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Corundum Impregnation Conditions for Preparing Supported Ni Catalysts for the Synthesis of a Uniform Layer of Carbon Nanofibers

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Abstract—Impregnation techniques for corundum (S_{BET} = 0.5 m^2/g) as a support for Ni catalysts for C_3–C_4 alkane pyrolysis into catalytic filamentous carbon (CFC) are compared. The effects of the following factors on the uniformity of the active component (Ni) deposition on the inert support and on the CFC yield (g CFC)/(g Ni) are reported: (1) pH of the nickel nitrate solution, (2) presence of aluminum(III) nitrate in the solution, (3) addition of viscosifying agents (glycerol, glucose, sucrose) to the solution, (4) catalyst calcination conditions before pyrolysis, and (5) catalyst drying technique. The surface morphology of the Ni catalysts and of the carbon deposits resulting from the catalytic pyrolysis of C_3–C_4 alkanes in the presence of hydrogen has been investigated by scanning electron microscopy. The optimum way of preparing the supported Ni catalysts is by carrying out the incipient wetness impregnation of corundum with a nickel nitrate solution (0.05–0.1 mol/l) containing glycerol (20–25 vol %), drying the product in a microwave oven, and burning away the glycerol before alkane pyrolysis.

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The problem of preparing supported catalysts with a preset distribution and particle size of the active component is still a challenge [1]. The active component distribution in the support pellet can be uniform or crustlike. In turn, crustlike distributions can be like an eggshell, a white in an egg, or a yolk in an egg [1]. Impregnation, which is the most widespread and the simplest way of obtaining supported catalysts, suffers from the following serious drawback: the active component distribution over the cross section of the pellet is nonuniform because of the transfer of part of the solution to the pellet periphery during drying [1, 2]. This disadvantage manifests itself most clearly for macrostructured and macroporous (sintered) supports with a small specific surface area (<1 m^2/g), such as cordierite monoliths [1], and when there is no adsorption interaction between the support and the active component compounds. Obviously, the active component distribution depends strongly on the deposition conditions, the viscosity of the solution, and catalyst drying conditions. For the active component distribution in the Ni catalyst prepared by impregnation of cordierite honeycomb monoliths, the drying conditions are of crucial significance [3]. For example, drying in a microwave oven and prolonged lyophilic drying afford the most uniform nickel distribution over the length of the honeycomb monolith. After conventional drying in an air atmosphere or in flowing air, the active component is nonuniformly distributed in the catalyst [3].

Carbon–mineral composites in the shape of honeycomb monoliths, rings, and "openwork" foamed pieces are of interest as supports and adsorbents. Uniform thin carbon layers of various morphologies, such as pyrocarbon and catalytic filamentous carbon (CFC), have been synthesized on these composites. The carbon-coated supports retain their initial mechanical strength and macrostructure, and the carbon layer imparts them a high adsorption capacity. Earlier [4–7], we reported the synthesis of a CFC layer on the surface of Ni-containing inert supports with a specific surface area of <1 m^2/g (including honeycomb monoliths and foamed ceramics) by the pyrolysis of methane and C_3–C_4 alkanes. The catalysts were prepared by two methods, namely, impregnation (IMPR) with aqueous solutions of nickel(II) nitrate at 85°C [6, 7] and homogeneous deposition of nickel nitrate in the presence of a tenfold excess of urea at 85°C (HOMDEP) [5–7]. It was found that the catalysts prepared by the HOMDEP technique are more active in CFC synthesis: the carbon yield on Ni/α-Al_2O_3 was 76 g/(g Ni), which is ~2 times higher than the carbon yield attained with catalysts prepared by the IMPR method [7]. Under alkane pyrolysis conditions, particularly in the two-step pyrolysis of C_3–C_4 hydrocarbons with Ni(II) pre-reduction to nickel metal with hydrogen, CFC layers on the catalysts prepared by impregnation of macroporous supports with a small specific surface area (clayite, vermiculite, Al/Si ceramics) are synthesized nonuniformly, as was demonstrated by examination of carbonized catalyst pel-

lets and their cleaved surfaces [4, 6]. Scanning electron microscopy (SEM) data confirmed that the synthesis of carbon nanofibers takes place nonuniformly, mainly on surface defects (pits and cracks), and carbon-free surface areas can clearly be seen in the micrographs [4, 6]. It was also discovered that Ni^0 particles can migrate over the sintered, smooth aluminosilicate (clayite, glass) surface to form larger particles in surface pits [4]. Evidently, the problem of synthesizing a uniform CFC layer on the surface of an inert sintered support, which is directly related to the distribution of catalytically active particles of Ni(II) compounds, can be solved by optimizing the catalyst impregnation conditions.

Here, we report a comparative study on the impregnation of corundum, an inert macroporous support with a specific surface area of 0.5 m^2/g, as a method of preparing Ni catalysts for C_3–C_4 alkane pyrolysis. The purpose of this work was to optimize the support impregnation procedure, primarily for obtaining a uniform distribution of Ni particles, which are active in the synthesis of carbon nanofibers. We studied how the outcomes of the synthesis depend on the impregnation procedure (excess solution versus incipient wetness impregnation) and drying technique. In addition, we studied the effect of the composition of the nickel nitrate solution (pH, presence of viscosifying agents) on the uniformity of the CFC coating and on the carbon yield ((g CFC)/(g Ni)). The surface morphology of the supported catalysts and carbon deposits synthesized by C_3–C_4 alkane pyrolysis in the presence of hydrogen was studied by SEM with energy-dispersive X-ray (EDX) microanalysis.

EXPERIMENTAL

The inert support for Ni catalysts was corundum shaped as rings with a height of 5–6 mm, an outer diameter of ~7 mm, and an inner diameter of 2.5 mm (OAO Katalizator, Novosibirsk). The specific surface area of the support was 0.5 m^2/g, its mean pore diameter was 2.9 μm, and its total pore volume was V_Σ = 0.4 cm^3/g. It was proved by X-ray diffraction that the parent support was α-alumina (corundum). Only traces of the θ-Al_2O_3 phase were detected. Note that the commercial support used in this study is very nonuniform.

Ni/corundum catalysts were prepared via two impregnation techniques. The first was excess solution impregnation (IMPR-1): 1 part support to 50 parts solution by weight were stirred vigorously for 5 h at 20–22°C, and the solid was then washed with distilled water and dried. The second technique was incipient wetness impregnation (IMPR-2): each ring, weighing 0.2–0.3 g, was impregnated with 100–150 μl of a solution of appropriate composition. The resulting catalysts were dried in three ways: (1) static conditions, IR lamp, drying time of at least 5 h; (2) dynamic conditions (nitrogen flow, 14 l/h), 85–120°C, 1 h; (3) microwave oven, 400–600 W, 5–10 min. The extent of drying in the microwave oven was monitored by weighing the catalysts prepared by the IMPR-2 method every minute. Catalysts prepared by homogeneous deposition [6] were used as references.

The initial concentration (C_0) of nickel nitrate in the impregnating solution was varied between 0.001 and 0.5 mol/l; that of aluminum nitrate, between 0.01 and 0.5 mol/l. The acidity of the solution was varied between pH 5.5 and 7.0 (0.05 M acetate buffer). pH was determined potentiometrically using a glass electrode and a pH meter. The viscosity of the solution was varied by adding glycerol (5–80 vol %), glucose (20 wt %), or sucrose (1 and 20 wt %). Hereafter, these compounds are referred to as polyols for the reason that their molecules have three, five, and nine OH groups, respectively. The polyols were either not burned away or burned away in steps by raising the temperature as follows: 300°C (1 h) ⟶ 500°C (1 h) (for glycerol and glucose); 300°C (1 h) ⟶ 400°C (1 h) ⟶ 600°C (1 h) (for sucrose). When a single-step burning procedure was used, the organic matter ignited as the temperature was being raised to 600°C over 0.5 h.

The nickel content (wt %) of the Ni/corundum catalysts was determined by atomic emission spectroscopy using an ASSIN instrument with a flame ionization detector. The error of analysis was 10–20 rel %.

The C_3–C_4 mixture was pyrolyzed in the presence of hydrogen at 500°C for 1 h in a fixed bed rector [5, 6]. The total amount of carbon synthesized on the support (C_Σ, wt %) was determined gravimetrically after calcination of the catalyst at 800°C for 3 h. The amount of synthesized carbon determined as the weight gain upon pyrolysis and the amount of carbon determined as the weight loss after the calcination of the catalyst coincided within the experimental absolute error (0.1–0.2%).

Catalytic activity was characterized by the filamentous carbon yield (Y) in terms of the mass of the resulting CFC (g) per gram of nickel. The amount of synthesized CFC (wt %) was estimated as $C_{CFC} = C_\Sigma - C_{pyr}$, where C_Σ is the total amount of the resulting carbon (wt %) and C_{pyr} is the amount of carbon that resulted from C_3–C_4 alkane pyrolysis on the nickel-free support. For corundum, C_{pyr} does not exceed 0.1%; therefore, for the Ni/corundum catalysts, it can be taken that $C_{CFC} \approx C_\Sigma$.

The specific surface area of corundum, supported catalysts (Ni/corundum), and carbonized catalysts (C/Ni/corundum) were measured by the thermal argon desorption technique using a SORBI-M instrument (ZAO META, Russia). The pore size distribution was studied by mercury porosimetry (AUTOPORE 9200 porosimeter, Micromeritics, United States).

The morphology of surface nickel compounds and CFC was studied by electron microscopy on JSM 6460

Table 1. Effect of the pH of the impregnating solution on the properties of the supported Ni catalysts prepared by the IMPR-1 method

pH	Ni content of the catalyst, wt % (chemical analysis data)		Carbon yield, Y, (g CFC)/(g Ni)	
	$C_0 = 0.01$ M	$C_0 = 0.1$ M	$C_0 = 0.01$ M	$C_0 = 0.1$ M
5.5	0.04	0.28	6.5	74.6
6.0	0.03	0.34	19.7	18.8
6.5	0.04	0.29	21.8	36.8
7.0	0.04	0.20	22.2	68.6
Distilled water, pH 5.7	0.04	0.20	12.5	38.9

LV (JEOL, Japan) and LEO 1430 (LEO, Germany) scanning electron microscopes fitted with an EDX attachment.

RESULTS AND DISCUSSION

Effect of the pH of the Impregnating Solution on the Properties of Ni/Corundum Catalysts

Compounds of transition metals, including Ni, form aqua, hydroxo, and oxo complexes in aqueous solutions. The homoligand aqua complex $[Ni(H_2O)_6]^{2+}$ is very labile: the rate constant of water exchange in this complex at 25°C is 10^4 s^{-1} [8]. It was demonstrated that, in the presence of solid oxyhydrate supports (including Al_2O_3), the hydrolysis of anionic Pt, Rh, Pd, and Ir complexes takes place at the solution/solid interface [9]. This process, called heterogeneous hydrolysis, is a typical heterogeneous acid–base reaction. It yields poorly soluble hydrated metal oxides on the support surface. Since this reaction takes place on active sites, specifically, surface OH groups, it is significant that its rate be well above the hydrolysis rate in the impregnating solution, which is decreased by lowering the pH of this solution [9]. We carried out experiments to see whether heterogeneous hydrolysis occurs in the Ni(II) salt solution/α-Al_2O_3 system. There was good reason to choose α-Al_2O_3 as the inert support. α-Alumina has a higher surface OH group concentration than any other crystalline phase of alumina [10]. It was indeed found that the concentration of basic sites on the corundum surface is 19.7 μmol/m^2, ~2 times higher than for the low-temperature alumina phases (γ, η).

It was demonstrated by examination of catalysts prepared by the IMPR-1 method that the supported nickel concentration is practically independent of pH and is primarily determined by the initial $Ni(NO_3)_2$ concentration in the solution (Table 1). It was discovered that the catalysts containing 0.01 wt % Ni (C_0 = 0.001 mol/l) are carbonized only slightly: the amount of synthesized carbon does not exceed 0.2 wt %. As the nickel content of the catalyst is increased, the amount and yield of synthesized carbon grow markedly. For the catalysts prepared by impregnation with aqueous $Ni(NO_3)_2$ solutions, the carbon yield increases on the average by a factor of ~3 as the amount of supported Ni is raised by a factor of ~5 (Table 1).

Although the supported nickel content of the catalyst is almost independent of the pH of the solution, the amount of synthesized carbon and CFC yield in most cases increase with increasing pH. Replacing the buffer solutions with solutions in distilled water did not exert any significant effect on the properties of the resulting catalysts (Table 1). It was observed that the pH of the aqueous 0.1 mol/l nickel nitrate solution decreases from 5.7 to 5.4 in 3 h and is then invariable for 20 h. The data on the effects of C_0 and pH on Y can likely be explained in terms of the difference between the particle sizes of the deposited Ni(II) compounds. As C_0 is raised and pH is shifted to higher alkalinities, increasingly larger particles of Ni(II) hydroxo compounds are deposited on the corundum surface. Earlier, we deduced from the results of previous studies [4–7] that the optimum particle size of supported Ni(II) compounds ensuring the highest catalytic activity is 200–500 nm. These particles afford carbon nanofibers 50–100 nm in diameter and 1–2 μm in length. A comparison between the activities of the Ni/corundum catalysts prepared by the HOMDEP method (0.1% Ni at C_0 = 0.01 mol/l [7]) and the IMPR-1 method (0.20% Ni at C_0 = 0.1 mol/l) demonstrated that the maximum carbon yields are similar in these cases (75–76 g/g); therefore, the size of the catalytic Ni particles deposited by the IMPR-1 method can be estimated at ~200 nm. Electron microscopic examination of the C/Ni/corundum catalysts prepared by the IMPR-1 method at C_0 = 0.001 mol/l and pH 5.5–7.0 revealed carbon formations resembling a "point of growth" of a carbon nanofiber <200 nm in diameter (Fig. 1a). It is likely because of the small size of the Ni particles that these catalysts were practically not carbonized, as was noted above. According to SEM data, the thickness of the carbon nanofibers and their weave density increase as pH is raised from 5.5 to 7.0 at C_0 = 0.01 mol/l (Figs. 1b, 1c). Examination of cleaved surfaces of C/Ni/corundum catalysts prepared by the IMPR-1 method showed that the active component is very nonuniformly distributed in the cross section of the annular pellet. The outer geometrical surface of the ring exhibits both white and velvety black areas, indicating intensive local CFC synthesis.

A comparison between the properties of the catalysts prepared by the IMPR-1 and IMPR-2 methods demonstrated that, for the IMPR-2 series, the carbon yield is independent of the pH of the impregnating solution and is 41 g/g (with data scatter of ±3 g/g),

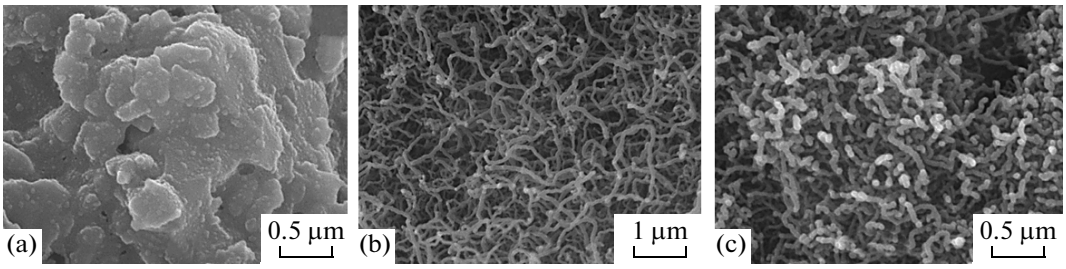

Fig. 1. Electron micrographs of the surface of C/Ni/corundum catalysts prepared by the IMPR-1 method: (a) $C_0 = 0.001$ mol/l, pH 5.5, 0.01% Ni, 0.2% C; (b) $C_0 = 0.01$ mol/l, pH 5.5, 0.04% Ni, 0.3% C; (c) $C_0 = 0.01$ mol/l, pH 7.0, 0.04% Ni, 0.9% C.

which is similar to the average value of $Y = 47$ (with data scatter of ±30 g/g) for the catalysts prepared using the excess solution impregnation technique (Table 1). The wide scatter of the experimental data for the IMPR-1 series is further indirect evidence of the very nonuniform distribution of the active component. Incipient wetness impregnation affords a more uniform distribution of Ni particles over the corundum surface. This is confirmed by the examination of cleaved surfaces of carbonized catalyst pellets of the IMPR-2 series. Thus, the uniformity of active component distribution in the alkane pyrolysis catalysts can be studied visually by estimating the uniformity of carbon synthesis in the cross section of a catalyst pellet.

Our results indicate that no heterogeneous Ni(II) hydrolysis with the formation of tightly bound surface hydroxides takes place on the α-alumina surface. As a consequence, as the catalyst is dried, the active component is distributed nonuniformly, which is evident from the examination of the cleaved surface of the pellets.

Effect of Al(III) Compounds in the Impregnating Solution on the Properties of Ni/Corundum Catalysts

Catalysts for alkane pyrolysis, which yields a nanoporous carbon support as pellets 0.2–3 mm in diameter formed by the interweaving and densification of synthesized carbon nanofibers, are prepared by the coprecipitation of aluminum and transition metal (Fe, Ni, Cu) hydroxides. Under optimized conditions, the carbon yield in this case is over 200 g/g [12]. In addition, it can be assumed that aluminum compounds have a higher alumina affinity than nickel compounds and that, in coprecipitation, catalytically active Ni particles will be more strongly bound to the Al_2O_3 surface.

We carried out comparative experiments, preparing Ni catalysts by the HOMDEP and IMPR-2 methods using impregnating solutions containing both Ni(II) and Al(III) nitrates. Initially, we determined the catalytic activity of the support impregnated with 0.5 mol/l aluminum nitrate (without nickel) in C_3–C_4 alkane pyrolysis in the presence of hydrogen. It was found that, under the conditions examined (500°C, 1 h), $C_{pyr} = 0.5\%$. According to chemical analysis, the Ni content of the catalyst obtained by the IMPR-2 method is independent of the aluminum concentration in the solution, which is natural for this impregnation technique, and is 0.12 wt %. By contrast, the Ni content of the catalyst prepared by the HOMDEP method decreases as the $Al(NO_3)_3$ concentration is raised and is 0.09, 0.02, and 0.007 wt % for aluminum nitrate concentrations of 0, 0.01, and 0.1 mol/l, respectively. For the HOMDEP series, as the $Al(NO_2)_3$ concentration in the solution is increased, the amount of synthesized carbon decreases sharply. For $Al(NO_2)_3$ concentrations of >0.1 mol/l, C_{CFC} does not exceed 0.5%, which is equal to C_{pyr} for the nickel-free support. Therefore, in the case of the HOMDEP catalysts prepared in the presence of aluminum(III) nitrate, aluminum hydroxide is mainly deposited on the corundum surface and the major pyrolysis product is pyrocarbon, while the activity of supported nickel is close to zero. Consequently, the presence of aluminum(III) nitrate in the impregnating solution exerts an adverse effect in the preparation of Ni catalysts for hydrocarbon pyrolysis and CFC synthesis. The catalytic activity of the Ni/corundum catalysts prepared by the IMPR-2 method decreases by a factor of ~2 as the $Al(NO_2)_3$ concentration is raised from 0 to 0.1 mol/l and remains invariable in the aluminum nitrate concentration range from 0.1 to 0.5 mol/l (Fig. 2).

Examining the cleaved surfaces of carbonized catalyst pellets prepared by the IMPR-2 method, we found that, with impregnating solutions containing $Al(NO_2)_3$, nickel deposition and carbon formation in the pellet bulk take place more uniformly and intensively, although C_Σ is smaller by a factor of ~2. Electron microscopic studies confirmed that, as the Al(III) ion concentration in the solution is raised, comparatively short carbon nanofibers are increasingly more uniformly synthesized on the corundum surface (Figs. 3a1, 3a2). For low aluminum concentrations, both accumulations of comparatively long carbon nanofibers (Figs. 3b1, 3b2) and CFC coatings were observed on the corundum surface. Thus, even though it leads to a more uniform nickel distribution in corundum, the presence of aluminum(III) nitrate in the impregnating solution is undesirable because it markedly reduces the activity of the resulting catalyst.

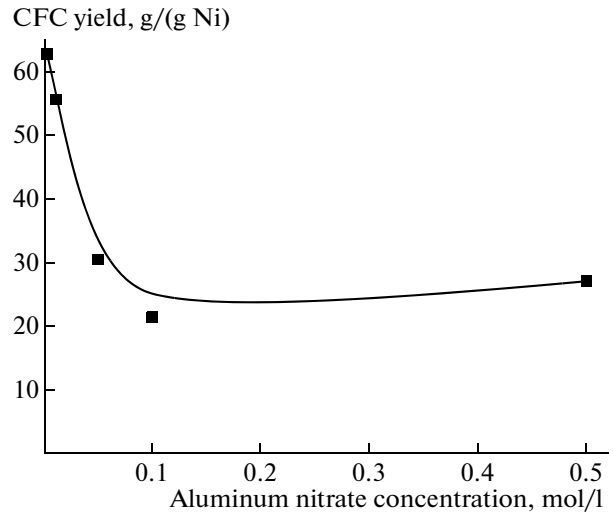

Fig. 2. Carbon yield as a function of the aluminum nitrate concentration in the impregnating solution for the supported Ni catalysts prepared by the IMPR-2 method (C_0 = 0.1 mol/l $Ni(NO_3)_2$).

Effect of Viscosifying Agents in the Impregnating Solution on the Properties of Ni/Corundum Catalysts

In order to attain a uniform active component distribution over the cross section of the corundum pellet, we used nickel nitrate solutions more viscous than their aqueous counterparts. The viscosity of the aqueous solutions was increased by adding glycerol (up to 80 vol %), glucose (20 vol %), or sucrose (up to 20 vol %). The kinematic viscosity (η) of the 20% solutions of glycerol (η^{20} = 0.1769 mPa s [13]) and sucrose (η^{20} = 1.945 mPa s [14]) is, respectively, ~2 and ~20 times higher than the viscosity of water (η^{20} = 0.1 mPa s). In impregnation, these compounds fill the pore space of the support pellet, so it is important to know the conditions under which they can be burned away from the Ni catalysts before pyrolysis. When glycerol (or sucrose) was not burned away, the resulting amount of carbon was equal to the stoichiometric amount of carbon in the polyol. For example, for the catalyst prepared by the IMPR-2 method in the presence of 20% glycerol, C_Σ = 2.1% (calculated amount of 2.6%). For the catalyst prepared in the presence of 20% sucrose, the resulting amount of carbon is 5–8%, which checks well with the amount of graphite-like carbon (6–10%) resulting from sucrose decomposition (500°C, H_2) in a sucrose-impregnated support [15]. The polyols were burned away from the catalysts in steps via programmed temperature rise. The study of the effect of the calcination temperature on the pyrolytic activity of the Ni catalysts (0.10–0.13% Ni) prepared in the absence of a polyol demonstrated that, as the temperature is raised, the amount of carbon (wt %) decreases as follows: 3.0–7.9 without heating $\longrightarrow$ 2.6 for 300°C $\longrightarrow$ 2.6 for 600°C $\longrightarrow$ 0.2 for 800°C; that is, the catalytic activity falls sharply at 800°C. The dark gray and light gray catalysts heat-treated at 300–600°C, which contained nickel as NiO, turned white at 800°C. This might indicate the interaction between Ni and Al_2O_3 and, as a consequence, catalyst deactivation. With the polyols burned

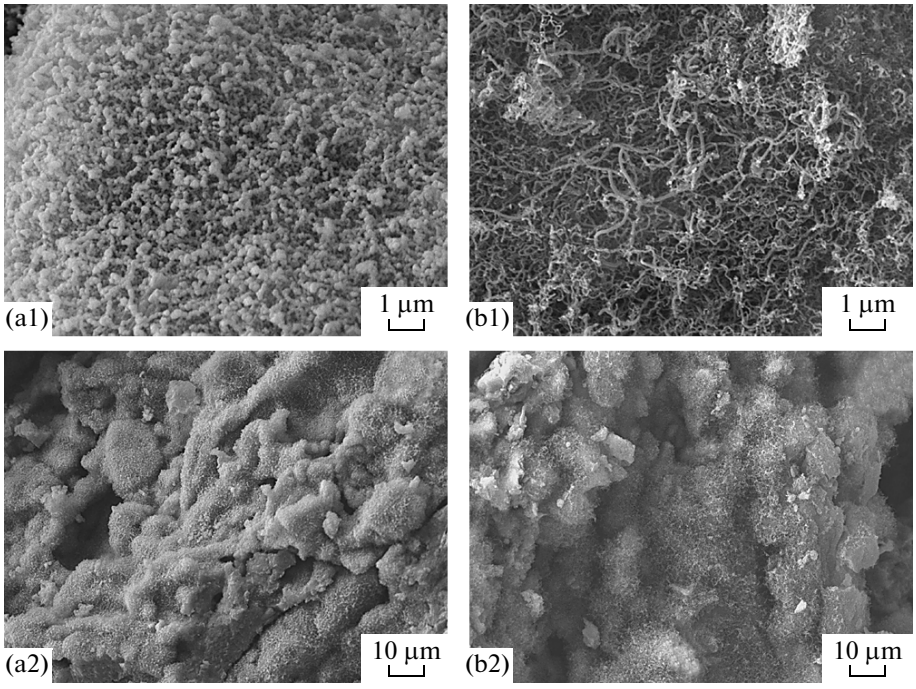

Fig. 3. Electron micrographs of the surface of C/Ni/corundum catalysts prepared by the IMPR-2 method in the presence of $Al(NO_3)_3$ at concentrations of (a1, a2) 0.5 mol/l (0.12% Ni, 3.3% C) and (b1, b2) 0.01 mol/l (0.12% Ni, 6.7% C).

away in a single step by rapidly raising the temperature to 500–600°C, the amount of synthesized carbon did not exceed 0.2 wt %. This can be due to catalyst deactivation at the high temperature developed as a result of polyol ignition. In subsequent experiments, the Ni catalysts prepared in the presence of polyols were heat-treated in steps before C_3–C_4 alkane pyrolysis. It was demonstrated by mercury porosimetry that, after polyol burning, the specific surface area of the catalysts was 1.0–1.2 m^2/g (0.5 m^2/g for corundum) and their total pore volume was 0.6–1.0 cm^3/g (0.4 cm^3/g for corundum).

As can be seen from the data presented in Table 2, the amount of carbon synthesized on the catalysts prepared by the IMPR-2 method in the presence of glycerol (20 vol %) depends on the nickel nitrate concentration in the impregnating solution and the maximum Y value is 76 g/g (as in the case of the catalyst prepared by the HOMDEP method [7]). A comparison between the Y values for the Ni/corundum catalysts with the same nickel content (0.10–0.13% Ni) prepared in the absence of glycerol (~30 g/g) and in the presence of 20% glycerol with subsequent stepwise polyol burning (~40 g/g) shows that glycerol does not exert any significant effect on the pyrolytic activity of the Ni catalysts. Note also that the nickel content of the catalysts determined by chemical analysis after glycerol burning was 2–4 times lower than the nickel content calculated from incipient wetness impregnation data. This might indicate nickel carry-over from the catalyst.

The amount of carbon synthesized on the catalysts prepared by the IMPR-2 method depends on the glycerol concentration in the solution, and the plot illustrating this dependence has a well-defined peak at 20–25 vol % (Fig. 4). The decrease in catalytic activity above the glycerol concentration of >20 vol % can likely be explained in terms of the dependence of the viscosity of the solution on the glycerol concentration. The viscosity of glycerol solutions increases linearly up to a glycerol concentration of 20–25% and then rises sharply (Fig. 4, top) [13]. Under the burning conditions, the viscous solution (>40% glycerol) filling the pore space of the pellet likely undergoes intensive carbonization and the resulting graphite-like deposits block active sites, thus deactivating the catalyst. Indeed, the electron microscopic examination of the surface of the Ni/corundum catalysts prepared in the presence of glycerol revealed smooth areas (Fig. 5a) hiding supported nickel, as was determined by EDX analysis. The SEM image of the surface of the C/Ni/corundum catalyst prepared without burning away the glycerol (Fig. 5b) shows features resembling the "points of growth" of carbon nanofibers. However, it was demonstrated by additional experiments that extending the pyrolysis time to 3 h does not increase the amount of synthesized carbon. Upon the stepwise burning of glycerol, separate smooth areas covered with graphite-like carbon appear on the C/Ni/corundum surface along with carbon formations with a well-defined filamentous structure (Fig. 5c). Electron microscopic studies demonstrated that the synthesis of carbon nanofibers on the Ni/corundum catalysts prepared in the presence of 20% sucrose (Fig. 5d) proceeds less intensively than on the catalysts prepared in the presence of 20% glycerol with subsequent glycerol burning (Fig. 5c) and more intensively than on the catalysts prepared in the presence of 20% glycerol without its burning before C_3–C_4 alkane pyrolysis (Fig. 5b). Note that the morphology of the smooth areas covered with graphite-like carbon is similar to the morphology of the surface of graphitized supports obtained by sucrose decomposition in the presence of hydrogen at 500°C [15].

Table 2. Dependence of the amount of synthesized carbon and of the texture parameters of the carbonized catalysts prepared by the IMPR-2 method in the presence of glycerol (20 vol %) on the nickel nitrate concentration in the solution

C_0, mol/l	C_{CFC}, wt %	S^*_{sp}, m^2/g	D^*_{por}, mean, nm	D^*_{por}, on surface, nm
0.01	0.23	–	–	–
0.05	4.25	6	180	9
0.1	9.20	–	–	–
0.5	20.02	26	61	8

* Determined by mercury porosimetry.

On the catalysts prepared by the impregnation of corundum with nickel nitrate in the presence of a polyol, CFC forms uniformly, mainly in the internal

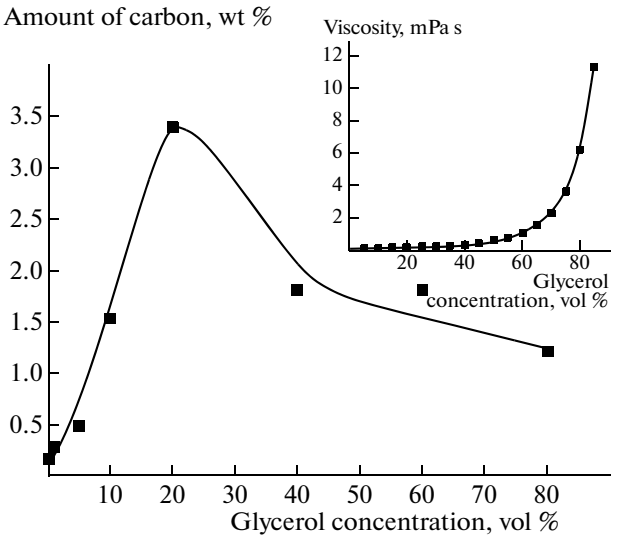

Fig. 4. Amount of carbon synthesized on catalysts prepared by the IMPR-2 method as a function of the glycerol concentration in the impregnating solution. The Ni content of the catalyst is 0.03–0.05 wt %.

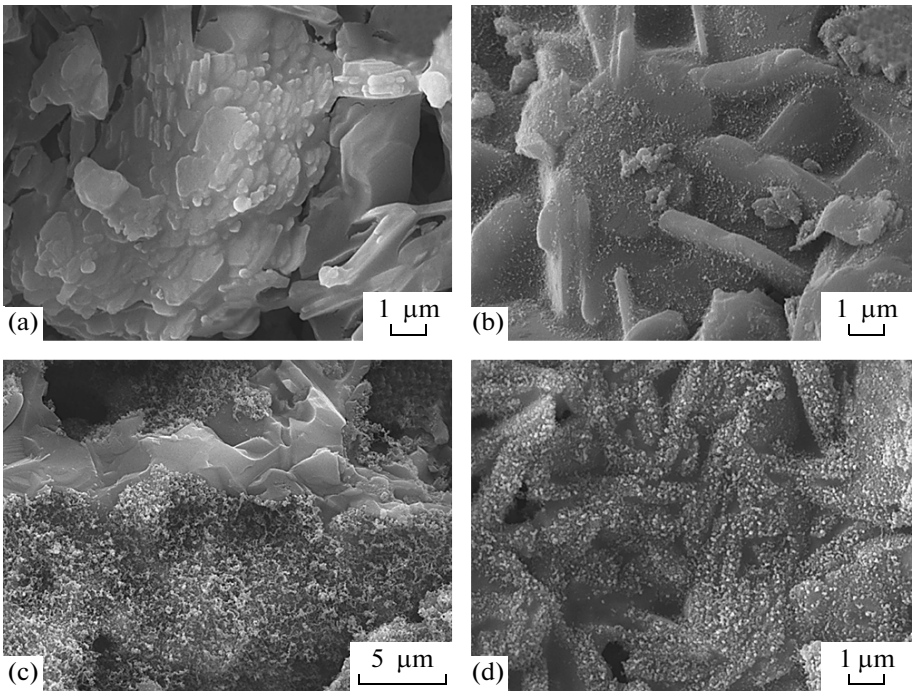

Fig. 5. Electron micrographs of the surface of (a) the Ni/corundum catalyst before pyrolysis and (b–d) C/Ni/corundum samples: (a) 0.3% Ni, 20% glycerol, stepwise heat treatment; (b) 0.1% Ni, 20% glycerol, no heat treatment, 2.1% C; (c) 0.05% Ni, 20% glycerol, stepwise heat treatment, 9.2% C; (d) 0.02% Ni, 20% sucrose, stepwise heat treatment, 0.9% C.

pore space of the ring (not on its geometrical surface), and this can clearly be seen on cleaved surfaces of the pellets, which are velvety black. As the amount of CFC increases, the specific surface area of the catalyst increases and the pore diameter decreases (Table 2), in agreement with the results reported in our earlier work [7]. At a CFC content of >20 wt %, the mechanical strength of the pellets decreases and the corundum rings shatter because of the bulk synthesis of carbon.

The effect of polyols on the impregnation process can manifest itself not only as an increase in the viscosity of the solution, but also as complexation with metal ions followed by the binding of the resulting complexes to the support surface. Indeed, it follows from a review by Alekseev et al. [16] that carbohydrates can form complexes with iron-family metal ions, including Ni^{2+}. The stability constants of these complexes are as large as $\sim 10^4$–10^5. If carbohydrate molecules can adsorb onto the support surface, then the strength of binding of the active component as the metal–carbohydrate complex will obviously be greater. However, it was demonstrated by the example of glucose that carbohydrate molecules do not actually adsorb onto the corundum surface. (Glucose before and after adsorption on corundum was quantified with a high accuracy using the glucose oxidase method.) Therefore, the tight binding of the metal–carbohydrate complexes is unlikely and the main role of the polyols is to increase the viscosity of the impregnating solution.

By comparing the activities of the catalysts prepared by the IMPR-1 method using a glycerol-, glucose-, or sucrose-containing solution (20%), it was established that, with an increasing viscosity of the solution, the amount of synthesized carbon increases (Table 3) and carbon formation in the pellet bulk becomes more uniform. Therefore, it is pertinent to prepare Ni/corundum catalysts using viscosified impregnating solutions since this makes active component deposition on the surface of macroporous inert supports more uniform.

The above data suggest that, from the standpoint of the uniformity of active component distribution in corundum with a specific surface area of <1 m^2/g, the best method of preparing Ni catalysts for C_3–C_4 alkane pyrolysis is incipient wetness impregnation with a nickel nitrate solution (0.05–0.1 mol/l) containing 20–25 vol % glycerol. The optimum nickel content maximizing the Y value is 0.1–0.3%.

Effect of Drying Conditions on the Properties of Ni/Corundum Catalysts

In the drying of catalysts prepared by the impregnation of a macroporous (or macrostructured) sintered support with an aqueous solution of a salt of an active component inert toward surface OH groups (such as nickel nitrate, which, as was mentioned above, does not undergo heterogeneous hydrolysis), the liquid phase can move in the pellet in the following

Table 3. Effect of the presence of polyols in the impregnating solution on the properties of the Ni catalysts prepared by the IMPR-1 method

Composition of the impregnating solution	η^{20}, mPa s	Ni, wt % (chemical analysis)	C_{CFC}, wt % (experiment)	Y, (g CFC)/(g Ni)
Distilled water	0.1	0.01	0.11	11.0
Glycerol*	0.1769	0.02	0.19	9.5
Glucose*	–	0.02	0.52	26.0
Sucrose*	1.945	0.02	0.86	43.0

* Polyol concentration of 20 vol %, stepwise burning out.

ways: (1) downward flow of the solution under the action of gravity; (2) water evaporation from the pellet surface, taking place mainly in its outer part under heating or in a flowing inert gas, leading to an increase in the concentration of nickel nitrate and to the crystallization of the salt; (3) motion of the solution under the action of capillary forces. Obviously the rate ratio of these processes governs the distribution of the active component during catalyst drying.

For the Ni/corundum catalysts (0.05–0.06 wt % Ni) prepared by the IMPR-1 method, the carbon yield depends on the drying technique. Drying with an IR lamp (for at least 5 h) or air drying to constant weight at 20–22°C (20–22 h) ensures a carbon yield of ~18 g/g, which is higher than the Y value for the Ni/corundum catalysts dried in flowing nitrogen, ~3 g/g. In the latter case, as the drying temperature is raised from 85 to 120°C, the CFC yield decreases monotonically to ~2 g/g. Visual examination of cleaved surfaces of carbonized catalyst pellets demonstrated that, in the case of drying in flowing nitrogen, the active component is very nonuniformly distributed in the pellet bulk. For the Ni/corundum catalysts (0.01 wt % Ni) prepared by the IMPR-1 method and dried in a microwave oven, Y reaches a record value of ~100 g/g, far exceeding the Y value of 18 g/g attained with IR drying. As the initial nickel nitrate concentration in the solution is increased to 0.1 mol/l, the difference between the Y values attained with different drying techniques becomes less significant, taking on a value of 45–47 (g CFC)/(g Ni).

Figure 6 illustrates the effect of the drying technique on the amount of synthesized carbon for the Ni/corundum catalysts prepared by incipient wetness impregnation with solutions containing different nickel nitrate concentrations. The maximum amount of CFC is obtained on the catalysts dried in flowing nitrogen at 85–100°C (Fig. 6, curve *3*); however, the active component in these catalysts is distributed nonuniformly. Carbon in these catalysts (14.8 wt %) is localized only on the outer surface of the pellets and crumbles away readily under mechanical action. Drying in flowing nitrogen affords the highest rate of water evaporation from the outer surface of the pellet, and this leads to the observed result.

The catalysts dried in the microwave oven differ insignificantly from the IR-dried samples in terms of the mount of synthesized carbon (Fig. 6, curves *2* and *1*, respectively). However, with the analyses for Ni taken into account, the average Y value for the microwave-dried samples is ~2 times larger than the same parameter for the IR-dried samples: at $C_0 = 0.1$ mol/l, $Y = 47$ and 24 (g CFC)/(g Ni), respectively. Examination of cleaved surfaces of the pellets indicates that both drying techniques afford a uniform distribution of the active component of the corundum surface. A comparison between these two drying techniques suggests that the main advantage of microwave drying is the short drying time—a few minutes rather than hours. Water evaporation in a microwave oven occurs simultaneously in the corundum pellet bulk and on the ring surface, and this likely ensures the uniform distribution of the active component throughout the catalyst pellet.

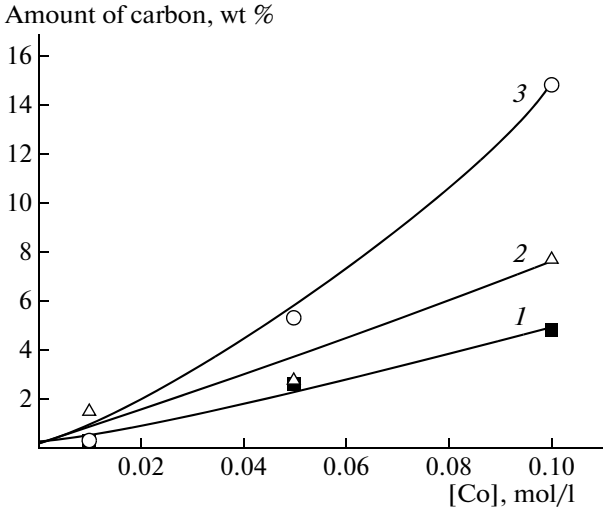

Fig. 6. Amount of carbon synthesized on catalysts prepared by the IMPR-2 method and dried (*1*) with an IR lamp, (*2*) in a microwave oven, and (*3*) in flowing nitrogen as a function of the nickel nitrate concentration in the impregnating solution. The Ni content of the catalyst is 0.03–0.05 wt %.

CONCLUSIONS

Impregnation as a method of preparation of supported catalysts needs the impregnation conditions to be optimized with account taken of the nature of the support and active component, as well as the texture characteristic and macrostructure of the support. For preparing active Ni/corundum catalysts for C_3–C_4 alkane pyrolysis in the presence of hydrogen, the optimum conditions ensuring a uniform active component distribution and a high CFC yield are as follows: (1) incipient wetness impregnation; (2) nickel nitrate concentration of 0.05–0.1 mol/l in the impregnating solution; (3) 20–25 vol % glycerol in the impregnating solution, which has to be burned away; (4) rapid drying of the resulting catalysts in a microwave oven. Under these conditions, the active component is distributed most uniformly and the highest carbon yield is 76 (g CFC)/(g Ni). The acidity of the nickel nitrate solution in the pH 5.5–7.0 range has no effect on the supported nickel content of the catalyst and on the carbon yield. The addition of an Al(III) compound to the solution afford a more uniform active component deposition, but decreases the catalytic activity by a factor of >2. Catalyst drying in a microwave oven ensures, on the average, a 2 times higher carbon yield than drying with an IR lamp.

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