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Functionalized nanocarbon materials as catalysts for the ethanolysis of furfuryl alcohol

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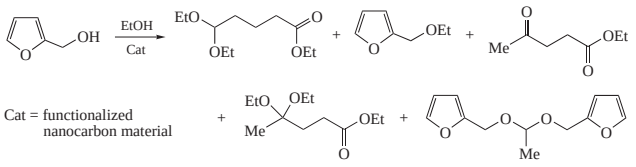
The functionalized nanocarbon materials were prepared and their structure was characterized by a set of physicochemical methods. The materials were tested as catalysts for the ethanolysis of furfuryl alcohol. The synthesis of 2-ethoxymethylfuran and ethyl levulinate in high yields was performed at 100–130 °C.



In the past decades, a great number of synthesized nanocarbon modifications were studied due to enormous interest in the development of new highly dispersed carbon materials and their use as the components of catalytic systems. Among them are nanocarbon fibers, fullerenes, single-walled and multiwalled carbon nanotubes, graphene-like materials, and different amorphous structures based on carbon black.[1] So-called graphene oxide, a material prepared by the exfoliation of graphite oxide, is one of the most promising materials based on the nanomodifications of graphite. Because of its highly developed surface functionalized by oxygen-containing groups (the most hydroxyl and epoxy groups are located on the basal plane, whereas carbonyl, carboxyl, and lactone groups occur on the edges of graphene plates), this nanocarbon material (NCM) is considered not only as a support for catalytically active particles but also as a mild acid catalyst active in acid–base transformations.[2] The sulfonation of graphene oxide makes it possible to obtain materials with high catalytic activity, which is caused by a considerable density of acid sites. These catalytic systems are very promising, in particular, in the conversion of renewable raw materials into motor fuel components.[3]

Furfuryl alcohol is a readily available and inexpensive raw material, which is obtained from different agricultural wastes and wood. Recently, methods for the synthesis of levulinic acid esters from furfuryl alcohol have been actively developed; these esters can be used in the perfumery and as precursors for the preparation of motor fuels.[4] Various substances,[5] including mesoporous hollow carbon spheres functionalized by arylsulfonic acids[6] and graphene oxide,[7] were tested as catalysts for the conversion of furfuryl alcohol into alkyl levulinates.

In this work, we studied the catalytic transformations of furfuryl alcohol in the presence of ethanol on functionalized nanocarbon materials (F-NCMs).†

The characteristics of the F-NCMs were studied by FTIR and Raman spectroscopy (Figure 1), elemental analysis (Table 1), X-ray diffraction (XRD), and electron microscopy (Figure 2).

According to the IR- and Raman-spectroscopic data (see Figure 1), the O-NCM and S-R-NCM samples are disordered imperfect oxidized carbon structures with high concentrations of sp^3-hybridized carbon atoms. The O-NCM sample was characterized by high concentrations of C=O (1726 cm^{-1}) and C–O (1100 cm^{-1}) bonds [Figure 1(*a*)] and a large quantity of the ether groups Ph–O–Ph (1266 cm^{-1}); it contained carboxylate groups (1726 cm^{-1}) and ether bonds with sp^3-hybridized carbon atoms (a region of 1000–1100 cm^{-1}). Absorption bands at 3100–2800 and 730 cm^{-1} are indicative of the presence of C–H bonds at both

† *Preparation of the oxidized nanocarbon material (O-NCM)*. The structural fine-grained extrapure-grade artificial graphite of GMZ KNPS brand was oxidized according to a modified Hummers' method[8] with different pretreatment of the graphite material, which included the ultrasonication of a graphite powder fraction in distilled water with the addition of a sulfonol surfactant using a MEF-93 probe ultrasonic disperser (22 kHz, 600 W) for 1 h. The incompletely oxidized starting graphite was separated from the finely dispersed suspension by centrifugation. FTIR (ν/cm^{-1}): 3330 (OH), 1726 (C=O), 1636 (OH bending), 1090 (C–O). Raman (ν/cm^{-1}): 1350 (D band), 1584 (G band), and I_D/I_G ratio of 1.2. XRD data: 11.5°.

Preparation of the reduced sample (R-NCM). A weighed portion of dispersed O-NCM was reduced with sodium borohydride in accordance with a published procedure.[9]

Preparation of the sulfonated samples (S-NCM). The oxidized and reduced NCM samples were treated with oleum according to a published procedure.[10]

S-O-NCM. FTIR (ν/cm^{-1}): 2000–3000 (OH), 1760 (C=O), 1571 (sp^2-hybridized C=C in-plane vibrations), 1150 (S=O). Raman (ν/cm^{-1}): 1360 (D band), 1620 (G band), and I_D/I_G ratio of 0.83.

S-R-NCM. FTIR (ν/cm^{-1}): 3330 (OH), 1150 (S=O), 760 (S–O). Raman (ν/cm^{-1}): 1355 (D band), 1607 (G band), and I_D/I_G ratio of 0.8.

The total concentration of protogenic functional groups was determined using a reported procedure.[11,12] According to the elemental analysis and X-ray fluorescence analysis (Thermo Scientific ARL Perform'X X-ray fluorescence sequential spectrometer) data, the sulfur contents of the S-O-NCM and S-R-NCM samples were 2.42 and 5.43%, respectively (Table 1).

Reaction between furfuryl alcohol and ethanol. The experiments were carried out in a 20-ml steel autoclave with intense stirring (700 rpm) at 100–130 °C for 3–7 h. The furfuryl alcohol : catalyst weight ratio was 4 : 1, and the furfuryl alcohol concentration in the initial mixture with ethanol was 4 wt%. Before the reuse, the catalyst was washed twice with ethanol and dried at 100 °C. The products were analyzed carried out by a GC/MS technique (Finnigan MAT 95 XL instrument).

Table 1 Chemical and textural characteristics of F-NCMs.

Sample	Element[a] (wt%)			Acid sites[b]/ mmol g^{-1}	S_{BET}[c]/ m^2 g^{-1}	V_{mp}[c]/ cm^2 g^{-1}
	C	H	S			
O-NCM	74.28	0.77	0.48	0.7	21	0.02
R-NCM	87.01	0.60	0.03	–	79	0.11
S-O-NCM	69.35	1.10	2.42	2.7	10	0.01
S-R-NCM	74.32	3.85	5.43	3.6	25	0.01

[a]Thermo Scientific FLASH 2000 Analyser (FPD). [b]Acid groups were determined by acid–base titration.[11,12] [c]ASAP 2020 Analyser (Micromeritics).

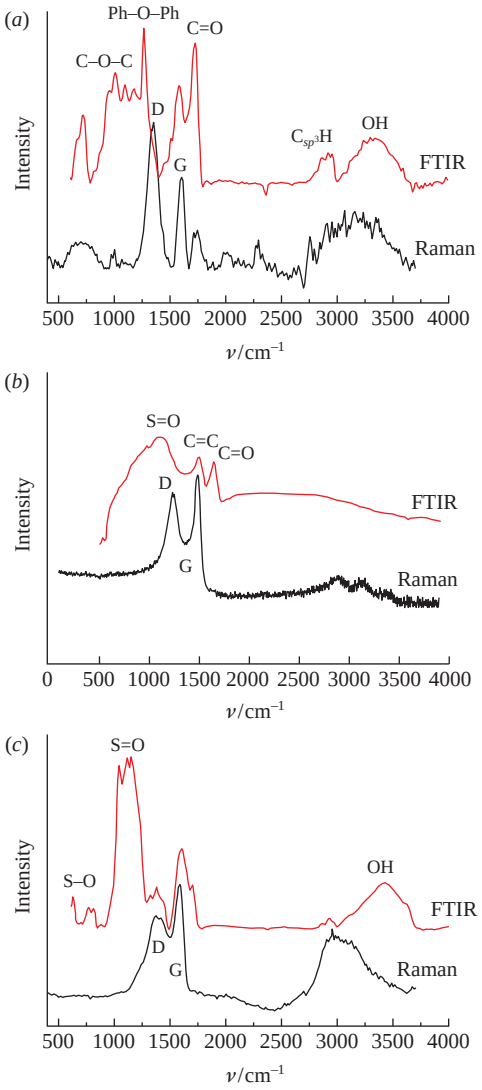


Figure 1 FTIR and Raman spectra of (*a*) O-NCM, (*b*) S-O-NCM and (*c*) S-R-NCM samples.

sp^3- and sp^2-carbon atoms. The S-O-NCM sample [Figure 1(*b*)] revealed large amounts of both carbonyl groups (1760 cm^{-1}) and SO_3H groups; the presence of SO_3H groups was evident from characteristic bands in the spectrum (1250–1100 cm^{-1}). Note that the sample contained a small amount of water. The S-R-NCM sample [Figure 1(*c*)] contained S–O and S=O bonds in large quantities.

According to the X-ray diffraction analysis, the average layer thickness of the O-NCM material was ~3.2 nm. Thus, the nanocarbon material obtained was multilayer cluster graphene oxide in which the number of layers varied from five to several tens; this was also confirmed by the transmission microscopy [Figure 2(*a*)]. Considerable peak spreading (2θ = 11.5°) can also

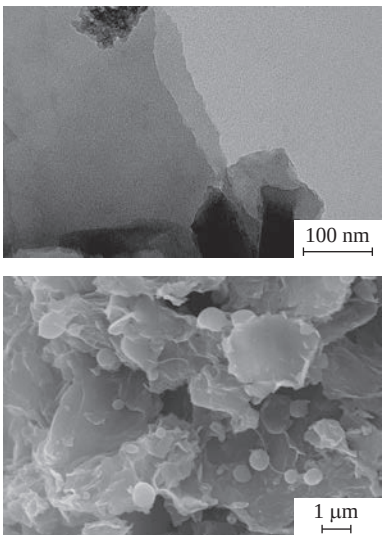
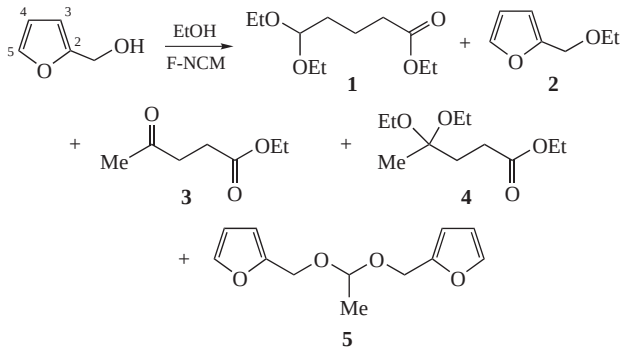


Figure 2 (*a*) TEM and (*b*) SEM images of the O-NCM sample.

be indicative of the defect crystal structure of the sample and some amorphization. The S-NCM exhibited the greatest acidity due to the predominant content of sulfo groups.

The catalytic activities of the F-NCM samples in ethanolysis of furfuryl alcohol were studied (Scheme 1). The main reaction pathway was the cleavage of the C–O bonds of the furan ring with the reduction of double bonds. The C^2–O bond cleavage led to ethyl 5,5-diethoxypentanoate **1**. 2-Ethoxymethylfuran **2**, the product of the intermolecular dehydration of furfuryl alcohol and ethanol, was detected in noticeable amounts. Products of C^5–O bond cleavage were ethyl levulinate **3** and its ketal **4**. The other products were formed in minor amounts, among them, acetaldehyde difurfuryl acetal **5**. Highly-boiling products could be furfural acetals (the mass spectra of a group of substances exhibited a peak with *m*/*z* of 112 $[C_5H_4O_3]^+$) and heavy aldehyde ethyl acetals, *e.g.* a derivative of 5-oxopentanoic acid (a peak with *m*/z 103 $[C_5H_{11}O_2]^+$). Figure 3 shows the distribution of the products of the ethanolysis of furfuryl alcohol on F-NCM.



Scheme 1 Main products of the ethanolysis of furfuryl alcohol on F-NCM.

In summary, the yield of the main reaction product, ethyl levulinate, increased with temperature and reaction time on all of the F-NCM samples. A maximum yield of ethyl levulinate (76%) was obtained on the S-O-NCM sample. The experimental results are consistent with the published data;[5(c),6,7] under optimal conditions, the yields of ethyl levulinate were 75, 81, 89 and 93% on sulfated metal oxide (SO_4^{2-}/TiO_2), carbon-based SO_3H catalyst, Amberlyst 15 and anhydrous benzenesulfonic acid, respectively. The reusability of the S-O-NCM sample was tested in three catalyst reuse cycles. It was found that, at a 100% conversion, the yield of ethyl levulinate decreased by 4 and 7% in the second and third runs, respectively, with an increase in

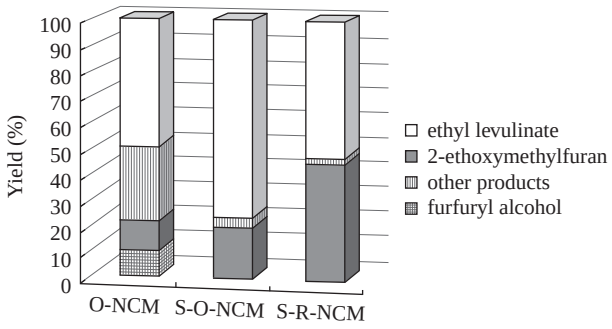


Figure 3 Yields of the products of furfuryl alcohol ethanolysis on F-NCM. Conditions: 130 °C, 7 h, furfuryl alcohol : Cat ratio of 4 : 1 (w/w).

the proportion of diethyl ether and 2-ethoxymethylfuran in the product mass.

The high catalytic activity of S-O-NCM may be caused by the synergetic effect of the presence of sulfo groups and other protogenic (carboxyl and phenol) groups in the catalyst and by their mutual arrangement and accessibility in a cluster of the multilayer nanocarbon material, which makes it possible to form hydrogen bonds with the initial reagents to increase their reactivity.

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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.2018.01.032.

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