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CHEMICAL KINETICS AND CATALYSIS

Catalytic Conversion of Aliphatic Alcohols on Carbon Nanomaterials: The Roles of Structure and Surface Functional Groups

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Abstract—Carbon nanomaterials with the structure of graphene and different compositions of the surface groups are used as catalysts for the conversion of C_2–C_4 aliphatic alcohols. The conversions of ethanol, propanol-1, propanol-2, butanol-1, butanol-2, and *tert*-butanol on carbon nanotubes, nanoflakes, and nanoflakes doped with nitrogen are investigated. Oxidized and nonoxidized multiwalled carbon nanotubes, nanoflakes, and nanoflakes doped with nitrogen are synthesized. X-ray diffraction analysis, X-ray photoelectron spectroscopy, scanning and transmission electronic microscopies, Brunauer–Emmett–Teller method, derivatographic analyses, and the pulsed microcatalytic method are used to characterize comprehensively the prepared catalysts. It was established that all of the investigated carbon nanomaterials (with the exception of nondoped carbon nanoflakes) are bifunctional catalysts for the conversion of aliphatic alcohols, and promote dehydration reactions with the formation of olefins and dehydrogenation reactions with the formation of aldehydes or ketones. Nanoflakes doped with nitrogen are inert with respect to secondary alcohols and *tert*-butanol. The role of oxygen-containing and nitrogen-containing surface groups, and of the geometrical structure of the carbon matrix of graphene nanocarbon materials in the catalytic conversion of aliphatic alcohols, is revealed. Characteristics of the conversion of aliphatic alcohols that are associated with their structure are identified.

Keywords: carbon nanomaterials, catalysis, alcohols, dehydration, dehydrogenation

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INTRODUCTION

Carbon materials, particularly activated carbons, have long been used in catalysis, both as supports and as catalysts. However, the nature of active sites of carbon catalysts has yet to be completely clarified. In contrast to activated carbons, the new generation of carbon nanomaterials (CNMs) has a definite regular structure. Due to their properties (nanodimensions, mesoporosity, and high specific surface), and to the presence of surface functional groups whose compositions are determined by their postsynthetic treatment [1], carbon nanomaterials are used in very different areas of physics, biology, and chemistry, especially in catalysis [2]. These materials are mainly used as active-phase carriers [3–7], since their functional groups serve as adsorption sites for deposited metal atoms, promoting their uniform distribution over the surface of CNMs. However, CNMs themselves serve as catalysts for a number of different processes, e.g., the oxidative dehydrogenation of ethylbenzene [8–11] and light alkanes [12, 13], and for the conversion of aliphatic alcohols [14]. The authors ascribe the catalytic properties of carbon nanomaterials in the above processes to the effect different functional groups have on their surfaces; however, data on the effect of the structure of a carbon matrix itself on one catalytic process or another are sparse and somewhat contradictory. In [14], we investigated the conversion of C_2–C_3 alcohols on nanodiamond (ND) and its oxidized and reduced forms, and showed that nanodiamond is a catalyst for the conversion of aliphatic alcohols, and the oxidative treatment of nanodiamond raises its catalytic activity without changing its high-level selectivity toward the conversion of alcohols into dehydrogenation products. This allowed us to draw conclusions regarding the formation of new catalytic sites on surfaces of ND in the form of bridging carbonyl groups. In this work, we studied the catalytic conversion of C_2–C_4 aliphatic alcohols on three types of nanocarbon materials (oxidized and nonoxidized carbon nanotubes (CNTs, sp^2-hybridization, bent structure), carbon nanoflakes (CNFs, sp^2-hybridization, planar structure), and nanoflakes doped with nitrogen (CNF-Ns). The conversion of aliphatic alcohols (dehydration and dehydrogenation), a reaction used in industry and fine chemical synthesis, is also a test reaction for the presence of acidic and basic sites on the surfaces of catalysts that allows us to correlate the catalytic properties of carbon nanomaterials with their surface chemistries [15–19].

Table 1. Elemental composition (at %) of nanocarbon catalysts by means of XPS

Catalyst	C	O	N	Cl
ND	91.08	7.16	1.74	0.02
CNT	98.89	0.64	0.36	0.02
CNT-AO	98.42	1.4	–	0.02
CNT-NO	89.59	9.35	0.62	0.02
CNF-N	87.34	2.43	9.76	0.02
CNF	98.2	1.8	0.1	0.02

The aim of this work was to study the role played by the geometrical structure of a carbon matrix (planar or bent), and by the composition of the surface functional groups of nanomaterials with the sp^2-carbon structure in the catalytic conversions of alcohols.

EXPERIMENTAL

Ethanol, propanol-1, propanol-2, butanol-1, butanol-2, and *tert*-butanol of special purity grade (Khimmed, Russia) were used as the substrates in the studied catalytic reactions. Oxidized and nonoxidized CNTs, CNF, and CNF-N synthesized in the present work were used as the catalysts. CNMs were synthesized in a reactor consisting of a quartz tube with an inner diameter of 50 mm and a length of 1.5 m, placed in a Carbolite TZF 12/100/90 tube furnace. For the synthesis of CNTs, a $Co_{0.03}Mo_{0.01}MgO$ catalyst was placed in the center of the reactor, and the furnace was heated to a temperature of 750°C for 1 h at a nitrogen flow rate of 200 mL/min. After achieving the set temperature, a nitrogen flow with a rate of 500 mL/min passed through a Drechsel flask filled with hexane was fed to the reactor for 5 h. Nondoped and doped CNFs were synthesized by the pyrolitic decomposition of benzene or acetonitrile, respectively, at a temperature of 900°C over fine-crystalline magnesia catalyst [20]. The obtained CNMs were refluxed in a 15% HCl solution in order to remove the catalyst, then washed with distilled water until neutral pH, and dried at 120°C to a constant weight. The carbon nanotube surfaces were functionalized via the oxidation of CNTs in air at 120°C for 5 h (CNT-AO), and by treating the CNTs with concentrated nitric acid for 9 h (CNT-NO). The obtained oxidized CNTs were washed with distilled water and dried at 120°C.

The purity of carbon nanomaterials was checked by means of synchronous thermal analysis on a STA449PCLUXX device (Netzsch) at an air flow rate of 40 mL/min and a heating rate of 10 K/min. The morphology of carbon nanomaterials was studied by means of scanning electron microscopy (SEM) on a JEOL JSM 6490 LV instrument (JEOL) equipped with an X-ray fluorescent detector. High-resolution electron microscopy studies were performed on a JEM 2100 F/Cs instrument (JEOL). The specific surface, pore structure and size were determined on an Autosorb-1E/QMS analyzer (Quantachrome) using low-temperature nitrogen adsorption data.

The elemental composition and composition of surface groups of the studied catalysts were determined by means of X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra DLD spectrometer using a monochromatic AlK_α radiation at transmission energies of 160 and 40 eV for separate lines. X-ray diffraction analysis (XRD) of carbon nanomaterials was performed on a DRON diffractometer with a CoK_α radiation source. The catalytic conversion of alcohol was investigated using the pulsed microcatalytic method [21]. A quartz tube 0.5 cm in diameter and 14.5 cm long was used as the pulse reactor. A weighed catalyst sample (~50 mg) was placed in the isothermal zone of the reactor (bed height, ~2.5 cm). The temperature in the reaction zone was maintained with an accuracy of ±1 K. Alcohol vapors were injected into the catalytic reactor with a syringe in amounts of ~5 μL. The volume of the injected sample depended on the equilibrium vapor pressure of each alcohol at room temperature. The carrier gas (nitrogen) flow rate was 50 mL/min. The mixture of the products and unreacted alcohol was transferred from the reactor to a column 1.3 m long and 0.5 cm in diameter, filled with a Porapak-N sorbent. The column temperature was 130°C. The products of the conversion of alcohols were analyzed on a Chrom-5 chromatograph equipped with a flame-ionization detector.

RESULTS AND DISCUSSION

SEM and transmission electron microscope (TEM) images of the carbon nanomaterial samples are shown in Fig. 1.

The oxidized and nonoxidized CNTs (Figs. 1a–1d) were more than 5 μm long and 18 to 25 nm in diameter. Carbon nanoflakes, both pure and doped with nitrogen, had identical morphologies and were obtained in the form of rectangular three-to-six-layered graphene planes with rounded corners. They were 25 × 25 nm in size (Figs. 1e and 1f).

The elemental compositions of the studied carbon nanomaterials, obtained from the XPS data, are given in Table 1. The least amount of oxygen is observed in nonoxidized CNTs, and some of the oxygen in the CNTs was, according to the XPS data, bonded with the metal that usually remains in nanotubes during synthesis. The largest content of oxygen was observed in UNT-NOs. The content of surface oxygen-containing groups in CNFs and CNF-Ns was negligible, but it was three to four times higher than in nonoxidized CNTs.

The surface oxygen atoms of CNTs were constituents of surface carbonyl, carboxylic, anhydride, and ester groups, which play the roles of Lewis acid and Lewis base sites in catalysis.

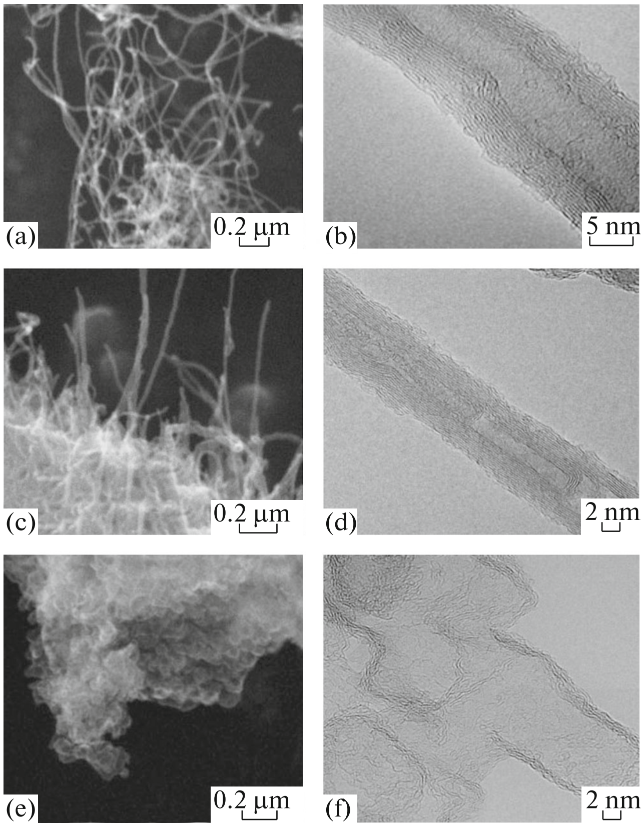

Fig. 1. Electron microphotographs of (a) CNT (SEM), (b) CNT (TEM), (c) CNT-NO (SEM), (d) CNT-NO (TEM), (e) CNF-N (SEM), and (f) CNF-N (TEM) carbon nanomaterials.

Analysis of the spectra of C 1*s*- and O 1*s*-electrons of CNF-Ns showed that the presence of oxygen was basically due to the C–O groups. Nonoxidized CNTs contain nitrogen in the form of pyridine surface groups and quaternary nitrogen, but the content of these groups was negligible (0.36%). The nitrogen content in the oxidized CNTs was higher (0.62%) and mainly represented by quaternary nitrogen (0.29%) and nitrogen bonded with oxygen in the form of NO_3 groups (0.21%). Most of the nitrogen in CNF-Ns fell on quaternary nitrogen included in the CNF structure (3.25%), and on the nitrogen of the surface pyridine groups (2.32%). The content of nitrogen bonded with oxygen was 2.08%.

Table 2. Surface characteristics of *sp*^{2}-carbon nanomaterials according to BET (*V* is pore volume, and *R* is pore radius)

sp^2-CNM	S_{sp}, m^2/g	*V*, cm^3/g	*R*, Å
CNT-AO	197	0.58	18.4
CNT-NO	249	0.58	4.95
CNF	326	2.36	18.6
CNF-N	456	4.88	15.8

The high-resolution O 1*s*- and N 1*s*-spectra are rather complex, and their convolution does not always give an unequivocal answer to the question of what the composition of one group or another is. The use of catalytic reactions, for which it is already known what functional groups are responsible for either catalytic process, allows us to specify the composition of functional groups. The conversion of aliphatic alcohols among such catalytic reactions is quite informative.

The catalytic properties of activated carbons in the conversion of aliphatic alcohols have been studied by many researchers [17, 18, 22–24]. To study these, activated carbons from different sources underwent additional oxidation treatment. It was found that activated carbon catalyzes the conversion of aliphatic alcohols with the formation of dehydration (olefins) and dehydrogenation (aldehydes and ketones) products.

The conversion of aliphatic alcohols on carbon nanomaterials with the *sp*^{2}-carbon structure, specifically CNT, CNF, and CNF-N, were studied in this work. These materials have mesoporous graphene structures with highly developed surfaces (see Table 2).

The conversion of C_2–C_4 alcohols on carbon nanotubes with minimum oxygen content (0.64%) was investigated in [25]. Nevertheless, nonoxidized CNTs yield high degrees of conversion, particularly in the case of secondary alcohols (propanol-2 and butanol-2) and *tert*-butanol.

The temperature dependences of the degree of conversion of alcohols on air-oxidized CNTs are shown in Fig. 2a. Comparison to the similar dependences given in [25] for the degree of conversion of alcohols on nonoxidized CNTs shows that raising the oxygen content on the CNT surfaces from 0.64 to 1.4% increases the degree of conversion. With primary alcohols, it grows substantially, by 35% on average. The temperature curves of the degree of conversion of secondary alcohols and *tert*-butanol, the catalytic activity of which on nonoxidized CNTs is already quite high, are shifted to the lower temperature region. The 100% conversion of *tert*-butanol is moved from 200°C for nonoxidized CNT to 120°C for CNF-AO with the formation of a single product, isobutene. The temperature dependence of the conversion of primary C_2–C_4 alcohols only is shown in Fig. 2b, since nearly 100% conversion is observed for secondary alcohols and *tert*-butanol over the investigated range of temperatures. The products of the conversion of C_2–C_4 alcohols and the selectivity of oxidized and nonoxidized CNTs toward the formation of dehydration and dehydrogenation products are given Table 3.

The main products of the conversion of primary alcohols on nonoxidized CNTs are aldehydes, the selective formation of which in a homologous series of primary alcohols is reduced upon an increase in the number of carbon atoms in an alcohol molecule. The oxidation of CNTs in air does not change the selectiv-

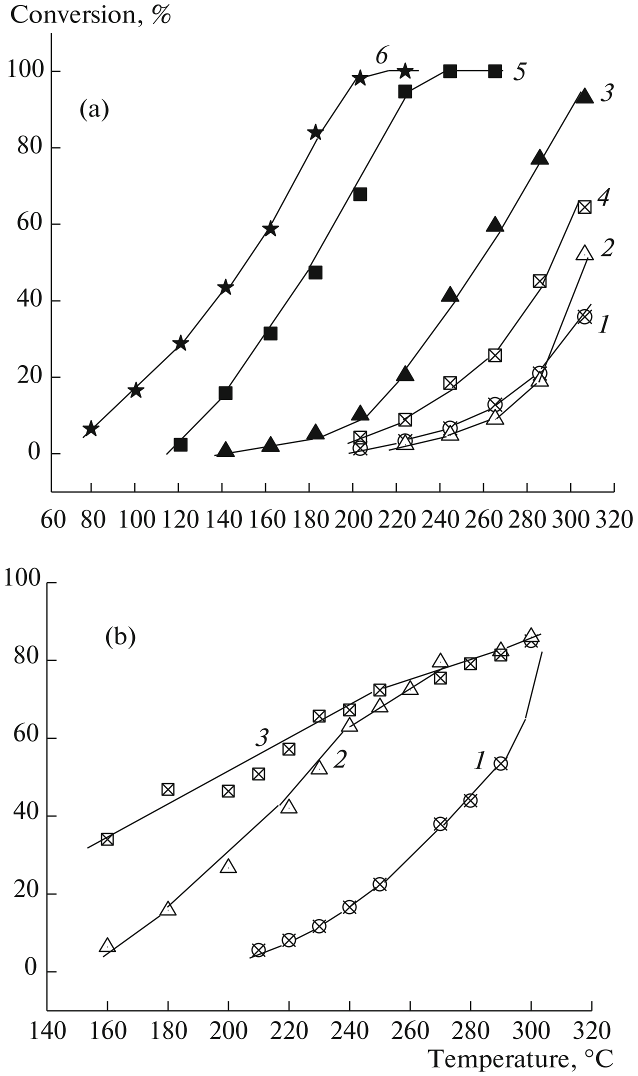

Fig. 2. Temperature dependences of the degrees of conversion of (*1*) ethanol, (*2*) propanol-1, (*3*) propanol-2, (*4*) butanol-1, (*5*) butanol-2, and (*6*) *tert*-butanol on oxidized CNTs; (a) the conversion of all C_2–C_4 alcohols on CNT-AO and (b) the conversion of primary C_2–C_4 alcohols on CNT-NO.

ity toward the formation of acetic aldehyde in the case of ethanol; it somewhat lowers the selectivity of the formation of propionaldehyde from propanol-1; and it substantially reduces the selectivity of the formation of butyraldehyde in the case of butanol-1 (from 71 to 48%). To a lesser extent, the oxidation of CNT in air affects the selectivity of the formation of conversion products from secondary alcohols. A high selectivity toward the dehydration products (70% for propanol-2 and 88% for butanol-2) is observed with nonoxidized CNTs and CNT-AO.

Oxidizing CNTs with nitric acid for 9 h greatly changed the selectivity of the formation of dehydration products from primary and secondary alcohols toward products of dehydration. With propanol-2, butanol-2, and *tert*-butanol, 100% conversion and 100% selectivity toward the formation of dehydration products were preserved over the investigated range of temperatures. The temperature dependences of the conversion of primary alcohols on CNT-NO are given in Fig. 2b. With ethanol, the selectivity toward the formation of dehydration products grew from 3% on nonoxidized and air-oxidized CNTs to 88% on CNT-NO. The selectivity toward the formation of dehydration products from propanol-1 and butanol-1 on CNT-NO was close to 100%, but considerably lower on nonoxidized and air-oxidized CNTs: 26% for propanol-1 and 28% for butanol-1 on nonoxidized CNTs, and 35% for propanol-1 and 52% for butanol-1 on air-oxidized CNTs.

Nondoped CNFs and CNTs (sp^2-hybridization) have the same carbon structure but different morphologies. The graphene layers in nondoped CNFs are planar, but are rolled into tubes in CNTs. The specific surface area of nondoped CNFs is much larger than those of any of the investigated types of CNTs. According to the XPS data, nondoped CNFs are 1.8% oxygen. This value exceeds the oxygen content in nonoxidized and air-oxidized CNTs. The surface characteristics of carbon nanomaterials with the sp^2-carbon structure, determined by the Brunauer–Emmett–Teller (BET) method, are given in Table 2. The specific surface area of nondoped CNFs considerably exceeds this value for nonoxidized and oxidized carbon nanotubes; nevertheless, nondoped CNFs displayed no catalytic activity in the conversion of the investigated C_2–C_4 alcohols. The large specific surface area and high porosity of carbon materials are still insufficient for displaying catalytic activity. The presence of oxygen-containing groups is also not enough for catalysis. It is important which kind of functional groups include oxygen. Based on the composition of products from the conversion of alcohols, and on an analysis of high-resolution XPS spectra, these are carboxylic, carbonyl, ester, and anhydride groups in the case of CNTs. The absence of catalytic activity of nondoped CNFs indicates these kinds of groups are not found on their surfaces. Oxygen-containing groups in CNFs are most likely C–OH groups, which are not active in acid–base catalysis. CNF-Ns have developed surfaces (456 m^2/g) and are 2.43% oxygen; this greatly exceeds the oxygen content in nonoxidized and air-oxidized CNTs. However, CNF-Ns are inert in the conversion of secondary alcohols and *tert*-butanol. They display catalytic activity only in the conversion of primary alcohols. The temperature dependences of the degrees of conversion of ethanol, propanol-1, and butanol-1 on CNF-N are shown in Fig. 3.

As can be seen from Fig. 3, the conversion of primary alcohols on CNF-Ns proceeds only at relatively high temperatures, and the degree of its completion is not as high as when using CNTs. The character of conversion differs from that on CNTs. While ethanol displays high selectivity toward the formation of acetaldehyde on nonoxidized and air-oxidized CNTs, the products of the conversion of ethanol on CNF-Ns are diethyl ether and, to a lesser extent, ethylene (Fig. 4). The concentration of acetaldehyde does not exceed 0.5%. As for propanol-1 and butanol-1, the selectivity toward the formation of dehydrogenation products in their conversion on CNF-Ns is in contrast higher than in their conversion on CNTs: the selectivity of the formation of propionaldehyde from propanol-1 is 89% at a 49% degree of conversion, and the selectivity of the formation of butyraldehyde from butanol-1 reaches 63 at a 66% degree of conversion. This difference in selectivity for ethanol is perhaps due to the character of its adsorption on CNF-N surfaces, which is determined in turn by the differences in the polarizability of alcohols growing along with the number of carbon atoms in the alcohol hydrocarbon chain. The probability of the dissociation of the adsorbed alcohol molecules increases upon an increase in polarizability. CNF-Ns are 9.76% nitrogen; based on the high-resolution XPS data, it is present on their surfaces in the form of quaternary nitrogen, the nitrogen of pyridine bases, and nitrogen bonded with oxygen. The conversion of linear C_1–C_4 alcohols on nonporous carbon fibers, and on CNFs synthesized from polyacrylonitrile and modified by means of electrochemical and oxidizing treatment, were investigated in [19] by means of programmed thermal desorption. In contrast to our results, the authors of that work did not observe the formation of dehydration products. The adsorption behaviors of linear alcohols on CNF-Ns and on nonporous carbon fibers are apparently different. The catalytic function was attributed to the formed oxygen-containing surface groups, while the effect of nitrogen-containing groups was not considered.

Table 3. Selectivity (*S*) and the composition of the products of conversion of C_2–C_4 aliphatic alcohols on oxidized and nonoxidized CNTs (α is the maximum degree of conversion)

Alcohol	T, °C	α, %	S_{H_2}, %	S_{H_2O}, %
CNT				
Ethanol	200–300	35.8	97.0	3.0
Propanol-1	220–300	53.0	74.0	26.0
Propanol-2	140–300	93.0	29.9	70.1
Butanol-1	200–300	64.5	71.4	28.6
Butanol-2	120–240	100	11.6	88.4
tert-Butanol	50–220	100	–	100
CNT-AO				
Ethanol	180–300	58.8	97.0	3.0
Propanol-1	160–300	73.6	65.3	34.7
Propanol-2	130–300	99.5	25.6	74.4
Butanol-1	120–280	100	48.2	51.8
Butanol-2	130–250	100	93.0	90.7
tert-Butanol	50–200	100		100
CNT-NO				
Ethanol	210–300	85.0	12.0	88.0
Propanol-1	160–300	86.0	7.2	92.8
Propanol-2	50–100	100		100
Butanol-1	160–300	71.0	3.4	96.6
Butanol-2	50–150	100		100
tert-Butanol	50–160	100		100

The characteristics of the conversion of aliphatic alcohols on CNTs and CNF-Ns are most likely associated with the structural features of their carbon matrices. As was mentioned above, CNTs consist of graphene planes, modified by rolling into tubes in which carbon is in the sp^2-hybridization state. The rolling changes their electronic properties in comparison to graphite and alters the π-electron cloud [9]. In addition, the rolling of graphene planes creates defects in the form pentagonal and heptagonal rings, and vacancies in the stable hexagonal carbon structure. The probability of defects forming in multiwalled CNTs is higher, since the rolling of each tube contributes to the formation of defect sites. As catalysts, CNTs thus contain two types of active sites: oxygen-containing surface groups, which are not so numerous in nonoxidized CNTs, and defects of the carbon structure itself. A less significant change in selectivity toward the formation of dehydration and dehydrogenation products during the conversion of alcohols on air-oxidized CNTs indicates that the ratio of Lewis acid and Lewis base sites basically remains unchanged upon an increase in the number of oxygen-containing groups; i.e., oxidation in air increases the number of both Lewis acid and Lewis base sites. Oxidizing CNTs with nitric acid for 9 h results in the oxidation of not only the available carbonyl, ester, and other groups that serve as Lewis base sites, but also in the formation of new Lewis acid sites. This is confirmed by the 100% conversion and 100% selectivity toward the formation of dehydration products from secondary alcohols and *tert*-butanol, and by the substantial increase in selectivity towards the formation of dehydration products from primary alcohols.

We may assume that the absence of catalytic activity in the conversion of alcohol on CNFs is associated with both the type of oxygen-containing groups and the lack of those defect sites that are available on the surfaces of CNTs. We also cannot exclude the possibility that the absence of catalytic activity is due to the character of adsorption of alcohol on CNFs. Despite the high specific surface areas of CNFs, alcohol molecules can be adsorbed but not chemisorbed on them with the formation of a catalytic complex. Doping CNFs with nitrogen adjusts their catalytic activity with respect to the conversion of alcohols. The catalytic activity in the conversion of primary alcohols and its absence in the conversion of secondary alcohols must

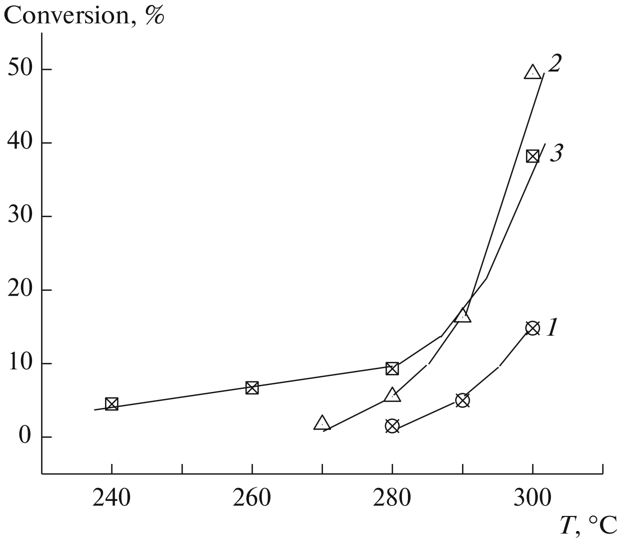

Fig. 3. Temperature dependences of the degrees of conversion of (*1*) ethanol, (*2*) propanol-1, and (*3*) butanol-1 on CNF-N.

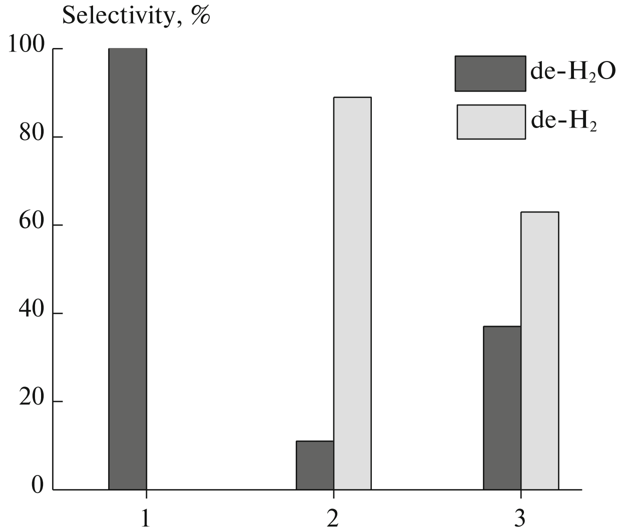

Fig. 4. Selectivity of CNF-N toward the formation of dehydration and dehydrogenation products in the conversion of primary alcohols at 300°C: (*1*) ethanol, (*2*) propanol-1, and (*3*) butanol-1.

be due to the presence of nitrogen groups in CNF-Ns, which include different forms of nitrogen contained both in the carbon matrix structure (quaternary nitrogen and the nitrogen of pyridine bases) and in the form of surface NO_2 and NO_3 groups bonded with carbon atoms. Nitrogen atoms provide additional electron density affecting the catalytic activity. However, the catalytic activity of CNF-Ns is apparent only in the conversion of primary alcohols with the formation of dehydrogenation products from propanol-1 and butanol-1. The bond dissociation energies of the O–H bonds in aliphatic alcohols are close; they vary from 104.7 kcal/mol for ethanol to 106.3 kcal/mol for *tert*-butanol [26]. The absence of catalytic activity of CNF-Ns in the conversion of propanol-2, butanol-2, and *tert*-butanol is most likely associated with the adsorption ability of nonlinear alcohols (secondary and tertiary) on CNF-Ns, which is determined in turn by the molecular structure of these alcohols; i.e., steric factors come into play.

CONCLUSIONS

Comparative analysis of the conversion of C_2–C_4 aliphatic alcohols on carbon nanomaterials with the sp^2-carbon configuration shows that CNTs are effective catalysts for the conversion of alcohols, while CNFs do not display catalytic activity. This leads us to conclude that the morphological features of the CNT carbon structure that are associated with its curvature resulting in the formation of defects which serve as catalytic active sites play a key role in catalysis. The structure of oxygen-containing surface groups in CNTs and CNFs are different. While CNTs contain surface functional groups able to serve as Lewis acid and Lewis base sites, the surface groups on CNFs display no such properties. Hence, both the carbon surfaces themselves and their oxygen-containing groups perform catalytic functions in CNTs. The oxidation of CNTs leads to the appearance of new catalytic sites, as is revealed in increased activity and a change in selectivity toward the formation of dehydration products. CNF-Ns synthesized by the pyrolysis of acetonitrile contain nitrogen in their elemental composition, the presence of which affects their catalytic function. Only primary alcohols are converted on CNF-Ns, making this a characteristic trait of the conversion of C_2–C_4 alcohols on such catalysts. Propanol-2, butanol-2, and *tert*-butanol are apparently not converted on CNF-Ns, due to the nonlinear structure of these alcohols.

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