0) affected the yield of carbon (which is equal to the weight (g) of synthesized filamentous carbon per gram of metal catalyst), the initial rate of CFC formation, the rate of catalyst deactivation, and the size (length and diameter) of the synthesized carbon nanofiber. There are only a few scientific publications devoted to studies of the dependence of the yield of carbon on the conditions of the catalytic pyrolysis of various hydrocarbons [1–3].

Recently, attention was focused on the synthesis of a CFC layer on the surfaces of inorganic supports with intricate geometric shapes (as honeycomb monoliths, stainless steel meshes, glass fiber, glass cloth, and special metal filters) [18–22]; this considerably extends the range of materials for various practical applications. For example, Keller et al. [18] described CFC-containing glass cloth, which was prepared by the pyrolysis of an ethane–hydrogen mixture on a supported Ni catalyst at 700°C. This glass cloth was used as a support for a photocatalyst based on TiO_2.

The aim of this work was to study the effect of the conditions of CFC synthesis on a supported Ni catalyst upon the following characteristics of ceramic supports (ceramic foam, glass foam, and haydite): (1) the specific surface area, (2) the yield of carbon ((g carbon)/(g nickel)), and (3) the morphology of a surface CFC layer studied by scanning electron microscopy. The goal was also to examine the resulting supports as adsorbents for the preparation of heterogeneous biocatalysts for the hydrolysis of dextrins and the inversion of sucrose by the immobilization of enzymatically active substances (glucoamylase, yeast membranes, and nongrowing baker's yeast cells exhibiting invertase activity).

EXPERIMENTAL

Ceramic aluminosilicate supports with various geometric shapes (honeycomb monoliths, foam materials, and granules) were used as starting matrices for the supporting of a nickel catalyst and the synthesis of CFC. The honeycomb monoliths (M) were prepared from a mixture of natural minerals (clay, talc, and amorphous alumina) taken in a stoichiometric ratio corresponding to the cordierite phase $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ using extrusion molding. The resulting monoliths were calcined at 900 and 1200°C. In accordance

Table 1. Examples of the practical applications of CFC

Adsorbate	Area of application	Characteristics	References
Hydrocarbons (benzene, chlorobenzene, pentane, hexane, and heptane)	Gas chromatography	Benzene retention volume of 1.8×10^{10} cm^3/m^2	[4]
Nickel	Catalyst for methane decomposition	Nickel content of 40%; Yield of secondary carbon, 224 g/(g Ni)	[5, 6]
Palladium	Catalyst for nitrobenzene and 1,3-butadiene hydrogenation	Amount of supported Pd, 0.25–5.8%	[1, 7]
Heteropoly acid $H_3PW_{12}O_{40}$	Catalyst for butanol esterification with acetic acid	Adsorption of the heteropoly acid, 50–100 mg/g	[8, 9]
Hydrogen and methane (adsorption)	Fuel cells	25–35 (mg H_2)/(g carbon)	[10]
Hydrogenase from *Thiocapsa roseopersicina*	Electrocatalyst in biofuel cells	Tunneling mechanism of electron transfer between the electrode and the enzyme active site	[11]
Biologically active compounds	Biotechnology and biocatalysis	Albumin adsorption, 3.7 mg/(m^2 accessible surface area); Rhodococcus adsorption, 1.6 g/(m^2 accessible surface area)	[12, 13]

with the calcination temperature, the honeycomb monoliths were designated as M/900 and M/1200, respectively. The ceramic foam (F) (Powder Metallurgy Research Institute, Minsk, Belarus) had a cellular macrostructure as a three-dimensional network with an average cell size of ~2 mm and ~70% open porosity. The calcination temperature of this support was 1400°C.

The following granulated supports were also used in this study: haydite (H) as granules 2–3 mm in diameter (OOO SKhP Elita-Flora, Tomsk, Russia) and glass foam (G) as granules 3–4 mm in diameter (ZAO Penosital, Perm, Russia). Glass foam is a new fully inorganic heat-insulating material with a density of 100–600 kg/m^3 (htpp://extrotur.narod.ru/iglu/plan.htm). Its chemical resistance corresponds to the resistance of glass; glass foam has a rigid structure; it is noncombustible, steam-tight, and waterproof. Moreover, the manufacture of this material is environmentally oriented because any cullet including bottle glass and waste glass can be used for this purpose.

Nickel hydroxide was supported onto the surfaces of starting matrices by homogeneous precipitation. For this purpose, a solution of nickel nitrate (0.01 mol/l) and urea (0.1 mol/l) was prepared in a glass vessel, and a starting matrix was placed in this vessel in an amount corresponding to a ratio of 1 part of the matrix by weight to 6–8 parts of the solution by volume. This vessel was heated in a water bath to 85 ± 1°C and kept for 3 h at the specified temperature. The matrix with supported nickel (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 nickel (wt %) precipitated on the surface was determined by atomic absorption spectrometry on an ASSIN instrument with a flame-ionization detector.

The synthesis of CFC was performed by the pyrolysis of a propane–butane-containing gas mixture at 500°C in a fixed-bed reactor. The fixed catalyst bed was formed using a packing material of stainless steel mesh, which was placed in a horizontally arranged quartz tube reactor 200 mm in length and 30 mm in diameter. 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. In the reactor, the catalyst removed from the desiccator 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°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; procedure 3, the two-stage synthesis of a CFC layer involved a stage of the prereduction of nickel hydroxide with hydrogen at 500°C for 0.5 h followed by a stage of 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) the increase in the catalyst weight, which was measured before and after pyrolysis, or (2) the 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 was taken into consideration and the weight loss of the starting support under conditions of pyrolysis (500°C; 1 h) and annealing (800°C; 3 h) was also determined. The experimental error was 2%.

Table 2. Changes in the characteristics of supports depending on procedures used for the synthesis of a CFC layer on the support surfaces

Support (S_{BET}, m^2/g)	Procedure*	Nickel content, %	Carbon content,	Yield of carbon, (g C)/(g Ni)	S_{sp}, m^2/g
M/900 (24)	1	0.49	4.25	8.7	47
	2		7.22	14.7	52
	3		0.28	0.6	26
M/1200 (0.1)	1	0.07	1.59	22.7	5
	2		2.18	31.1	8
	3		0.52	7.4	3
F (0.2)	1	0.18	5.54	30.8	23
	2		4.35	33.5	21
	3		6.44	35.7	23
G (0.4)	1	0.29	13.63	47.0	44
	2	0.17	4.84	28.5	30
	3		0.78	4.6	12
H (1)	1	0.09	2.54	28.2	10
	2		1.36	45.3	9
	3		1.28	14.2	6

* 1, pyrolysis of a propane–butane mixture (without hydrogen); 2, pyrolysis of a hydrogen–propane–butane mixture; 3, two-stage procedure with the prereduction of nickel hydroxide.

The productivity of the synthesis of CFC was characterized by the yield of carbon (Y), which is equal to the weight (g) of synthesized filamentous carbon per gram of nickel metal.

The specific surface areas of supports were measured using the thermal desorption of argon on a SORBI-M instrument (ZAO Meta, Russia). The pore-size distribution was determined by mercury porosimetry on an AUTO-PORE 9200 Instrument (Micromeritics, USA). The crushing strength of supports under static conditions was measured on an MP-2S strength meter (Experimental Plant of the Siberian Division of the Russian Academy of Sciences, Novosibirsk, Russia).

The electron-microscopic studies of the morphology of a carbon layer on the surfaces of supports were performed with the use of JSM 6460 LV (JEOL, Japan) and LEO 1430 (LEO, Germany) instruments.

As a result of the synthesis of CFC on the surfaces of aluminosilicate supports, adsorbents for the immobilization of enzymatically active substances having biocatalytic activity in the hydrolysis of carbohydrate substrates, such as dextrins (glucoamylase enzyme) and sucrose (yeast membranes and nongrowing baker's yeast cells) were prepared. The adsorption of enzymatically active substances was performed under batch conditions as described elsewhere [23–26]. The enzymatic activity of heterogeneous biocatalysts (immobilized enzymatically active substances), which is equal to the rate of hydrolysis (μmol/min) of substrates at saturation concentrations (zero-order reaction in the Michaelis–Menten kinetics), was measured in a circulation system with a differential gradientless reactor under conditions described previously [23–26] in the absence of external-diffusion limitations for enzymatic reactions. The stability was determined on keeping in a buffer solution at 18–22°C measuring the residual activity at regular intervals and comparing it with the initial activity of the freshly prepared biocatalyst. The half-inactivation time ($t_{1/2}$) of the biocatalyst, that is, the

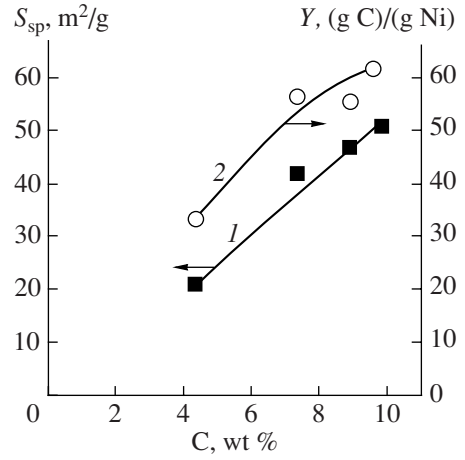

Fig. 1. Dependence of (*1*) the specific surface area (S_{sp}) of ceramic foam and (*2*) the yield of carbon (Y) on the amount of carbon synthesized on a Ni catalyst (0.13–0.16%) under conditions of hydrogen–propane–butane pyrolysis (procedure 2) at 500°C.

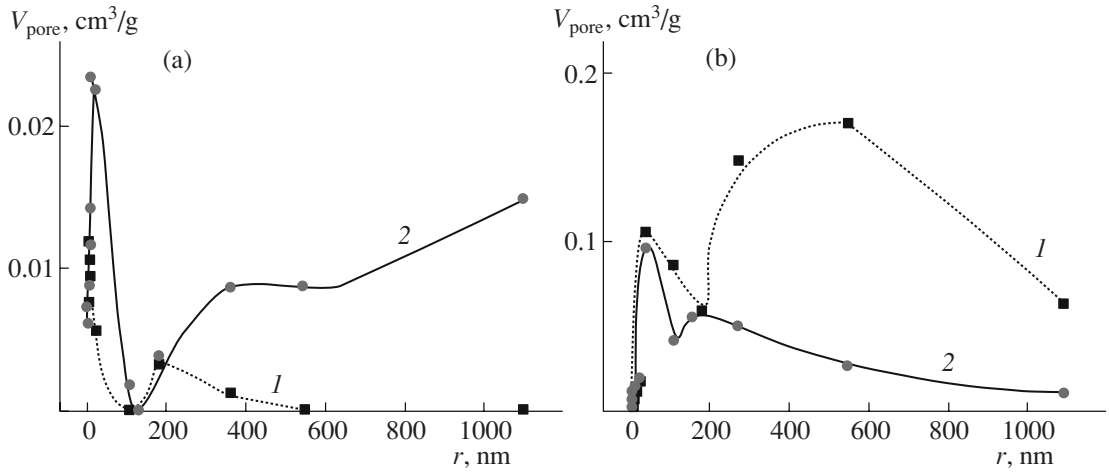

Fig. 2. Pore-size distribution diagrams of (a) glass foam (*1*) without carbon and (*2*) with 2.4% CFC; (b) haydite (*1*) without carbon and (*2*) with 3.2% CFC.

time during which the initial activity decreased by a factor of 2, was taken as a measure of stability.

RESULTS AND DISCUSSION

We studied the texture characteristics of adsorbents and found that the synthesis of a CFC layer was accompanied by a considerable (by a factor of tens) increase in the specific surface areas of parent supports regardless of the conditions of pyrolysis of a propane–butane mixture (Table 2). The specific surface area of the carbon layer varied from 250 to 550 m^2/(g C), as estimated with consideration for the increase of the specific surface area of the parent support and the weight of synthesized carbon. As the amount of synthesized carbon increased by 1 wt %, the specific surface areas of supports increased, on average, by 3–4 m^2 (see Fig. 1, curve *1* for ceramic foam). A comparative analysis of pore-size distribution diagrams for glass foam demonstrated that the pore structure of this support dramatically changed and became bidisperse upon the synthesis of a CFC layer (Fig. 2a). In this case, both mesopores of ~20 nm and macropores of >200 nm appeared (it is likely that the former appeared because of the synthesis of carbon nanofibers and the interlacing of nanofibers in a CFC layer and the latter resulted from the synthesis of CFC in supermacropores of >2 μm). An analogous analysis for haydite showed that the average pore radius of this support decreased from 118 to 32 nm upon the synthesis of CFC; that is, mesopores were predominant in the pore structure of the CFC-containing haydite. In this case, the fraction of macropores (>100 nm) considerably decreased (Fig. 2b) because of the synthesis of CFC in these pores. In was found that the cellular structure of ceramic foam, as well as the mechanical strength of inorganic supports, remained unchanged upon the synthesis of CFC (Table 3).

Table 3. Mechanical strengths of inorganic supports

Support	CFC content, wt %	Crushing strength, kgf/cm^2
F	–	20.4
	2.4	18.8
H	–	33.7
	3.6	36.2

We studied the parameters affecting the yield of carbon and found that this yield depended on not only the conditions of pyrolysis of a propane–butane mixture but also on the concentration of supported nickel. Thus, on ceramic foams with equal concentrations of supported nickel (~0.15%), the yield of carbon proportionally increased with the amount of synthesized carbon (Fig. 1, curve *2*). As the concentration of nickel was increased from 0.13 to 0.37%, the amount of synthesized CFC increased (from 7.4 to 12.7%, respectively). However, in this case, the yield of carbon decreased by a factor of ~1.7; this was likely due to the greater nickel particle size at a concentration of 0.37%. It is known from published data that these catalysts exhibit a lower specific catalytic activity as a consequence of their encapsulation by graphene layers and the blocking of active sites accompanied by catalyst deactivation in the course of propane–butane pyrolysis. A study of the morphology of the CFC layer by scanning electron microscopy demonstrated that the carbon nanofibers synthesized on ceramic foam with a low concentration (0.13%) of supported nickel (Fig. 3a) were shorter than those on ceramic foam with a higher nickel concentration (0.37%) (Fig. 3b) and the size of carbon nanofibers depended on the particle size of the nickel catalyst, analogously to published data [15–17].

The conditions of propane–butane pyrolysis had almost no effect on the characteristics of adsorbents prepared based on ceramic foam, whereas they exerted a considerable effect on the characteristics of adsor-

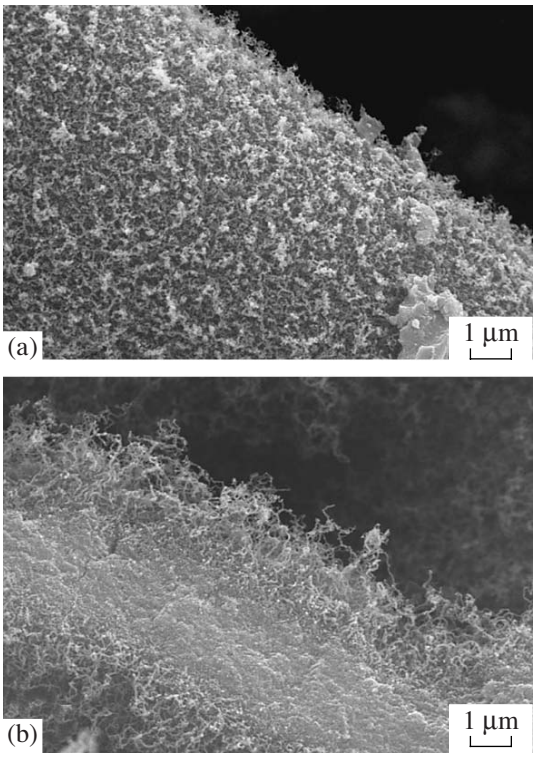

Fig. 3. Electron micrographs of the surface of ceramic foam with a CFC layer synthesized on supports containing (a) 0.13 and (b) 0.37 wt % nickel under conditions of hydrogen–propane–butane pyrolysis (procedure 2).

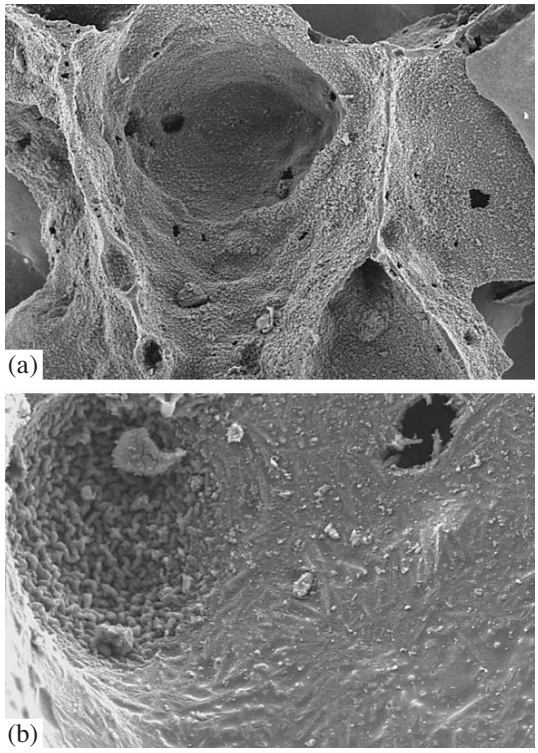

Fig. 4. Electron micrographs of the surface of glass foam with a CFC layer synthesized using (a) procedure 2 or (b) procedure 3.

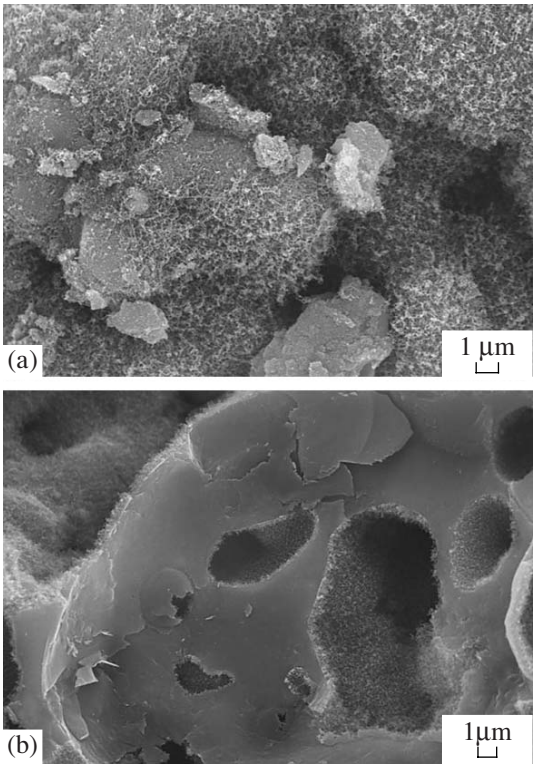

Fig. 5. Electron micrographs of the surface of haydite with a CFC layer synthesized using (a) procedure 1 or (b) procedure 3.

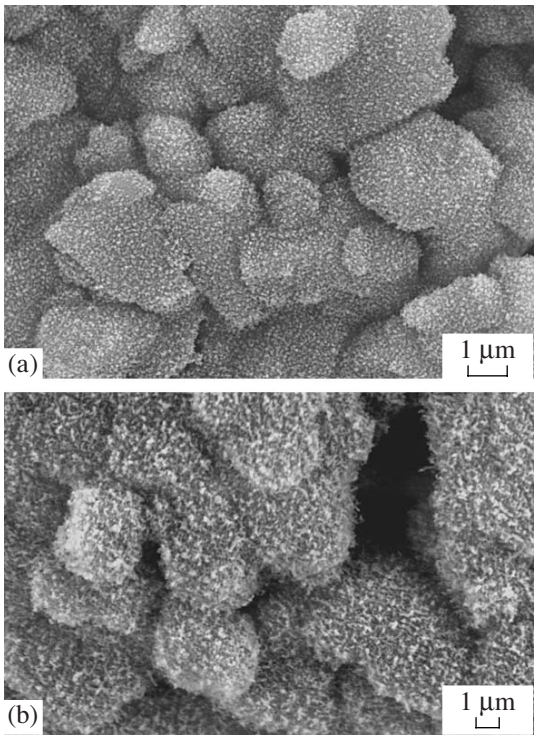

Fig. 6. Electron micrographs of the surface of ceramic foam with a CFC layer synthesized using (a) procedure 1 or (b) procedure 2.

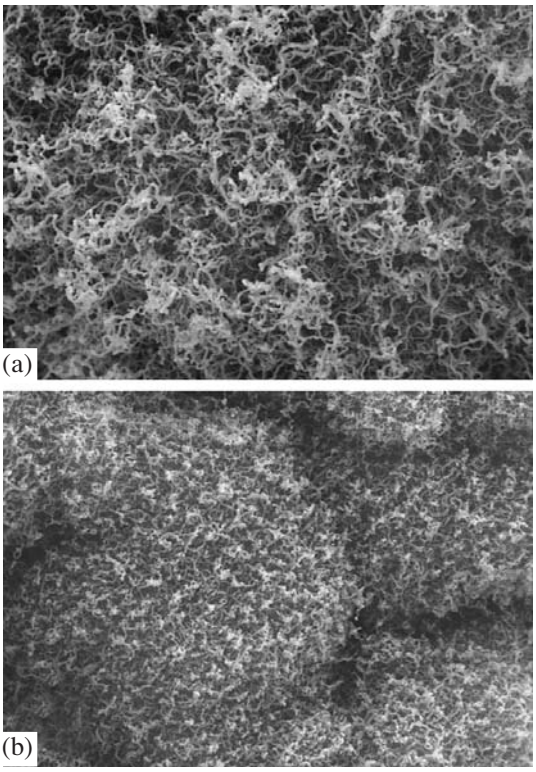

Fig. 7. Electron micrographs of the surface of glass foam with a CFC layer synthesized in accordance with (a) procedure 1 or (b) procedure 2.

bents prepared based on honeycomb monoliths, glass foam, and haydite (Table 2). Pronounced differences in the characteristics of adsorbents were observed upon the two-stage synthesis of CFC with the prereduction of supported nickel hydroxide with hydrogen (procedure 3). We found that, under conditions of the two-stage synthesis of CFC on M, G, and H supports, the specific surface area, the amount of synthesized carbon, and the yield of carbon considerably (several times) decreased (Table 2). Moreover, electron-microscopic studies demonstrated that, unlike procedure 2 with glass foam (Fig. 4a) and haydite (Fig. 5a), nonunifom coverage with carbon nanofibers (Figs. 4b, 5b) was observed in two-stage procedure 3 (Figs. 4b, 5b): the micrographs exhibited regions of the parent support with no carbon. It can also be seen that the CFC layer was nonuniformly synthesized on these supports. These results can be explained by the fact that Ni^0 particles formed at the stage of nickel hydroxide reduction with hydrogen weakly interacting with the support and migrating over the sintered smooth surfaces of G and H and aggregated to form coarser particles with lower catalytic activity, which was observed under the test conditions (Table 2). As for ceramic foam, it is likely that the adhesion of nickel metal particles to the surface of this support was comparatively strong and the aggregation of metal particles did not occur. As a consequence, the catalytic activity and the yield of carbon remained unchanged under varied synthesis conditions (Table 2); moreover, carbon nanofibers were nonuniformly distributed on this support (Fig. 6).

We found that, in the absence of hydrogen from the gas mixture used for pyrolysis, the intense synthesis of relatively long carbon nanofibers was also observed on haydite (Fig. 5a) and glass foam (Fig. 7a). In these cases, the amount of carbon on the support and the yield of carbon were comparatively high (Table 2). Evidently, the reduction of nickel hydroxide to Ni^0 and the synthesis of CFC occurred simultaneously in the pyrolysis of a propane–butane mixture with the formation of

Table 4. Biocatalytic properties of the enzyme glucoamylase, yeast membranes, and nongrowing baker's yeast cells immobilized on CFC-containing ceramic supports

Support	S_{BET}, m^2/g	Glucoamylase		Yeast membranes		Nongrowing baker's yeast	
		activity* (adsorption, mg/g)	stability $t_{1/2}$, month	invertase activity* (adsorption, mg/g)	stability $t_{1/2}$, month	invertase activity* (adsorption, mg/g)	stability $t_{1/2}$, month
M/900	47.0	45 (0.1)	20	16 (<0.1)	3.5	1.5 (<0.1)	6
M/1200	0.8	50 (<0.1)	18	7 (<0.1)	0.5	1.3 (<0.1)	3
F	16.0	29 (1.1)	14	18 (1)	4.0	19 (1.4)	5
G	12.0	60 (5.4)	8	–	–	–	–
H	22.0	12 (6.9)	1	29 (1)	1	–	–

Notes: M/900 and M/1200 are honeycomb monoliths calcined at 900 and 1200°C, respectively; F is ceramic foam; G is glass foam; and H is haydite.
Conditions for the determination of glucoamylase activity: 50°C; 0.05 M acetate buffer solution, pH 4.6; circulation rate through a biocatalyst bed, 30 ml/min; substrate, 5% solution of corn dextrins; specific activity of glucoamylase in solution, 300 $\mu mol\ min^{-1} \times (mg\ protein)^{-1}$.
Conditions for the determination of invertase activity: 50°C; 0.05 M acetate buffer solution, pH 4.6; circulation rate through a biocatalyst bed, 30 ml/min; substrate, 20% sugar syrup; specific activity of yeast membranes in a suspension, 17 $\mu mol\ min^{-1}$ (mg dry membranes)$^{-1}$; specific activity of baker's yeast in a suspension, 12 $\mu mol\ min^{-1}$ (mg dry cells)$^{-1}$.
Conditions for the determination of stability: 18–22°C; 0.05 M acetate buffer solution, pH 4.6.
* $\mu mol\ min^{-1}$ (g biocatalyst)$^{-1}$.

carbon and hydrogen (procedure 1). Table 2 and electron micrographs indicate that the synthesis of CFC on glass foam in accordance with procedure 1 occurred most intensely; in this case, the weight of synthesized carbon increased because of the elongation of carbon nanofibers (Fig. 7). Although, as noted above, the conditions of the CFC synthesis on ceramic foam had almost no effect on the characteristics of the support (Table 2), the electron micrographs exhibited considerable differences in the morphology of synthesized CFC layers. Thus, unlike G and H supports, a denser layer of comparatively short carbon nanofibers (Fig. 6a) was synthesized on ceramic foam upon the pyrolysis of the propane–butane mixture (procedure 1) unlike the pyrolysis of the hydrogen–propane–butane mixture (procedure 2) (Fig. 6b). It is likely that, with the simultaneously occurring processes of reduction and pyrolysis (procedure 1), the synthesis of CFC on ceramic foam occurred at several active sites rather than at a single site of a supported nickel catalyst particle with the formation of comparatively short carbon nanofibers.

We found that the yield of carbon and the amount of synthesized carbon were practically the same as the pyrolysis temperature was increased from 500 to 550°C. In the subsequent experiments, we prepared adsorbents using procedure 2, which consisted in the pyrolysis of the hydrogen–propane–butane mixture on a nickel catalyst at 500°C. We also found that the pyrolysis of the propane–butane mixture did not occur on the test aluminosilicate supports in the absence of a supported nickel catalyst.

The CFC-containing ceramic supports prepared in this work were considered from the standpoint of their practical applications as adsorbents for the immobilization (binding) of enzymatically active substances (enzymes, cell membranes, and whole microorganisms) and the preparation of heterogeneous biocatalysts for various hydrolysis processes. An analysis of texture characteristics and physicochemical properties allowed us to assume that these adsorbents exhibit a high potential for use in biotechnology and biocatalysis. First, the adsorbents prepared exhibited an optimum pore structure with a bimodal pore-size distribution. Thus, the stability of a biocatalyst considerably increased upon enzyme adsorption in the mesopores of the CFC layer because of the multipoint interaction of a protein molecule with the adsorbent surface. Transport macropores or channels or the holes of the parent support facilitated the mass transfer of the substrate to the immobilized enzyme to reduce the diffusion limitations of the enzymatic reaction and to increase the apparent rate of substrate conversion. Second, according to published data and our experimental results, the adsorption of enzymes and microorganisms on a carbon surface allows one to retain their biocatalytic activity at a high level because of the favorable hydrophilic–lipophilic balance. Third, because the macrostructure and mechanical strength of honeycomb monoliths and ceramic foam were fully retained upon the synthesis of the CFC, this allowed us to construct new types of high-productivity vortex reactors on this basis; these reactors were specially designed for heterogeneous biocatalytic processes controlled by the diffusion of a substrate to an immobilized enzyme.

The CFC-containing adsorbents prepared in this study were used in the processes of starch saccharification (dextrin hydrolysis) [23, 24] and sucrose inversion [25, 26]. In 2004 and 2005, de Lathouder et al. [27, 28] also demonstrated that honeycomb monoliths on the surface of which CFC layers were synthesized are effective supports for the adsorption immobilization of enzymes (lipase and lactase); stable heterogeneous biocatalysts with high enzymatic activity can be prepared based on these supports.

As can be seen in Table 4, the adsorption capacity of CFC-containing honeycomb monoliths for the enzyme glucoamylase, yeast membranes, and baker's yeast cells decreased as the calcination temperature was increased. Thus, the adsorption on M/1200 cordierite monoliths was extremely low; this was likely due to the low specific surface area. In spite of this fact, the activity of biocatalysts prepared based on these supports for the processes of dextrin hydrolysis and sucrose inversion was relatively high. An analysis of pore-size distribution diagrams demonstrated that macropores, through which a substrate was transferred to an immobilized enzyme, were predominant in the carbon layer synthesized on M/1200 cordierite. The presence of macropores is particularly important for the mass transfer of high-molecular-weight dextrin; therefore, the activity of biocatalysts prepared by the adsorption of glucoamylase on the M/1200 cordierite monolith was higher than that on the M/900 aluminosilicate monolith, although the adsorption on the former was low (Table 4). It is obvious that the relatively high glucoamylase activity of a biocatalyst prepared on CFC-containing glass foam was due to the high adsorption of the enzyme on the given support (Table 4). Although the adsorption of glucoamylase and yeast membranes on CFC-containing haydite was high, the biocatalysts prepared exhibited insignificant activity and the lowest stability (Table 4); this was likely due to the nonuniform coverage of haydite with carbon nanofibers and the occurrence of parent support regions (with no carbon).

The biocatalysts prepared by the immobilization of larger biologicals, such as yeast membranes and nongrowing baker's yeast cells of size 1–2 μm, for the process of sucrose inversion exhibited maximum invertase activity and stability on CFC-containing ceramic foam (Table 4); this was likely due to the more efficient adsorption on the given support.

Analysis of the experimental results demonstrated that, for enzymes, the size of synthesized carbon nanofibers had almost no effect on the properties of the resulting biocatalysts. For yeast membranes and whole microorganisms, it was reasonable to synthesize a layer of short carbon nanofibers on the surface of aluminosil-

icate supports because this CFC layer exhibited an optimum roughness, which was responsible for the strong immobilization of microorganisms on the support surface [13] and, consequently, the high stability of the biocatalysts prepared.

Undoubtedly, the synthesis and use of CFC-containing adsorbents in biotechnology is a promising area of application for the development of commercially attractive heterogeneous biocatalytic processes.

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