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# Catalytic Conversion of C<sub>2</sub>–C<sub>3</sub> Alcohols on Detonation Nanodiamond and Its Modifications

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## Abstract

The catalytic activity of detonation nanodiamond and its modifications obtained through treatment with hydrogen or air at elevated temperatures is studied in the conversion of C<sub>2</sub>–C<sub>3</sub> alcohols. The catalysts were characterized by means of electron microscopy, optical (FTIR) spectroscopy, elemental analysis and pulse microcatalytic method. It has been established that nanodiamond exhibits high catalytic activity in the conversion of alcohols. The oxidizing and reducing treatment of nanodiamond changes its activity and selectivity, and the activity of oxidized nanodiamond is considerably higher than that of reduced nanodiamond.

*Keywords:* catalysis, nanodiamond, alcohol, dehydrogenation, dehydration.

## INTRODUCTION

Detonation nanodiamond has a number of unique and specific properties that distinguish it from diamonds of other types, since many of its properties are determined more by the state of the surface than the properties of diamond crystals and diamond powders [1, 2]. A feature of this material is that it combines the mechanical, thermal, radiation and chemical stability of diamond and the lability of a functional surface coating. The latter creates the prerequisites for creating new functional materials based on it and its application in various fields of science and technology [3]. Expanding studies of nanodiamond properties could lead to the discovery of its new properties and, hence, new fields for its application, e.g., as sorbents for the sorption of radionuclides and for purification and separation of proteins; in developing biosensor controls and biochips for use in microbiology and medicine; and in catalysis.

The carbon materials used in catalysis usually have a graphite structure (activated coal, soot, activated carbon fibers, carbon aerogels and xerogels, etc.) [4]. Most often they are used as carriers of an active phase - metals and oxides. The authors of many works consider that the feature of the structures formed by carbon atoms in the state of  $sp^2$  hybridization favors the manifestation of specific catalytic activity. In fact, in connection with obtaining various forms of nanocarbon (including carbon nanotubes), their catalytic activity, even without deposited metals, has been recently revealed. Examples of the catalytic action of various metal free forms of nanocarbon in the oxidative dehydrogenation of ethylbenzene were presented in [5]. The authors of [4, 5] believe that the manifestation of the catalytic properties of nanocarbon is due to the presence of certain functional groups on its surface.

The diamond materials formed by carbon atoms in the state of  $sp^3$  hybridization and having another crystal structure were hardly used in catalysis before the appearance of detonation nanodiamond. With its high specific surface, nanodiamond was mainly used as a nanostructured carrier for the metal phase in catalysts for the hydrodechlorination of organochlorine compounds [6] or the oxidative dehydrogenation of ethyl benzene [5]. The data on the catalytic activity of nanodiamond itself, metal free are extremely poor. The authors of [7] studied the oxidative dehydrogenation of ethylbenzene in its presence, and the kinetic parameters of this reaction in the presence of carbon nanotubes and nanodiamond, which appeared to be very close, were compared in [5, 8].

To test the catalytic activity of carbon materials and study the effect of the chemical state of the surface on their activity and selectivity, we usually use the model reaction of the conversion of aliphatic alcohols, which can transform in two directions: dehydrogenation and dehydration. The conversion of aliphatic alcohols on carbon materials subjected to different oxidizing treatments was investigated in [9–16]. It was shown in [10] that the products of the conversion of propanol-2 on activated coals obtained from lignocellulose and treated with  $H_3PO_4$  were only products of dehydration. The formation of products of dehydration only was also observed [14–16] in the conversion of methanol and ethanol on activated coals oxidized by various types of oxidizers. The conversion of butanol-2, propanol-2, methanol, and ethanol on activated coals obtained from poly(furfuryl-alcohol) proceeded with the formation of products of the dehydration and dehydrogenation [11–13], and the oxidizing of the catalyst increased the yield of products of dehydration. All of the authors who have studied the conversion of alcohols on carbon catalysts are of the same opinion that the active centers of the reaction of dehydration on the carbon surface are carboxyl groups [9, 10], while the simultaneously present Lewis acidic and basic centers are responsible for the reaction of the dehydrogenation

of alcohols [11–13].

It is known [1, 2] that the chemical state of the surface of nanodiamond, just as for other carbon materials, is determined by the conditions of their preliminary processing (modification). The purpose of this work is to learn whether nanodiamond (without metal deposited on it) exhibits catalytic activity in the conversion of alcohols, and how preliminary gas phase thermal treatment (modification) affects it.

## EXPERIMENTAL

UDA STP brand detonation nanodiamond manufactured by JSC Diamond Center (St. Petersburg, Russia) was used in our experiments. The content of diamond carbon in the nanodiamond was 98.2%, that of nondiamond was 1.1%, and that of incombustible residue was 0.7% (ignoring heteroatoms of H, O, and N). Nanodiamond was reduced on a flowing apparatus at 800°C for 5 h. The nanodiamond powders were oxidized with air on the same apparatus at 450°C for 5 h. Aliphatic C<sub>2</sub>–C<sub>3</sub> alcohols were selected to study the catalytic activity of nanodiamond: ethanol, propanol-1 and propanol-2. All of the alcohols were of chemically pure grade.

Electron microscopy images of the nanodiamond particles were obtained on transmission (LEO912 AB OMEGA) and scanning (Hitachi S520) electron microscopes. The elemental analysis of the nanodiamond samples was performed on an EA 1105 C–H–N–O–S analyzer (Carlo Erba). The chemical composition of the surface of the nanodiamond samples was analyzed using Auger spectra obtained on a Microlab MK II spectrometer (VG Scientific) with monochromatized X ray AlK $\alpha$  radiation (1486.6 eV). The technique for sample preparation is described in [17]. Infrared (IR) spectra of the nanodiamond samples were recorded in tablets with KBr on a ThermoNicolet IR200 IR spectrometer with Fourier transform. The resolution was 4 cm<sup>-1</sup>; the scan number, 32. The absorption bands were assigned using the data in [18, 19]. The specific surface of the nanodiamond samples after their preliminary heating at 120°C in a vacuum of 10<sup>-3</sup> mm Hg was determined by BET from the low temperature adsorption of nitrogen with an accuracy of  $\pm 1$  m<sup>2</sup>/g.

The catalytic conversion of alcohols on nanodiamond was studied using pulse microcatalytic method. This technique is described in detail in [20]. A catalytic setup was assembled on the basis of a Chrom-5 chromatograph. The pulse reactor was a quartz tube with the diameter of 0.5 cm and 14.5 cm long. A sample of nanodiamond (50 mg) was placed in the isothermal zone of the reactor (layer height, ~2.5 cm). The temperature in the reaction

zone was maintained with an accuracy of  $\pm 1$  K. Alcohol vapors were introduced in the catalytic reactor by means of a syringe. The volume of introduced probe depended on the value of the equilibrium pressure of each alcohol at room temperature [21]. The amount of introduced alcohol was 5  $\mu\text{mol}$ . The flow rate of the carrier gas (nitrogen) was 30 ml/min. Products of the conversion of alcohols were analyzed on the Chrom-5 chromatograph with a flame ionization detector. Mixture of the products and nonreacted alcohol from the reactor passed into a chromatographic column 1.3 m long with a diameter of 0.5 cm and containing Porapak N. The temperature of the column was 130°C.

## RESULTS AND DISCUSSION

Our nanodiamond samples were grey powders in which diamond particles were aggregates with sizes of up to 100  $\mu\text{m}$  (Fig. 1a). According to the data from transmission electron microscopy, these aggregates consisted of primary particles with approximately spherical form  $\sim 5$  nm in size (Fig. 1b). It should be noted that the size distribution was rather narrow: all of the primary particles had almost the same size of  $\sim 5$  nm. It should be noted that large aggregates ( $>20$   $\mu\text{m}$ ) are mechanically fragile and are easily destroyed by mechanical, chemical or ultrasonic impact to aggregates with sizes of 50–100 nm, which are more stable under these conditions. According to the data from transmission electron microscopy, the size of the primary diamond particles after gas phase treatment did not change. The values of the specific surface of nanodiamond and its modifications are given in Table 1. The increase in the specific surface could be related to the destruction of the aggregates due to the change of the nature of the functional groups upon treatment and the reduction in the strength of the linkage of particles in aggregates. The change in the constant  $C$  value in the BET equation indicates a change in the adsorption properties of the nanodiamond surface as well. The structural characteristics of the modified nanodiamonds are described in detail in [22].

The functional coating of the diamond particles in the initial samples was formed during its purification with diluted nitric acid. The intense band of the surface hydroxyl groups coupled by the hydrogen bonds and adsorbed water with a wide maximum at  $3400\text{ cm}^{-1}$  is present in the absorption spectrum of the initial nanodiamond (spectrum *I* in Fig. 2). Low intensity bands are observed in the region of the valence vibrations of the C–H bonds ( $2800\text{--}3000\text{ cm}^{-1}$ ). The  $1737\text{ cm}^{-1}$  band is due to the presence of carbonyl groups ( $>\text{C}=\text{O}$ ) on the surface. The deformation vibrations of hydroxyl groups, both on the sample surface and in the water

adsorbed on it, are observed at  $1617\text{ cm}^{-1}$ . After treating of nanodiamond with air (spectrum 2), the band at  $1737\text{ cm}^{-1}$  corresponding to the vibration of the carbonyl groups is shifted considerably to the higher wavenumbers ( $1791\text{ cm}^{-1}$ ), indicating the formation at  $400^\circ\text{C}$  of the bridging C–O–C bonds adjoining the carbonyl groups [23], e.g.,



The absorption band of the carbonyl groups completely disappears in the IR spectrum (spectrum 3) after modification of the nanodiamond by hydrogen, but intense absorption bands at  $2941$  and  $2877\text{ cm}^{-1}$  appear, indicating the formation of new C–H bonds on the  $sp^3$  hybridized carbon atom. The elemental composition of both the nanodiamond and its surface after gas phase treatment changed as well. The obtained data are given in Table 2.

The conversion of alcohols on the nanodiamond samples described above was studied at temperatures of  $180\text{--}350^\circ\text{C}$ . It was established that the catalytic conversion of ethanol, propanol-1, and propanol-2 in the presence of nanodiamond and its modified forms proceeds via two channels: (a) dehydration with the formation of ethylene (from ethanol), propylene (from propanol-1 and propanol-2), and dipropyl ether (from propanol-1), and (b) dehydrogenation with the formation of acetaldehyde (from ethanol), propanal (from propanol-1), and acetone (from propanol-2). The temperature dependences of the conversion of these alcohols and the selectivity of their transformations over the products of dehydrogenation in the presence of nanodiamond and its modifications are given in Fig. 3.

#### Study of the catalytic conversion of alcohols.

The temperature dependences of the degree of conversion were revealed on the basis of the obtained data. The comparative characteristics of the conversion of alcohols in the presence of the modified forms of nanodiamond are presented in Table 3. In contrast to the data on the conversion of alcohols on the carbon suppresses the process of the dehydrogenation), in the case of nanodiamond the selectivity to the products of the dehydrogenation of the conversion of  $\text{C}_2\text{--C}_3$  alcohols is considerably higher. It can be seen in Fig. 3 and Table 3 that the oxidizing treatment of the nanodiamond surface with oxygen of air considerably increases the conversion of propanol-2, from 28 to 100% at  $330^\circ\text{C}$ . The selectivity towards acetone rises from 88.9 to 94.2%. The conversion of propanol-1 also increases on the oxidized nanodiamond, from 28.5 to 92.6%. The reduction of the selectivity to propanal for propanol-1 at high temperatures is related to the formation of the dipropyl ether and is probably due to features of the

adsorption of propanol-1 on active nanodiamond centers that favor the occurrence of intermolecular dehydration. The conversion of ethanol and its selectivity to acetaldehyde (which is close to 100%) are the same on both nonmodified and oxidized nanodiamond forms, while the reducing treatment leads to a decrease in conversion, preserving the selectivity to acetaldehyde.

The authors of [10–16] explained the preferable formation of products of the dehydration of alcohols on the activated coals by the formation of carboxyl groups on carbon surfaces, which are strong acid centers. A comparison of the IR spectra of initial nanodiamond and its oxidized form shows the formation of surface carbonyl groups of the bridging type. The treatment of nanodiamond with hydrogen leads to the reduction of the carbonyl groups, and this dramatically reduces the degree of conversion of all the investigated alcohols. Nanodiamond and its modified forms exhibit high selectivity to the products of dehydrogenation in the conversion of alcohols. This is apparently related to the features of the nanodiamond structure where carbon, unlike activated coal and carbon nanotubes, is in the state of  $sp^3$  hybridization, and the functional groups are distributed over the entire surface of the nanodiamond particles.

In studying the conversion of  $C_2$ – $C_3$  alcohols, we established that detonation nanodiamond is an active catalyst in the conversion of alcohols. Oxidizing treatment of a nanodiamond surface with atmospheric oxygen considerably raises its catalytic activity in the conversion of  $C_3$  alcohols and does not affect the conversion of ethanol. This is due to the appearance of new active centers in the form of the bridging type carbonyl groups for  $C_3$  alcohols on the nanodiamond surface as a result of oxidation. Treating a nanodiamond surface with hydrogen leads to a lowering of the catalytic activity of the nanodiamond due to a reduction in the number of carbonyl groups. In addition, we have shown that in contrast to activated coals, the conversion of alcohols on nanodiamond leads to the preferable formation of products of dehydrogenation.

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**Table 1.** Change of the specific surface ( $s_{sp}$ ) of UDA STP and constant  $C$  in the BET equation after the modification of nanodiamond

Nanodiamond	$s_{sp} \pm 1, \text{m}^2/\text{g}$	$C$
Initial	240	458
Reduced	253	349
Oxidized	254	572

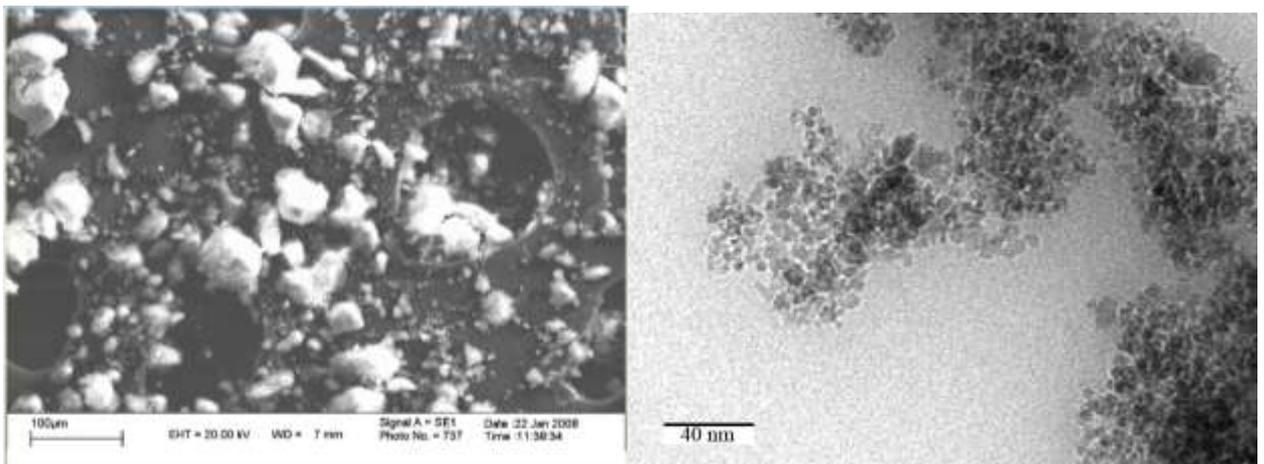
**Table 2.** Effect of gas phase treatment on the general elemental composition of nanodiamond and the elemental composition of its surface

Nanodiamond	General composition, wt %				Surface composition, at %		
	C	N	H	O + i.r.	C	O	N
Initial	88.4	3.2	0.2	8.2	89	9	2
Oxidized	87.8	2.9	0.1	9.2	86	12	2
Reduced	91.6	2.4	0.5	5.5	98	1	1

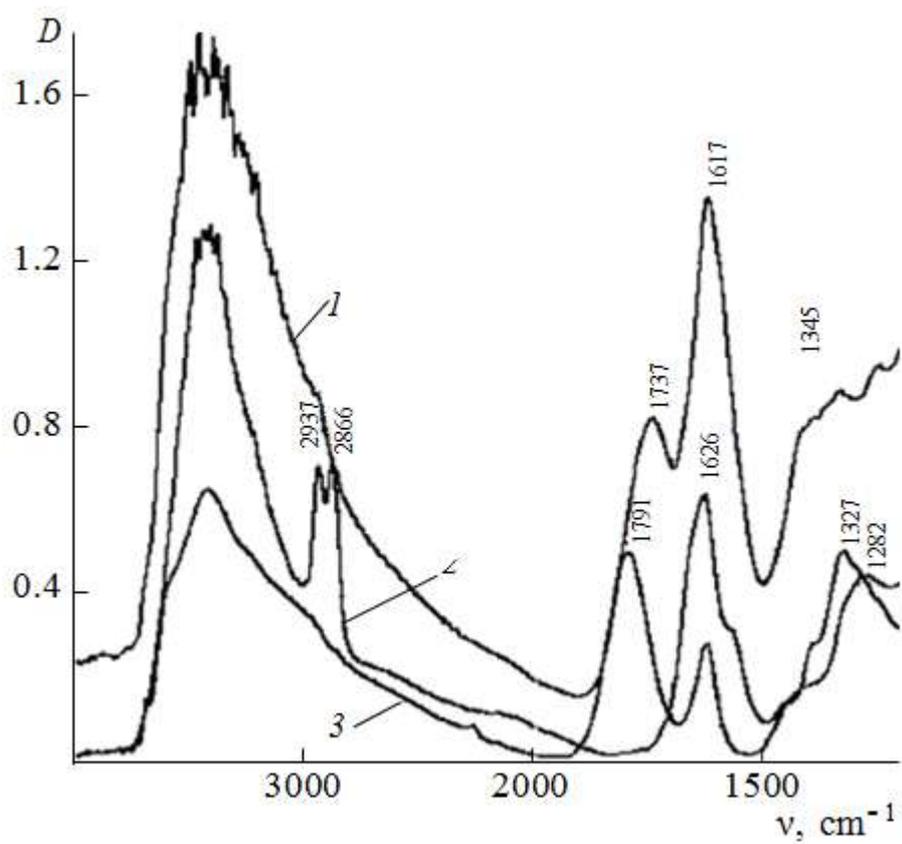
Note: The oxygen content in the general composition was calculated from the difference. Since the content of incombustible residue (i.r.) in the samples was constant (~1 wt %), the numbers in this column characterize the change in the oxygen content.

**Table 3.** Comparative characteristics of the conversion of alcohols in the presence of nanodiamond (ND): temperature at the start of conversion ( $T_{\text{start}}$ ); degree of conversion at 330°C ( $\alpha$ ); yield of the products of the dehydrogenation ( $y_1$ ) and dehydration ( $y_2$ ) at 330°C; selectivity of reaction to the dehydrogenation channel at 330°C ( $S$ )

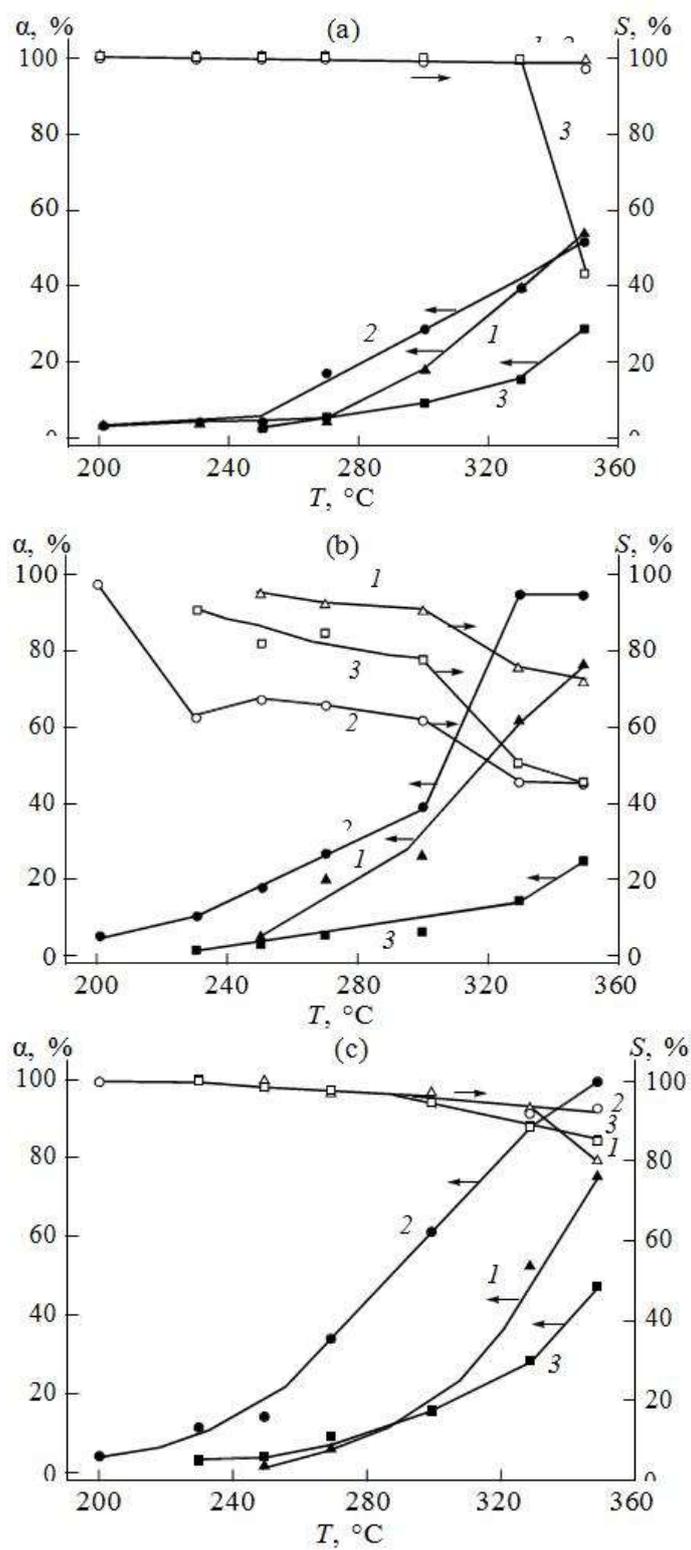
Alcohol	$T_{\text{start}}$ , °C	$\alpha$ , %	$y_1$ , %	$y_2$ , %	$S$ , %
Initial ND					
Ethanol	250	39.9	39.5	0.4	99.0
Propanol-1	220	28.5	23.4	5.1	82.1
Propanol-2	230	28.0	24.9	3.1	88.9
Oxidized ND					
Ethanol	200	39.7	39.4	0.3	99.2
Propanol-1	200	92.6	44.0	48.6	47.5
Propanol-2	200	100	94.2	5.8	94.2
Reduced ND					
Ethanol	250	15.5	15.4	0.1	99.3
Propanol-1	250	10.5	7.3	3.2	69.5
Propanol-2	250	17.0	15.8	1.2	92.9



**Fig. 1.** Microphotos of a sample of the initial nanodiamond, obtained on (a) scanning and (b) transmission electron microscopes.



**Fig. 2.** IR absorption spectra of nanodiamonds: 1, initial; 2, reduced; 3, oxidized.



**Fig. 3.** Temperature dependence of the conversion of (a) ethanol, (b) propanol-1, and (c) propanol-2, and selectivity to the products of the dehydrogenation in the presence of nanodiamonds: 1, initial; 2, oxidized; 3, reduced.