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Preparation and Characterization of Nanoporous Carbon Supports on a Nickel/Sibunit Catalyst

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Abstract—A nanoporous composite carbon material was developed; this material was prepared by the synthesis of catalytic filamentous carbon (CFC) on a Ni catalyst supported onto the Sibunit carbon support. The texture characteristics (specific surface area and pore structure) of this material were studied. The effects of the conditions of supporting bivalent nickel compounds from aqueous or water–ethanol solutions in the presence of urea and the pretreatment of the parent Sibunit (oxidation and reduction) on the yield of synthesized carbon were considered. The distribution of Ni inside a Sibunit granule was studied using energy dispersive X-ray microanalysis. The surface morphology of the Ni/Sibunit catalyst, as well as the synthesized carbon layer, was studied by scanning electron microscopy. It was found that a maximum yield of carbon (50–60 g/(g Ni)) was obtained on the precipitation of nickel compounds from water–ethanol solutions with an ethanol concentration of 5 to 50 vol %. The preliminary surface oxidation or reduction of the parent Sibunit resulted in a considerable decrease in the yield of carbon (by a factor of 2 or more). The parent Sibunit phase occurred within the prepared nanoporous carbon material, whereas a shell formed by CFC occurred on the outside.

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INTRODUCTION

The properties of new synthetic porous carbon materials, including those prepared based on catalytic filamentous carbon (bulk CFC), have been intensively studied in the past decades [1–3]. The reactions and possible mechanisms of hydrocarbon conversion on iron subgroup metals (Ni, Co, Fe, and their alloys) with the formation of various carbon filament nanostructures have been described [4, 5]. The development of novel carbon–carbon composite materials is a comparatively new area; it considerably extends the range of supports and adsorbents, which can be applied in actual practice.

Vieira et al. [6] prepared and studied a new CFC on Ni/graphite composite carbon–carbon material; plates and rings of various sizes were made of this material in order to use them in catalytic reactors. The carbon yield of 224 g/(g Ni) was reached in the study of the secondary synthesis of CFC and the preparation of CFC on Ni/CFC supports [7].

Previously, we studied the synthesis of thin CFC layers on the surfaces of inorganic oxide supports (aluminum oxides and aluminosilicates) with various texture characteristics and various geometric shapes (honeycomb monoliths, foam materials, and granules) [8–10]. For this purpose, we performed the pyrolysis of a propane–butane mixture on Ni and Co catalysts prepared by the homogeneous precipitation of nitrates in the presence of urea [11]. Nickel was found a more active pyrolysis catalyst than cobalt: the synthesis of carbon nanofibers occurred on it at a lower temperature, and the yield of synthesized carbon was ~40 g/(g Ni) [8–10]. As a result of the studies, CFC on Ni (or Co)/ceramic (or Al_2O_3) composite carbon–mineral supports were obtained, in which the adsorption properties of porous active carbon were combined with the mechanical strength of ceramic materials. These supports can be used, for example, in biocatalysis and biotechnology [8–10].

Carbon supports with regulated pore structures specially designed for supporting active catalyst components are widely used. Among them, the best studied are bulk CFC and Sibunit [1, 3]. For example, active Pd/CFC catalysts for hydrogenation processes were prepared by supporting Pd onto bulk CFC [12–14]. Noble metals (Pt, Pd, Au, and Ru) supported on Sibunit are active catalysts for various hydrogenation and hydrodechlorination processes [15–17].

Likholobov et al. [3] described a CFC on Ni/Sibunit composite carbon–carbon material with a globular fibrous texture prepared by the pyrolysis of methane at 550–650°C on Ni supported on Sibunit by impregnation. As a result of the synthesis of carbon, the specific surface area increased to 194 m^2/g, as compared with 54 m^2/g in the parent Sibunit; the total pore volume increased from 0.1 to 0.28 cm^3/g, and the micropore volume increased from 0.0024 to 0.0132 cm^3/g. An interesting CFC in Ni/Sibunit carbon–carbon material was obtained in the case that nickel particles were localized in intraglobular cavities, which were formed upon the combustion of soot [3, 18].

The aim of this work was to prepare and characterize a new CFC on Ni/Sibunit composite carbon–carbon material, to study the effects of the surface pretreatment of the parent Sibunit and the conditions of supporting bivalent nickel on the texture characteristics of the resulting supports and on the yield of carbon, and to examine the distribution of Ni in a granule using energy dispersive X-ray (EDX) microanalysis and scanning electron microscopy along with the study of the morphology of the Ni/Sibunit catalyst and the surface layer of filamentous carbon.

EXPERIMENTAL

To prepare a supported Ni catalyst, we used the mesoporous carbon support Sibunit (IPPU, Siberian Branch, Russian Academy of Sciences, Omsk) as granules of 1–3 mm. The specific surface area (S_{sp}) of the parent support was 650 m^2/g, as measured using the BET method from the thermal desorption of argon on a SORBI-M instrument (ZAO META, Russia). The specific surface area without considering micropores (S_{nm}), the total pore volume (V_Σ), and the average pore diameter (d) were 260 m^2/g, 0.72 cm^3/g, and 11 nm, respectively, as found by mercury porosimetry on an AUTO-PORE 9200 instrument (Micromeritics, the United States).

Before supporting nickel compounds, the parent Sibunit was pretreated in accordance with the following procedures: (I) oxidation with boiling 20% HNO_3 for 1 h, (II) oxidation with atmospheric oxygen at 350°C for 1 h, and (III) reduction in a flow of hydrogen at 500°C for 4 h. The specific surface areas of the parent supports pretreated in accordance with procedures I, II, and III were 350, 540, and 500 m^2/g, respectively. The values of S_{nm} for the supports treated in accordance with procedures I and III were 5.6 and 38 m^2/g, respectively. Nickel was supported on the surface of Sibunit by the homogeneous precipitation of the hydroxo compounds of nickel from a 0.01 M solution of $NiNO_3$ in the presence of urea (0.1 mol/l) at 85°C [11]. A tenfold excess of urea was added to aqueous or water–ethanol solutions of nickel nitrate; the ratio between the support weight (g) and the impregnating solution volume (ml) was 1 : 10. The rate of formation of hydroxyl ions in the hydrolysis of urea (1 mol/l; 85°C) was determined potentiometrically by measuring pH with a pH meter with a glass electrode. The concentration of ethanol in the impregnating solutions was varied from 5 to 75 vol %. From a survey of published data made by Komova et al. [11], it follows that an organic solvent (in the majority of cases, ethanol) is added to the impregnating solution in the case that the support exhibits pronounced hydrophobic properties. Ethanol provides a better wetting of the hydrophobic support surface with an aqueous solution of nickel nitrate; because of this, the dispersity of supported nickel is increased [19, 20]. Sibunit with supported nickel compounds was washed with distilled water and dried under an IR lamp for 2–3 h. Then, the resulting catalyst was cooled and kept in a desiccator.

The total concentration of supported nickel (wt %) was determined by atomic absorption spectrometry on an ASSIN instrument with a flame-ionization detector. The granules of Ni/Sibunit catalysts were thoroughly ground before analysis.

The distribution of Ni in a catalyst granule was determined on a cleavage using a JSM 6460 LV scanning electron microscope (Jeol, Japan) with an EDX spectrometer.

The synthesis of filamentous carbon was performed in a single-step process of the catalytic pyrolysis of propane–butane in the presence of hydrogen (without the preliminary reduction of supported nickel compounds to Ni^0). The pyrolysis was performed at 500°C for 1 h in a catalytic fixed-bed reactor. The synthesis conditions were described in detail elsewhere [8–11].

The amount of synthesized carbon (wt %) was determined gravimetrically from the equation $\Delta = \frac{m - m_0}{m} \times 100$, where m_0 and m are the weights of the Ni/Sibunit catalyst before and after pyrolysis, respectively. In the calculation of Δ, the hygroscopicity of the parent Sibunit and the catalysts, which was evaluated from the weight loss (Δ_1) after drying at 200°C for 4 h (to constant weight), as well as the weight loss (Δ_2) of dried supports and catalysts under conditions of pyrolysis (500°C; 1 h) in a flow of nitrogen, was taken into consideration. It was found that the hygroscopicity of the parent support and the catalysts was no higher than 0.7% and the weight loss of the parent Sibunit under conditions of pyrolysis was close to zero ($\Delta_2 = 0.06\%$). The value of Δ_2 for the Ni/Sibunit catalysts was 0.5–1.6%; in this case, the maximum weight loss was observed upon supporting nickel compounds from highly concentrated solutions of ethanol (70 ± 5 vol %). Thus, in the calculation of the amount of synthesized carbon, the value of Δ was taken to be $\Delta = \Delta_\Sigma - \Delta_1 - \Delta_2$, where Δ_Σ is the total increase in the catalyst weight (wt %) in the course of pyrolysis of a propane–butane mixture.

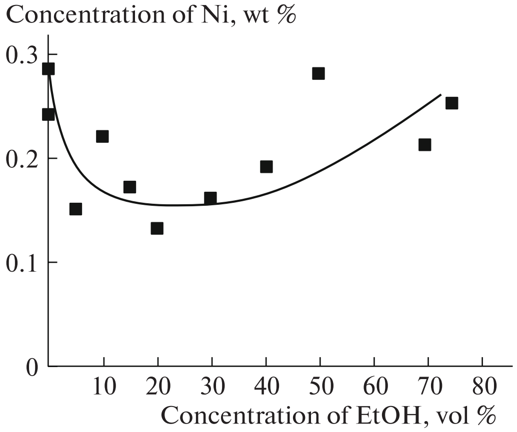

Fig. 1. Dependence of the concentration of nickel supported on Sibunit on the concentration of ethanol in the impregnating solution.

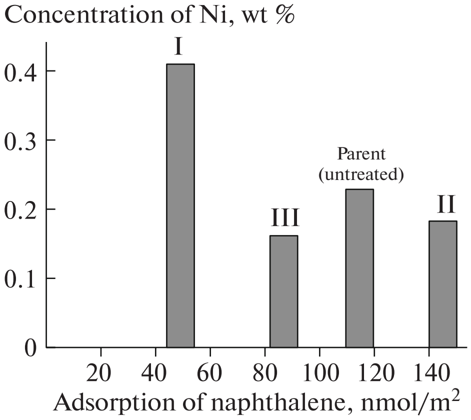

Fig. 2. Dependence of the concentration of supported nickel on the conditions of the surface pretreatment of parent Sibunit: (I) oxidation with boiling nitric acid, (II) oxidation with atmospheric oxygen at 350°C, and (III) reduction with hydrogen at 500°C.

The activity of the Ni/Sibunit catalysts in the synthesis of CFC was characterized by the yield of carbon, which was taken equal to the ratio of the weight of synthesized carbon to the weight of supported nickel.

The hydrophobicity of the surface was evaluated from the amount of naphthalene adsorbed from a saturated aqueous solution of this substance at 20–22°C. The concentration of naphthalene was determined from the absorbance at a wavelength of 220 nm using the molar absorption coefficient of 1.32×10^5 l cm^{-1} mol^{-1}. A weighed portion of the support with a total surface area of 1 m^2 (as measured using the BET method) was placed in a solution of naphthalene, deaerated with a water-jet pump to increase surface wettability, and kept in this state for 10 min. The amount of adsorbed naphthalene (in nmol/m^2) was calculated from the decrease in the concentration of naphthalene in solution with consideration for naphthalene adsorption on the glass surface of laboratory vessels. To perform the electron-microscopic studies of the Ni catalyst and to examine the morphology of a synthesized carbon layer, JSM 6460 LV (JEOL, Japan) and LEO 1430 (LEO, Germany) scanning microscopes were used. Scale labels in the micrographs have the dimensionality of μm.

RESULTS AND DISCUSSION

It was found that the concentration of Ni supported on the surface of the parent Sibunit by homogeneous precipitation depends on the concentration of ethanol in the impregnating solution. In the ethanol concentration range from 5 to 50 vol %, the Ni content reached a minimum and was, on the average, 0.17% (Fig. 1). To explain the found dependence, data on the hydrophilic–hydrophobic properties of support surfaces were used [21, 22]. According to these data, the concentration of acid–base sites on the surface of Sibunit is lower than that on the surface of mesoporous aluminum oxide by a factor of 5; that is, Sibunit is more hydrophobic than θ-Al_2O_3. From Fig. 1, it follows that the concentration of Ni on the surface of Sibunit was higher upon supporting the metal from purely aqueous solutions of $NiNO_3$, that is, under conditions of a higher hydrophobicity of this support. On the average, this concentration was 0.25%. Kovalenko et al. [10] studied the supporting of nickel compounds onto aluminum oxides and found that the Ni content of mesoporous aluminum oxide was, on the average, 0.17% as in the region of a minimum in Fig. 1. If nickel compounds were precipitated from highly concentrated water–ethanol solutions, the metal content was also ~0.25% (Fig. 1) as upon precipitation from an aqueous solution. This can suggest that, at an ethanol concentration in solution higher than 50 vol %, the hydrophobicity of the Sibunit surface increased, probably, because of the polylayer adsorption of alcohol molecules. In the first adsorption layer, the OH groups of ethanol and oriented toward the aqueous solution (the Sibunit surface becomes more hydrophilic as compared to that in the aqueous solution). In the second adsorption layer, the C_2H_5 groups of methanol are oriented toward the aqueous solution (the Sibunit surface becomes more hydrophobic).

To test the hypothesis that the hydrophilic–hydrophobic properties of a surface affect the efficiency of supporting nickel, we performed a pretreatment of the surface of the parent Sibunit using various procedures. With the use of support I (oxidation with boiling nitric acid), the nickel content of Sibunit reached a maximum (0.4–0.5%), whereas the adsorption of naphthalene reached a minimum (Fig. 2). Upon the treatment of the support by procedures II (oxidation with oxygen at 350°C) and III (reduction with hydrogen at 500°C),

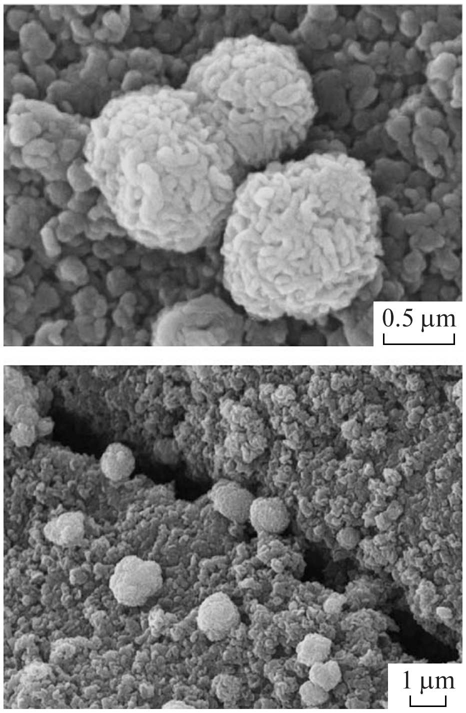

Fig. 3. Electron micrographs of the surface of Sibunit (untreated) with Ni compounds (0.28 wt %) supported from aqueous solutions (with no ethanol).

differences in the concentrations of supported Ni and in the adsorption of naphthalene became not so significant, as compared with the corresponding values for the untreated parent Sibunit (Fig. 2). The supports are arranged in the following order of increasing hydrophobicity: I < III < Sibunit (untreated) < II. As noted above, the most reliable fact with respect to this order of supports is an increase in the nickel content on the surface of deeply oxidized and the least hydrophobic Sibunit I.

The electron-microscopic studies demonstrated that, upon supporting nickel compounds from aqueous solutions (without ethanol) on the surface of the parent Sibunit, relatively coarse aggregates of size to 1 μm were formed; these aggregates consisted of flake particles (Fig. 3). If ethanol was present in a solution of nickel nitrate along with urea, the particle size decreased with ethanol concentration and comparatively small flake nanoparticles of Ni compounds were predominant on the surface (Fig. 4).

To determine why differences in the particle size and morphology of supported Ni^{2+} compounds occurred, we studied the dependence of the rate of urea hydrolysis at 85°C on the ethanol concentration in the impregnating solution. The initial rate of formation of hydroxyl ions dramatically decreased as the concentration of ethanol was increased; finally, this rate approached zero (Fig. 5). This fact allowed us to assume that Ni^{2+} from aqueous solutions in the pres-

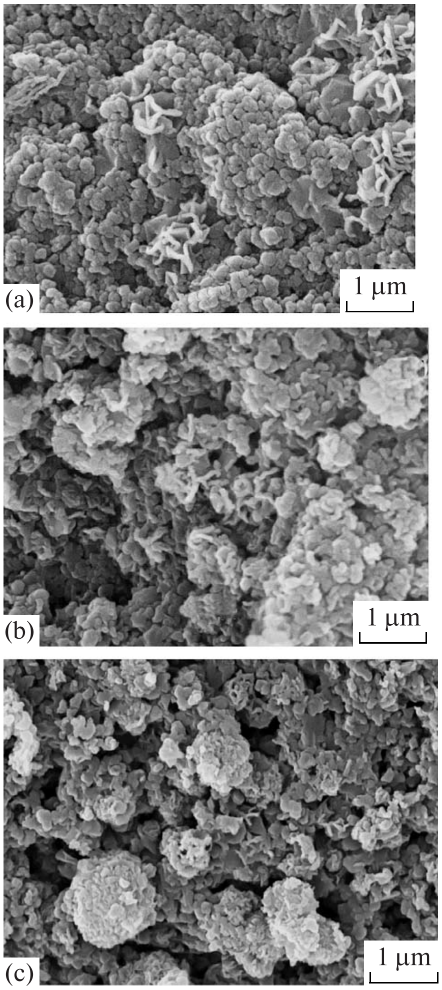

Fig. 4. Electron micrographs of the surface of Sibunit (untreated) with Ni compounds supported from water–ethanol solutions with the following ethanol concentrations, vol %: (a) 20 (0.13% Ni), (b) 50 (0.28% Ni), and (c) 75 (0.25% Ni).

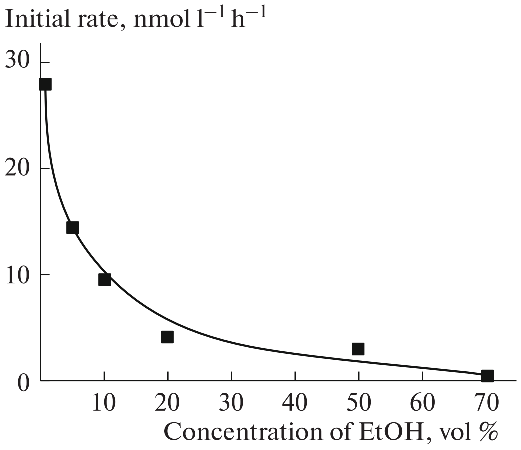

Fig. 5. Dependence of the initial rate of urea hydrolysis (solution concentration of 1 mol/l) at 85°C on the concentration of ethanol.

Texture characteristics of supports and Ni/Sibunit catalysts

Porous carbon material sample	Concentration of ethanol in the solution of $Ni(NO_3)_2$, vol %	Concentration, wt %		S_{sp}, m^2/g		S_{nm}, m^2/g	V_{Σ}, cm^3/g	d_{av}, nm
		Ni	CFC	with Ni	with CFC			
Parent Sibunit	–	–	–	–	–	260	0.72	11
Sibunit I	–	–	–	–	–	5.6	0.6	427
Sibunit III	–	–	–	–	–			
Ni on parent Sibunit	0	0.28	8.1	702	675	–	–	–
	20	0.13	7.9	708	618	261	0.62	10
	50	0.28	12.3	631	697	240	0.60	10
Ni on Sibunit I	0	0.27	3.7	347	484	–	–	–
Ni on Sibunit II	0	0.18	6.0	541	551	–	–	–
Ni on Sibunit III	0	0.16	6.3	483	668	–	–	–

ence of urea was deposited on the surface of Sibunit as the hydroxide $Ni(OH)_2$ (solubility product of 2×10^{-16}), whereas it was mainly deposited as $Ni(NO_3)_2$ from water–ethanol solutions.

The morphology of the Sibunit surface changed most significantly upon oxidation with boiling nitric acid (procedure I). Upon this treatment, the specific surface areas of the support measured by the BET

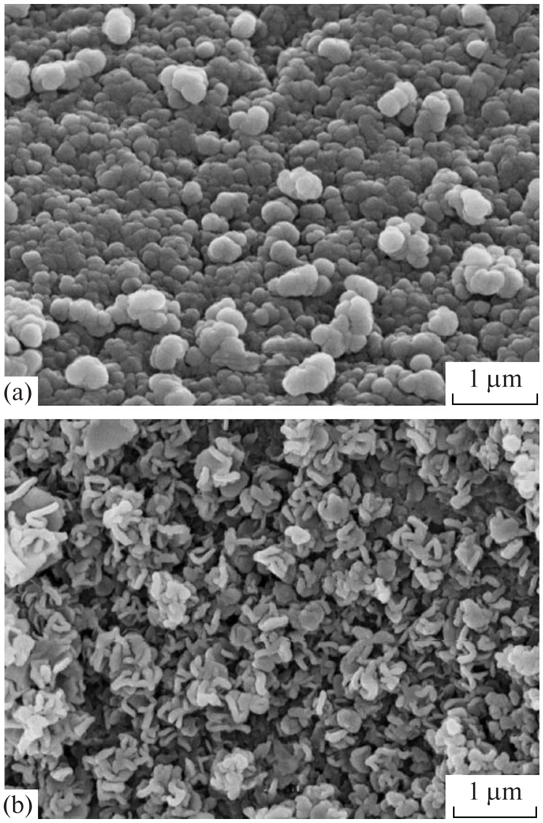

Fig. 6. Electron micrographs of the surface of Sibunit with supported Ni compounds: (a) Sibunit I (0.55% Ni) and (b) Sibunit III (0.16% Ni).

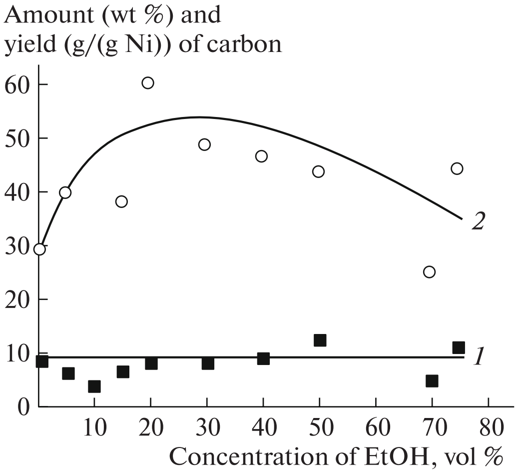

Fig. 7. Dependence of the (*1*) amount and (*2*) yield of synthesized carbon on the concentration of ethanol in solution.

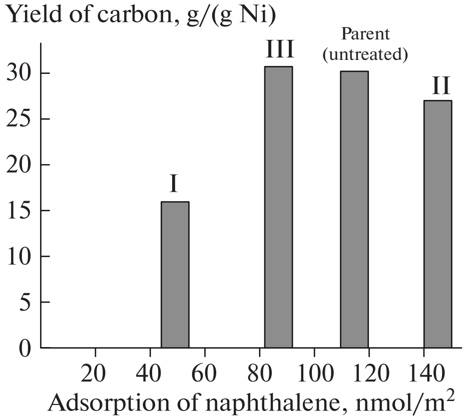

Fig. 8. Dependence of the yield of carbon on the pretreatment conditions and the hydrophobicity of the Sibunit surface: (I) oxidation with boiling nitric acid, (II) oxidation with atmospheric oxygen at 350°C, and (III) reduction with hydrogen at 500°C.

method and mercury porosimetry decreased from 650 to 350 and from 260 to 5.6 m^2/g, respectively. In this case, the average pore radius increased from 11 to 430 nm (see the table). As a result of the deep oxidation of carbon microglobules, the surface became smoother. Upon the precipitation of Ni compounds from aqueous solutions (with no EtOH) on Sibunit I, comparatively coarse particles of size ~0.5 μm were formed (Fig. 6), which are smaller than those upon precipitation on the parent Sibunit under the same conditions by a factor of ~2 (see Fig. 3). As can be seen in Fig. 6b, comparatively small nickel particles of size 0.1–0.2 μm were predominant on the reduced carbon surface of support III.

The study of the texture characteristics of the supports and catalysts showed that, upon supporting Ni onto the surface of untreated Sibunit, the specific surface area of the support remained almost unchanged (see the table). It is likely that this can be explained by a low (>0.5%) metal content. As noted above, the specific surface area of Sibunit decreased most significantly upon its oxidation with boiling nitric acid. The catalyst prepared with the use of support I was characterized by the lowest S_{sp} (table).

The total amounts of carbon formed on the parent Sibunit and supports II and III were almost independent of the conditions of supporting Ni, and they were 10 ± 2 wt % (Fig. 7, curve *1*; table). The maximum yield of carbon (to 60 g/(g Ni)) was observed at ethanol concentrations from 10 to 50 vol % in a solution of nickel nitrate (Fig. 7, curve *2*). A comparison between Figs. 1 and 7 indicates that the positions of maximums and minimums in the curves are coincident. An increase in the yield of carbon as the ethanol concentration was increased to 50 vol % can be due to the fact that smaller particles of supported nickel compounds were formed as a consequence of a decrease in the rate of urea hydrolysis in water–ethanol solutions (see Fig. 5). This was supported by the results of electron-microscopic studies (Fig. 4). A decrease in the yield of carbon upon supporting Ni from highly concentrated water–ethanol solutions (70–75 vol % EtOH) can be explained by, first, a change in the nature of nickel compounds (as noted above, this is $Ni(NO_3)_2$ in the case under consideration) and, second, the possible adsorption of ethanol molecules on the carbon surface, which results in catalyst deactivation under conditions of pyrolysis.

Kovalenko et al. [10] found that the Ni/Al_2O_3 catalyst prepared by impregnating a support with nickel nitrate (with no urea) exhibited a lower activity than an analogous catalyst prepared by the homogeneous precipitation of nickel compounds in the presence of urea. Because Ni^0 is the active component of a catalyst for the pyrolysis of a propane–butane mixture and the synthesis of CFC, the observed difference can be explained, for example, by different temperatures of formation of the precursors NiO_x ($x \approx 1$). Indeed, $Ni(NO_3)_2$ consecutively decomposes at 200–250°C to $Ni(NO_2)_2$ and then at 300–350°C to NiO_x, whereas the dehydration of $Ni(OH)_2$ with the formation of the hydroxo compounds of bivalent nickel and, finally, NiO_x occurs at a lower temperature (150–230°C).

As noted above, the second reason for the decrease in the yield of carbon upon supporting nickel compounds from highly concentrated water–ethanol solutions is the possible adsorption of the alcohol on the carbon surface. An estimation of the weight loss (Δ_2) of Ni/Sibunit catalysts in a flow of nitrogen at 500°C showed that Δ_2 monotonically increased with ethanol concentration in the impregnating solution and reached 1.6% in the case of a catalyst prepared by sup-

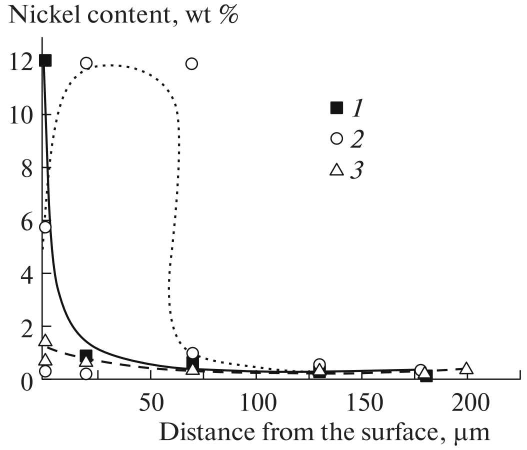

Fig. 9. Distribution of nickel in the depth of a support granule: (*1*) supporting onto the parent Sibunit from an aqueous solution (with no alcohol), (*2*) supporting onto the parent Sibunit from a 70% solution of ethanol, and (*3*) supporting onto Sibunit I from an aqueous solution.

porting Ni from a 70% solution of ethanol. In the decomposition of $Ni(NO_3)_2$ to NiO, when the concentration of supported Ni was ~0.2 wt %, the calculated value of Δ_2 was no higher than 0.1%. Assuming that the difference between the above values of Δ_2 was due to ethanol adsorption on Sibunit, the adsorption of EtOH can be estimated at ~10 mg/g. Evidently, adsorbed ethanol, as well as propane–butane, can undergo pyrolysis at 500°C; this pyrolysis is accompanied by a comparatively rapid carbonization of the catalyst. As a result, its catalytic activity in the synthesis of CFC and the yield of synthesized carbon decrease (Fig. 7, curve *2*).

A comparison between various procedures used for the pretreatment of the parent Sibunit surface demonstrated that the lowest carbon yield of 10–20 g/(g Ni) was obtained on the Ni/Sibunit I catalyst (Fig. 8). This fact may be explained by both a large particle size of supported Ni compounds (see Fig. 6) and a comparatively low catalytic activity of these compounds.

An analysis of texture characteristics indicated that the specific surface area and pore structure of Sibunit remained almost unchanged (table) in the synthesis of a CFC layer, as it was observed in a study of mesoporous supports [10]. The reason is that the relatively coarse particles of nickel hydroxide formed in aqueous solutions in the presence of urea cannot penetrate deep into a mesoporous support granule, and they are mainly deposited on the outer surface. The direct EDX study of the distribution of nickel in a granule showed that nickel was absent at a distance greater than 200 μm from the surface (Fig. 9). It was most uniformly distributed in a granule of deeply oxidized Sibunit I, which exhibited the lowest specific surface area and the greatest pore size among the test supports (see the table). In catalyst granules prepared by the precipitation of nickel compounds from highly concentrated water–ethanol solutions, nickel was detected at a larger distance from the granule surface than in the samples prepared by the precipitation of Ni from aqueous solutions (Fig. 9). This observation is consistent with a decrease in the size of supported particles as the alcohol concentration in solution was increased (see Fig. 4).

The electron-microscopic studies showed that the size and interweaving of synthesized carbon nanofibers was almost independent of the composition of the

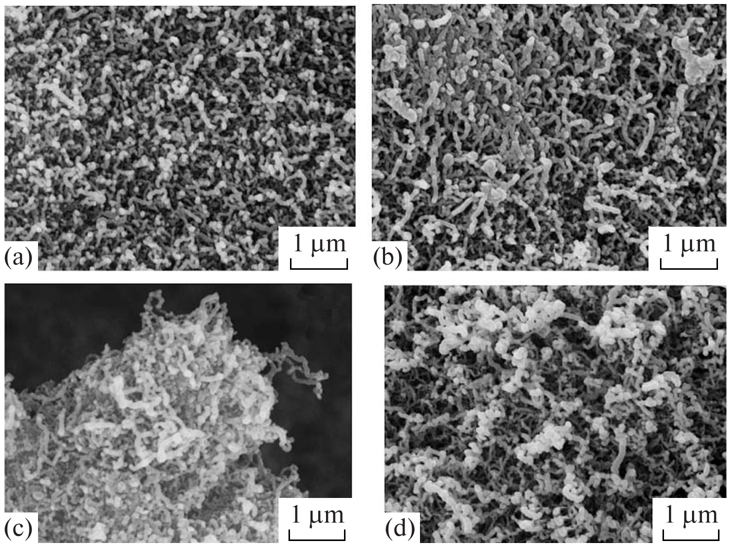

Fig. 10. Electron micrographs of carbon nanofibers synthesized on Ni/Sibunit catalysts prepared by supporting Ni from (a) aqueous and water–ethanol solutions with EtOH concentrations of (b) 20, (c) 50, and (d) 70 vol %.

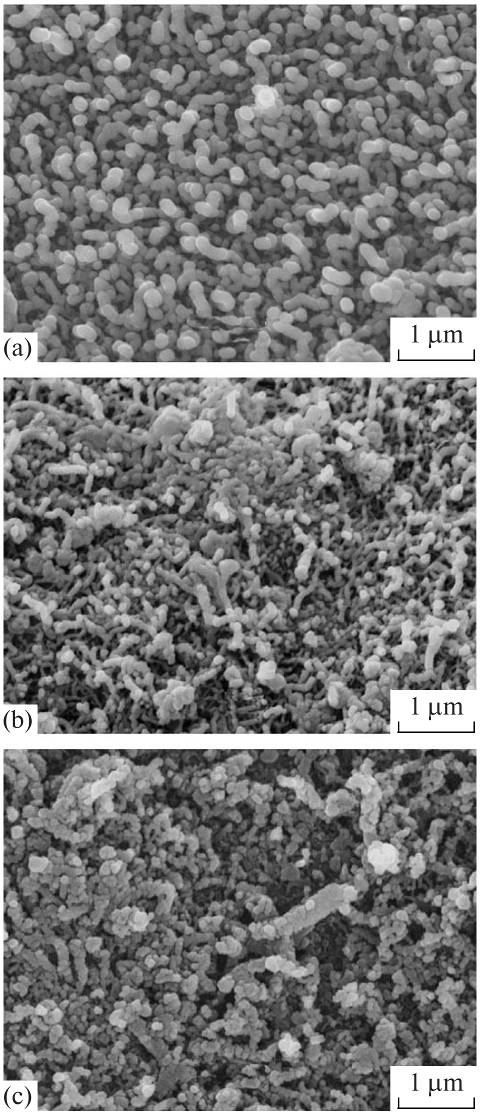

Fig. 11. Electron micrographs of carbon deposits on catalysts (a) I, (b) II, and (c) III.

impregnating solution used for the preparation of Ni/Sibunit catalysts (Fig. 10). Noticeable differences in the morphology of carbon deposits were detected by comparing the samples prepared by supporting Ni onto deeply oxidized or hydrogen reduced Sibunit. As can be seen in Fig. 11, larger carbon deposits were formed on catalyst I (as compared with nanofibers synthesized on the untreated parent Sibunit, Fig. 10a). Carbon deposits with various shapes and sizes were formed on catalysts II and III (Figs. 11b, 11c).

The electron-microscopic study of the cleavages of CFC on Ni/Sibunit support granules demonstrated that carbon nanofibers were mainly formed on the outer surface of a granule; the globular structure of Sibunit was retained within the granule (Fig. 12). Thus, the above new composite nanoporous carbon materials exhibited a shell structure with a two-phase composition.

Thus, in this work, we found that the composition of a solution used for the homogeneous precipitation of bivalent nickel compounds onto the carbon support Sibunit effects both the concentration of supported nickel and the yield of synthesized carbon. The maximum carbon yield of 50–60 g/(g Ni) was reached in the precipitation of nickel compounds from water–ethanol solutions with ethanol concentrations from 5 to 50 vol %. According to the results of electron-microscopic studies, the size of the resulting nickel nanoparticles was 0.5 μm. The morphology of the synthesized CFC layer, which was formed by chaotically interwoven carbon nanofibers to 1 μm in length, was independent of the conditions of supporting nickel onto Sibunit.

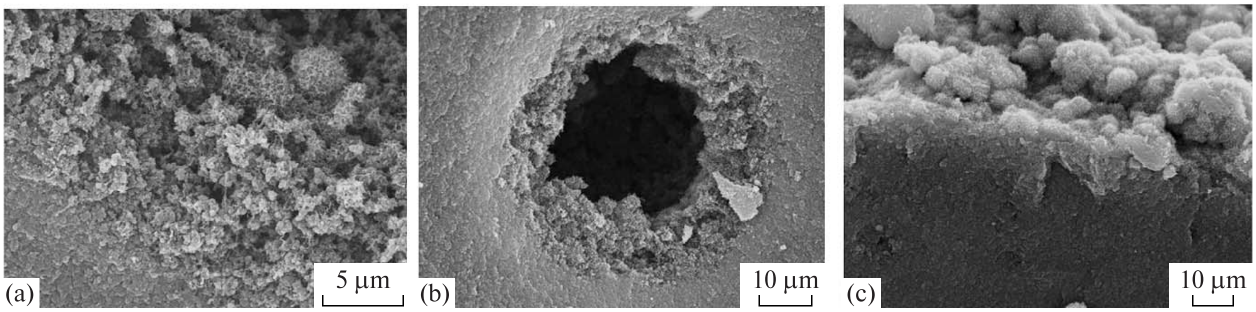

Fig. 12. Electron micrographs of the granule cleavages of CFC on Ni/Sibunit composite carbon materials.

The deep oxidation of the parent Sibunit with boiling nitric acid doubled the supported nickel content and decreased the yield of carbon by a factor of 2–4. The oxidation resulted in a change in the surface morphology of the parent Sibunit and in a considerable increase in the diameter of synthesized carbon nanofibers.

Nickel was mainly precipitated near the surface of a granule at a depth of no greater than 200 μm; nickel was not detected within the Sibunit granule. Because of this nonuniform distribution of nickel, carbon nanofibers were synthesized only near the surface of a granule, within which the globular structure of Sibunit was retained.

Undoubtedly, the composite carbon materials can find practical applications as adsorbents, supports, and catalysts because of their nanopore texture and shell structure. Macrostructured Sibunit as honeycomb monoliths can be used to produce composite supports with a uniform globular fibrous structure over the entire volume.

REFERENCES

1. Fenelonov, V.B., *Poristyi uglerod* (Porous Carbon), Novosibirsk: Inst. Kataliza, 1995.
2. Rakov, E.G., *Usp. Khim.*, 2000, vol. 69, no. 1, p. 41.
3. Likholobov, V.A., Fenelonov, V.B., Okkel, L.G., et al., *React. Kinet. Catal. Lett.*, 1995, vol. 54, no. 2, p. 381.
4. Chesnokov, V.V and Buyanov, R.A., *Usp. Khim.*, 2000, vol. 69, no. 7, p. 675.
5. Fenelonov, V.B., Derevyankin, A.Yu., Okkel, L.D., et al., *Carbon,* 1997, vol. 35, no. 8, p. 1129.
6. Vieira, R., Ledoux, M.-J., and Pham-Huu, C., *J. Appl. Catal. A: General*, 2004, vol. 274, nos. 1–2, p. 1.
7. Reshetenko, T.V., Avdeeva, L.B., Ismagilov, Z.R., et al., *Carbon,* 2004, vol. 42, no. 1, p. 143.
8. Kovalenko, G.A., Komova, O.V., Chuenko, T.V., et al., *Kinet. Katal.*, 2007, vol. 48, no. 5, p. 800 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 5, p. 749].
9. Kovalenko, G.A., Rudina, N.A., Chuenko, T.V., et al., *Kinet. Katal.*, 2007, vol. 48, no. 5, p. 808 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 5, p. 757].
10. Kovalenko, G.A., Chuenko, T.V., Rudina, N.A., and Perminova, L.V., *Kinet. Katal.*, 2008, vol. 49, no. 4, p. 529 [*Kinet. Catal.* (Engl. Transl.), vol. 49, no. 4, p. 506].
11. Komova, O.V., Simakov, A.V., Kovalenko, G.A., et al., *Kinet. Katal.*, 2007, vol. 48, no. 6, p. 860 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 6, p. 803].
12. Chesnokov, V.V., Prosvirin, V.V., Zaitseva, N.A., et al., *Kinet. Katal.,* 2002, vol. 43, no. 6, p. 838 [*Kinet. Catal.* (Engl. Transl.), vol. 43, no. 6, p. 838].
13. De Jong, K.P. and Geus, J.W., *Catal. Rev. Sci. Eng.*, 2000, vol. 42, no. 4, p. 481.
14. Chesnokov, V.V., Kuznetsov, B.N., Mikova, N.M., et al., *Ross. Khim. Zh.,* 2006, vol. 50, no. 1, p. 104.
15. Romanenko, A.V., Tyschishin, E.A., Moroz, E.M., et al., *Appl. Catal., A*, 2002, vol. 227, nos. 1–2, p. 117.
16. Simakova, I.L. and Semikolenov, V.A., *Kinet. Katal.*, 2000, vol. 41, no. 3, p. 421 [*Kinet. Catal.* (Engl. Transl.), vol. 41, no. 3, p. 383].
17. Bonarowska, M., Pielaszek, J., Semikolenov, V.A., and Karpinski, Z., *J. Catal.*, 2002, vol. 209, no. 2, p. 528.
18. Likholobov, V.A., *Soros. Obrazovat. Zh.*, 1997, no. 5, p. 35.
19. Park, C. and Keane, M.A., *J. Catal.*, 2004, vol. 221, p. 386.
20. Katsuomi Takehira, Takenori Ohi, Tetsuya Shishido, et al., *Appl. Catal., A,* 2005, vol. 283, p. 137.
21. Kovalenko, G.A., Kuznetsova, E.V., Mogilnykh, Yu.I., et al., *Carbon,* 2001, vol. 39, p. 1033.
22. Kovalenko, G.A. and Vanina, M.P., *Zavod. Lab.,* 1999, no. 9, p. 43.