

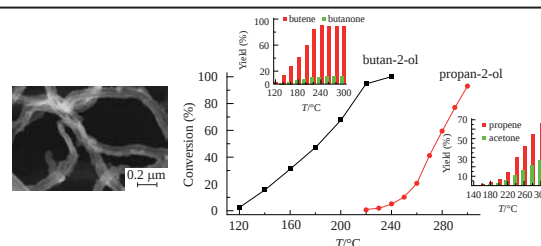
Catalytic conversion of propan-2-ol and butan-2-ol on carbon nanotubes with different carbon structures

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Cylindrical and conical carbon nanotubes were used as catalysts for the conversion of C_3 – C_4 secondary aliphatic alcohols. The effect of the oxidative and reductive treatment of carbon nanotubes on the catalytic activity, selectivity and the conversion of propan-2-ol and butan-2-ol related to the structure of carbon matrix was revealed.



Keywords: cylindrical and conical carbon nanotubes, alcohol conversion, secondary alcohols, catalysis.

In contrast to activated carbons, carbon nanomaterials (CNMs) have a well-defined organized microstructure, which depends on synthesis methods. These materials are used as catalyst supports^{1–5} because surface functional groups are adsorption centers for supported metal atoms. However, CNMs catalyze a number of processes such as the oxidative dehydrogenation of ethylbenzene^{6–11} and light alkanes^{12,13} and the conversion of aliphatic alcohols^{14,15} and furfuryl alcohol in the presence of ethanol.¹⁶ The catalytic properties of CNMs in these processes are due to various functional groups on their surface. Oxygen atoms in the carbonyl, carboxyl, anhydride and ether surface groups of CNMs play the role of Lewis acid and basic sites in catalysis.^{17,18} The effect of a carbon matrix on the catalytic conversion of secondary alcohols is poorly understood. It is well known that the dehydration and dehydrogenation of secondary aliphatic alcohols proceed at Lewis acid and basic sites, respectively.^{19–27} Carbon nanofibers structurally similar to the carbon skeleton (fishbone) of conical CNTs were used as carriers for an active metal phase.^{28–31} The catalytic activity of conical CNTs was reported previously.²⁷ The purpose of this work was to study the kinetics of propan-2-ol and butan-2-ol conversion on CNTs after oxidative and reductive treatments.

The catalytic experiments with propan-2-ol and butan-2-ol were performed using unoxidized and oxidized cylindrical and conical CNTs[†] synthesized according to a published procedure.³² The diameter of the unoxidized cylindrical CNTs was 5–30 nm, and the length varied from hundreds of nm to several microns. The diameter of the unoxidized conical tubes was 5–80 nm, and the length was several microns. The surface oxidation of cylindrical and conical CNTs was carried out by treatment with a concentrated solution of nitric acid followed by washing with distilled water and drying at 120 °C. The spent catalysts were regenerated by passing a flow of hydrogen through the reactor with a catalyst sample for 3.5 h at 300 °C and a flow rate of 70 ml min^{–1}. The micrographs

and compositions of CNT samples are given in Online Supplementary Materials.^{‡,§} The catalytic conversion of alcohols was investigated by a pulsed microcatalytic method.[¶] The apparent activation energies of the conversion of the alcohols were calculated using the Habgood–Bassett formula.¹⁴

An analysis of the high-resolution C 1s and O 1s spectra of cylindrical and conical CNTs has revealed that the surface oxygen atoms of the CNTs are the constituents of carbonyl, carboxyl, anhydride and ether surface groups, which serve as Lewis acid and basic sites in catalysis. Figure 1 shows the conversion of propan-2-ol and butan-2-ol on unoxidized cylindrical (0.64% O) [Figure 1(a)], unoxidized conical (2.35% O) [Figure 1(b)] and oxidized conical (9.41% O) CNTs [Figure 1(c)].

Selectivity for the products of propan-2-ol and butan-2-ol conversion is given in Table 1. On cylindrical CNTs, dehydration products (propene and but-2-ene) were predominantly formed. Selectivity for dehydration products increased with the oxygen content of surface functional groups. In the conversion of propan-2-ol on CNTcyl with 9.35% oxygen, 100% selectivity for propene was observed, and the conversion of butan-2-ol on CNTcyl occurred with 100% selectivity for but-2-ene already at an oxygen content of 1.4%. The conversion on unoxidized CNTcon

[†] The morphology of carbon nanomaterials was determined by scanning electron microscopy on a JEOL JSM 6490 LV (JEOL) instrument equipped with an X-ray fluorescence detector. High-resolution electron microscopy was performed on a JEM 2100 F / Cs (JEOL) instrument.

[§] The X-ray phase analysis of CNTs was carried out on a DRON diffractometer using CoK α radiation. The X-ray photoelectron spectroscopy was performed on a Kratos Axis Ultra DLD instrument with monochromatic AlK α radiation and transmission energies of 160 and 40 eV for individual lines.

[¶] The pulsed catalytic reactor was a quartz tube with a diameter of 0.5 cm and a length of 14.5 cm. A catalyst portion (~0.08 mg) was placed in the isothermal zone of the reactor. The analysis of alcohol conversion products was carried out on a Chrom-5 chromatograph with a flame-ionization detector and a Poropak-N column (length, 1.4 m; diameter, 0.5 cm) at a column temperature of 130 °C.

[†] High-purity propan-2-ol and butan-2-ol (Reakhim, Russia) were used. The purity of CNTs was determined by synchronous thermal analysis on an STA449PCLUX instrument (Netzsch).

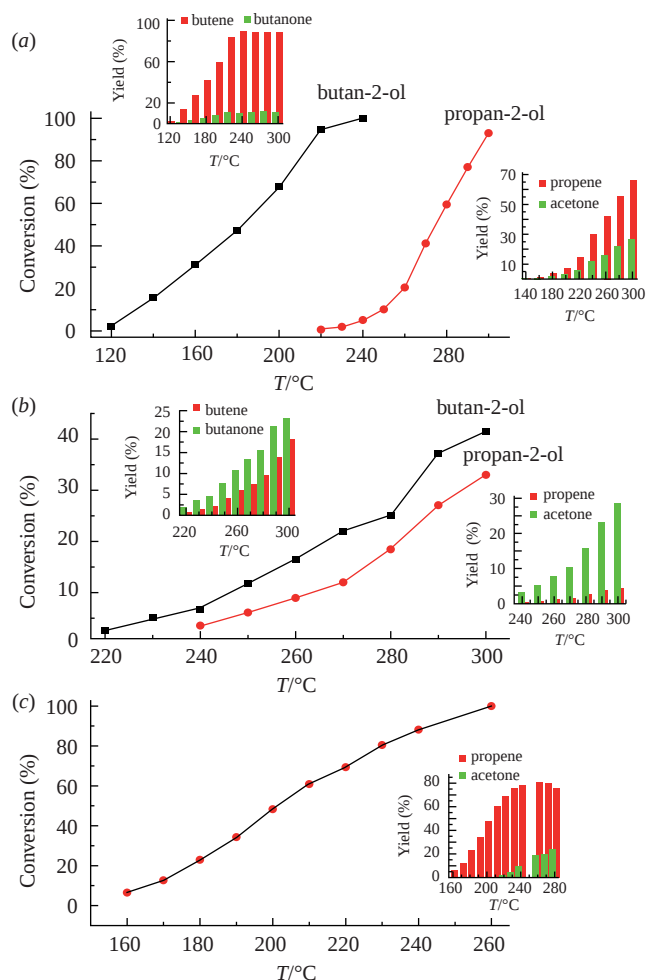


Figure 1 Temperature dependence of the conversion and product yields for propan-2-ol and butan-2-ol on (a) unoxidized cylindrical (0.64% O), (b) unoxidized conical (2.3% O) and (c) propan-2-ol on oxidized conical (9.41% O) CNTs. The conversion of propan-2-ol and butan-2-ol on oxidized cylindrical CNTs (9.35% O) was 100% over the entire test temperature range.

with 2.59% oxygen at 300 °C was 33% for propan-2-ol and 41.5% for butan-2-ol. For the conversion of propan-2-ol and butan-2-ol on unoxidized CNTcon over the entire temperature range, selectivity for dehydration products was 14 and 34%, respectively. Therefore, the surface groups of unoxidized CNTcon are predominantly Lewis base sites, but their number is small. The additional oxidation treatment of CNTcon (9.41% oxygen) leads to a 100% conversion of the alcohols and an increase in the selectivity for dehydration products of propan-2-ol and

butan-2-ol to 85 and 100%, respectively, which can be explained by a significant increase in the number of Lewis acid sites. In contrast to CNTcon, CNTcyl demonstrated a high conversion of the secondary alcohols even at a very low oxygen content (0.64%). An increase in the oxygen content to 1.4% changed the selectivity for dehydration products of propan-2-ol and butan-2-ol by ~5 and ~12%, respectively. A significant growth of oxygen content leads to 100% selectivity for dehydration products in both alcohols. This fact indicates that not only surface functional groups but also the carbon structures are involved in the catalytic conversion of alcohols in the form of defects caused by both the curvature and the influence of oxygen treatment. Unlike cylindrical CNTs, in which concentric cylinders of single-walled tubes with a inside channel are inserted each other, conical CNTs have a different configuration of concentric cones. The walls of conical CNTs are not parallel to the axis of the tube. They are structurally similar to nanofibers of the fishbone type. While cylindrical CNTs are graphene layers rolled up into tubes composed of carbon in the sp^2 hybridization state, conical CNTs contain carbon in the sp^3 hybridization state. Previously,³¹ we established that the carbon matrix structure affects the formation and the functional composition of the surface groups of carbon nanomaterials during their post-synthetic oxidative treatment. The reductive treatment of the test catalysts had different effects on the conversion and selectivity on conical and cylindrical CNTs. As an example, Figure 2 shows the temperature dependence of selectivity for acetone in the conversion of propan-2-ol on unoxidized CNTcon samples before and after treatment with hydrogen.

A study of the conversion of the alcohols on nanodiamond and its oxidized and reduced forms¹⁴ showed that the oxidative treatment of nanodiamonds leads to an increase in catalytic activity without changing the high selectivity for dehydrogenation products, which led to the conclusion about the nature of the surface functional groups of nanodiamonds, which are predominantly Lewis basic sites. The carbon structure of a nanodiamond (sp^3 hybridization), unlike CNTs, is not affected by either oxidizing or reducing treatment. The oxidative treatment of nanodiamonds affects only the composition of surface groups and leads to an increase in their number in the form of bridge-type carbonyl groups. Hydrogen treatment, on the contrary, reduces the catalytic activity of nanodiamonds because it leads to the destruction of catalytically active surface oxygen-containing groups. Unlike nanodiamonds, the reductive treatment of conical and cylindrical CNTs leads to an increase in the conversion of the secondary alcohols and in selectivity for dehydration products. The experimental results indicate that the treatment with hydrogen leads to the formation of new catalytic centers.

The nature of these centers was established by analyzing the conversion products. The treatment of unoxidized (0.64% O)

Table 1 Characteristics of the catalytic conversion of propan-2-ol and butan-2-ol on cylindrical and conical CNTs.

CNT	Oxygen content (%)	Propan-2-ol				Butan-2-ol			
		maximal conversion (%)/ T (°C)	selectivity (%)		E_a /kJ mol ⁻¹	maximal conversion (%)/ T (°C)	selectivity (%)		E_a /kJ mol ⁻¹
			propene	acetone			butene	butanone	
CNTcyl	0.64	93.2/300	72	28	74 ± 1	100/240	88	12	65 ± 2
	1.4	100/270	77	23	59 ± 2	100/240	100		36 ± 1
	9.35	100/130	100			100/90	100		
CNTcon	2.59	33.0/300	14	86	98 ± 3	41.5/300	34	66	86 ± 4
	9.41	100/250	85	15	54 ± 1	100/150	100		
HCNTcyl	0.64	97.5/250	100			100/90	100		
	1.4	100/250	100		69 ± 9	100/90	100		
HCNTcon	2.59	86.5/300	83	17	91 ± 1	100/300	91.5	8.5	78 ± 2
	9.41	100/230	95	5	43 ± 2	100/90	100		

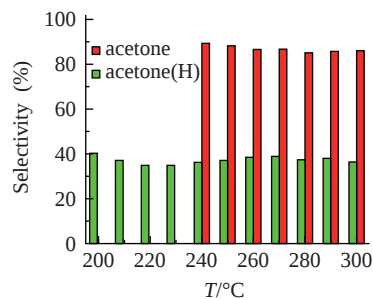


Figure 2 Temperature dependence of selectivity for acetone in propan-2-ol conversion on unoxidized CNTcon before and after treatment with hydrogen.

and oxidized (1.4% O) CNTcyl with hydrogen has little effect on the selectivity and conversion of propan-2-ol and butan-2-ol, whereas the reduction treatment of unoxidized CNTcon (see Figure 2) leads to an increase in selectivity for propene from 14 to 63% and an increase in conversion at 300 °C from 33 to 86%. In the conversion of butan-2-ol on unoxidized CNTcon treated with hydrogen, selectivity for dehydration products grows from 34 to 91%, and the conversion at 300 °C increases from 41 to 100%. Apparently, the treatment of cylindrical and conical CNTs with hydrogen not only affects the surface groups of these catalysts but also leads to a partial destruction of the carbon matrix, which results in the formation of new defect centers (Lewis acid sites) in the catalysis because the selectivity for dehydration products formed at Lewis acid sites changes drastically with increasing conversion. Conical CNTs with their specific carbon configuration are more susceptible to destruction than cylindrical

Table 1 summarizes the experimental results and the apparent activation energies of the conversion of the secondary alcohols on oxidized and nonoxidized CNTs calculated according to the Habgood–Bassett equation.¹⁴ The decrease in the activation energy of the conversion of propan-2-ol and butan-2-ol with an increase in the oxidation of CNTcyl is associated with the formation of new catalytic centers and new defects in the carbon structure as a result of oxidation. In the conversion of propan-2-ol, the apparent E_a decreases by a factor of almost 2 with an increase in the

degree of oxidation from 2.59 to 9.41. A study of the conversion of propan-2-ol on fresh CNTcon catalyst samples showed that the process occurred entirely in the pore-diffusion region (54 kJ mol⁻¹) [Figure 2(a)]. In the conversion of propan-2-ol on spent CNTcon samples at 190 °C, a transition of the process from the kinetic (108 kJ mol⁻¹) to the pore-diffusion region (54 kJ mol⁻¹) was observed [Figure 2(b)].

Hydrogen regeneration of the spent samples returns the process to the pore-diffusion region (43 kJ mol⁻¹) [Figure 3(c)]. In the conversion of butan-2-ol on CNTcyl, the apparent E_{act} decreases from 65 to 36 kJ mol⁻¹ with an increase in the degree of oxidation from 0.64 to 1.4%. Thus, the study of kinetic parameters (degree of conversion, selectivity, and apparent activation energy) in the catalytic transformation of the secondary alcohols allowed us not only to evaluate the nature and composition of surface functional groups in CNMs but also to control changes in their composition during oxidative and reductive treatments.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.032.

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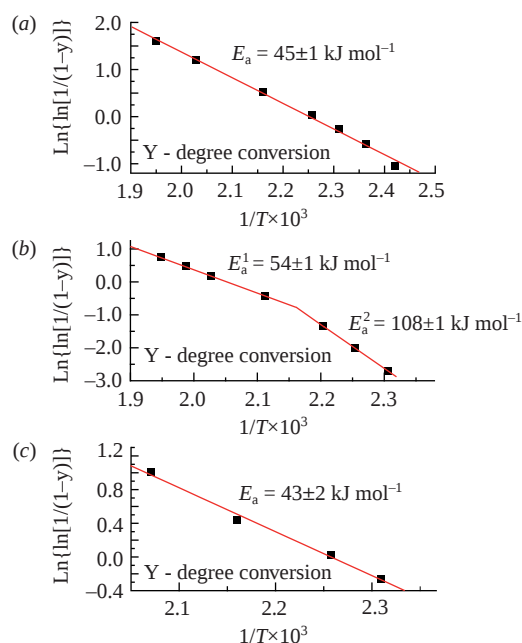


Figure 3 Temperature dependence of propan-2-ol conversion on (a) fresh, (b) spent and (c) regenerated CNTcon samples in the coordinates of the Habgood–Bassett equation.

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