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ScienceDirect
Mendeleev Commun., 2018, **28**, 646–647

Mendeleev
Communications

Catalytic approach to the estimation of the influence of carbon nanomaterial structures on surface functional groups

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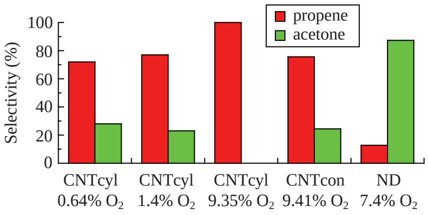
DOI: 10.1016/j.mencom.2018.11.028

A simple catalytic method is proposed for characterizing oxygen-containing surface groups formed upon post-synthetic treatment, control and regulation of their composition under oxidation. Using a pulsed microcatalytic method, we found that the carbon matrix structure plays a key role in the formation of the functional surface composition of carbon nanomaterials.



Carbon nanomaterials (CNMs) are of continuously growing interest due to their unique properties and the generation of their new forms.[1] As opposed to activated carbons, CNMs have a homogeneous carbon structure on a nanoscale; because of this, they find wide applications in physics, chemistry, biology, and various technological processes.[2–4] CNMs are used in catalysis due to their carbon matrix structures, mesoporosity, high specific surface areas, various surface groups (which depend on the conditions of their post-synthetic treatment), and inertness to aggressive media; moreover, they are relatively less expensive in comparison with inorganic oxides.[5,6] Metal-free carbon nanotubes (CNTs), nanofibers, and nanodiamonds (ND) are catalysts for the oxidative dehydrogenation of ethylbenzene[7–9] and butane[10,11] and the dehydrogenation of propane.[12] The catalytic properties of CNMs in these processes are attributed to the effect of functional groups on their surfaces, however the composition of these groups has not been so far associated with the structure of the carbon matrix. The conversion of C_2–C_3 alcohols on ND and its oxidized and reduced forms[13] and the catalytic transformation of C_2–C_4 alcohols on CNMs with planar and nonplanar graphene structures[14] were investigated. We noted the key role of a morphological feature of the structure of CNTs induced by its curvature, which resulted in the formation of topological defects, active centers in catalysis.

The purpose of this work was to investigate the influence of the CNM structure on the formation and composition of surface functional groups formed during the post-synthetic treatment of CNMs using a pulsed microcatalytic method. Oxygen surface atoms in the carbon materials are mainly the constituents of carbonyl, carboxyl, anhydride, and ether surface groups, which are Lewis acid and basic sites in catalysts. IR spectroscopy and chemical and potentiometric titration methods do not always allow one to distinguish the nature of these groups on the surface of CNTs.[15] The composition of oxygen-containing groups cannot also be unambiguously determined by high-resolution XPS. The use of catalytic reactions in which particular functional groups are responsible for one or another catalytic process makes it possible to clarify the nature of the surface functional groups of CNMs. Among these catalytic reactions, propan-2-ol conversion is a test reaction for the determination of Lewis acid and basic sites concentration on the surface of CNMs. It is well known[16–24] that the dehydration and dehydrogenation of aliphatic alcohols occur at Lewis acid and basic sites, respectively. The detonation ND and cylindrical (CNTcyl) and conic (CNTcon) CNTs were used in this work.[†] Using XRD analysis, we have shown that carbon in ND is located exclusively in the sp^3 hybridization, and carbon in cylindrical CNTs occurs in the sp^2 state. The carbon structure of conical CNTs is different from that of cylindrical CNTs. Graphene layers in conical CNTs are located obliquely to the axis of growth of the tubes. This explains the presence of sp^3-carbon atoms in the structure of conical CNTs.

Figure 1 shows the temperature dependence of propan-2-ol conversion on the surfaces of ND, CNTcon and CNTcyl, the latter containing different amounts of oxygen due to various ways of post-synthetic treatment.

The catalytic activity of CNMs is affected both by the carbon structure of the CNM and by the oxygen content of their surface groups. However, we compared the catalytic activity of CNMs with approximately the same oxygen contents but different carbon

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[†] The detonation ND was purchased from Diamond Center, St. Petersburg. The CNTcyl were synthesized by pyrolysis of hexane[25] and post-synthetic treatment under various conditions, and the CNTcon were synthesized by the pyrolysis of a mixture of benzene and ethanol in the presence of nickel acetylacetonate.[26] The post-synthetic treatment of CNTs and ND was carried out in a boiling solution of nitric acid. Propan-2-ol (Khimmed, Moscow) was used to test the composition of surface functional groups of CNMs. The purity of carbon nanomaterials was determined by synchronous thermal analysis using a STA449PCLUXX instrument (Netzsch). The morphology of the CNMs was determined by scanning electron microscopy using a JEOL JSM 6490 LV instrument equipped with an X-ray fluorescence detector. High-resolution electron microscopy was performed on a JEOL JEM 2100 F/Cs instrument. The specific surface areas, structures, and pore sizes were determined by the low-temperature adsorption of nitrogen on an Autosorb-1E/QMS analyzer (Quantachrome). The elemental composition and the composition of surface groups of the catalysts were determined by XPS on a Kratos Axis Ultra DLD instrument with a monochromatic AlKα source and a transmission energy of 160 eV or 40 eV for individual lines. The X-ray phase analysis of CNMs was carried out on a DRON diffractometer with a CuKα emitter. The catalytic conversion of propan-2-ol was studied by a pulsed microcatalytic method[16] and the conversion products were analyzed on a Chrom-5 chromatograph with a flame-ionization detector and a Porapak-N column (1.3 m in length and 0.5 cm in diameter). The column temperature was 130° C.

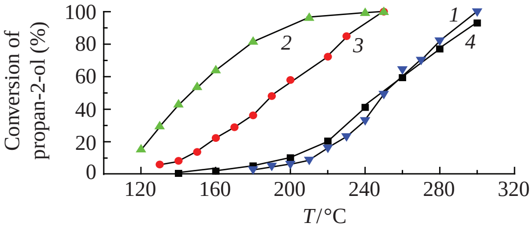

Figure 1 Temperature dependence of propan-2-ol conversion on (*1*) ND (7.4% O_2); (*2*) CNTcon (9.41% O_2); (*3*) CNTcyl (1.4% O_2); (*4*) CNTcyl (0.64% O_2). Cylindrical CNTs with an oxygen content of 9.41% showed a 100% conversion over the entire test temperature range.

structures and found that the activity of cylindrical CNTs with an oxygen content of 9.35% exceeds the activity of conical CNTs (9.4% O_2) and is significantly higher than the activity of ND (7.4% O_2), despite the fact that ND has the highest S_{BET} = 284 m^2 g^{-1}. For cylindrical and conical CNTs, the values of S_{BET} are 249 and 204 m^2 g^{-1}, respectively. This fact indicates that, in contrast to ND, not only the surface functional groups of CNTs, but also the *sp*^{2}-carbon structure itself in the form of defects due to its curvature participate in the catalytic process; in other words, the post-synthetic treatment of CNMs affects both the surface of the CNT and the carbon structure itself, creating new active centers. The oxidative treatment of ND has an impact on only its surface layer composition . However, the carbon matrix structure of the test CNMs significantly affects the nature of the surface groups, which is reflected in the composition of the products of propan-2-ol catalytic conversion.

Figure 2 shows the selectivity of propan-2-ol transformation into propene and acetone at 270 °C on ND, conical CNTs and cylindrical CNTs with different oxygen contents. In the latter case, selectivity for propene increased with the oxygen content. Conversion of propan-2-ol on CNTcyl (9.35% O_2) gives 100% yield of propene throughout the temperature range. Reaction of propan-2-ol on conical CNTs (9.41% O_2) affords propene and acetone with ~80% selectivity for propene. On the contrary, the process on ND (7.4% O_2), whose matrix consists of *sp*^{3}-hybridized carbon, leads to the preferential formation of acetone with ~85% selectivity over the entire test temperature interval. The functional covering of ND comprises carbonyl-containing groups. It was shown[10] that additional oxidative treatment of ND increases not only the catalytic activity but also selectivity (from 88 to 92%) for acetone formation from propan-2-ol. It can be assumed that post-synthetic oxidation treatment does not affect the carbon structure of ND, but only creates a surface layer incorporating oxygen-containing functional groups, mainly carbonyl groups of the bridging type, which are Lewis basic sites, whereas additional oxidative treatment leads to the formation of new carbonyl groups, which creates new active centers. Selectivity for the acetone formation from propan-2-ol on CNTcon is ~24%. This means that conical CNTs also contain bridging carbonyl groups remaining even under deep oxidation (9.4% O_2), which is associated with the presence of the *sp*^{3}-carbon in conical CNTs. The formation of acetone indicates that unoxidized cylindrical CNTs (0.64 and 1.4% O_2) contain the basic Lewis centers, and their number decreases with increasing oxidation level. In contrast to the bridging carbonyl groups in ND and CNTcon, the carbonyl groups of CNTcyl are easily oxidized. Deep oxidizing treatment of cylindrical CNTs (9.35% O_2) leads to the formation of only Lewis acid sites, as indicated by 100% selectivity for propene. Thus, the use of a simple catalytic method made it possible not only to characterize the surface oxygen-containing groups but also to estimate the impact of the carbon structure on the formation of the surface composition of CNMs after post-synthetic treatment.

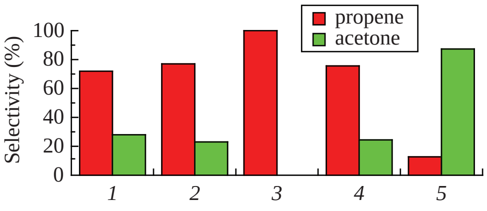

Figure 2 Selectivity of propan-2-ol conversion into propene and acetone at 270 °C on (*1*) CNTcyl (0.64% O_2); (*2*) CNTcyl (1.4% O_2); (*3*) CNTcyl (9.35% O_2); (*4*) CNTcon (9.41% O_2); and (*5*) ND (7.4% O_2).

This work was supported by the Russian Science Foundation (project no. 18-13-00217). The study was carried out using equipment purchased in the frame of the development program of the M. V. Lomonosov Moscow State University.

We are grateful to S. Chernyak and E. Arkhipova for the synthesis of CNM, F. Spiridonov for the RFA study, K. Maslakov, E. Nesterova, and S. Dvoryak for receiving the XPS spectra, and A. Egorov for the microelectrophotographic study of the CNM.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.028.

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Received: 7th June 2018; Com. 18/5603