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Hydrogenation of Unsaturated Compounds in the Presence of Palladium-Containing Modified Carbon Nanofibers

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Abstract—Palladium-containing carboxylated carbon nanofibers were studied as catalysts for hydrogenation of double bond >C=C< in olefins, unsaturated alcohols, and acids, as well as for hydrogenation of nitroarenes. The developed catalyst is 7 times more efficient than the industrial analog (Pd/C).

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Development and the reduced cost of production of carbon nanomaterials allows extention of their range of use. New opportunities of application of carbon nanomaterials may be opened by modifying their surface with various functional groups [1, 2]. For example, the modified carbon nanomaterials can attach on their surface the transition metals, and the obtained material can be used as the catalysts for organic synthesis [3–6]. In this work we investigated the use of palladium-containing carboxylated carbon nanofibers as a catalyst for the liquid-phase hydrogenation of double bond >C=C< in olefins, unsaturated alcohols and acids, as well as for nitroarenes hydrogenation.

Carbon nanofibers were obtained by pyrolysis of propane-butane mixture on a copper-nickel catalyst at 500°C. According to the scanning electron microscopy (Fig. 1), carbon nanofibers range in diameter from 40 to 500 nm and in length from 100 nm to 5 microns. The specific surface area of the material is 124 $m^2 g^{-1}$, and the content of the carbon nanofibers in it is approximately 90%.

The functionalization of carbon nanofibers was performed by treatment with concentrated sulfuric acid at 70°C with vigorous stirring for 24 h after which the material was filtered off, washed successively with water, ethanol, and dried in air. The resulting material was investigated by a complex of physicochemical methods.

The IR spectra of the functionalized carbon nanofibers contain the signal at 1713 cm^{-1}, confirming the presence of carboxy groups [7, 8], whereas in the spectrum of the initial sample this peak is not present.

In the Raman spectra (Fig. 2) there is an increase in the intensity of the D and G modes at 1362 and 1584 cm^{-1}, which indicates a violation of the hexagonal symmetry of graphene caused by the appearance of a covalent bond on the nanofibre sidewall [7, 8].

According to X-ray diffraction, the sample contains the allotropic carbon which is common for the carbon nanofibers (26.15 eV) (Fig. 3).

In the X-ray photoelectron spectrum C1*s* there is a peak at 285 eV corresponding to the sp^2-hybridized carbon, which is typical for the flat nets of graphite, graphene and nanotubes [9], as well as the signal at 288 eV, indicating the presence of carboxy groups on the surface of carbon nanofibers. This is also confirmed by the presence of peaks of O1*s* line at 532 and 534 eV. Thus, the formation of carboxy groups on the surface of the carbon nanofibres was confirmed.

C1*s*	O1*s*	Pd3*d* 5/2	Cl1*s*
285, 288	532, 534	335, 338	198
285, 288	526, 532, 534	335, 338	–
285, 288	526, 532, 534	335, 338	–

Fixing palladium on the oxidized carbon nanofibers was carried out by treating them in 1 N solution with 2% solution of $PdCl_2$ while stirring for 60 min at 20°C. The material was then filtered off, washed successively with water, ethanol, and dried in air. The presence of

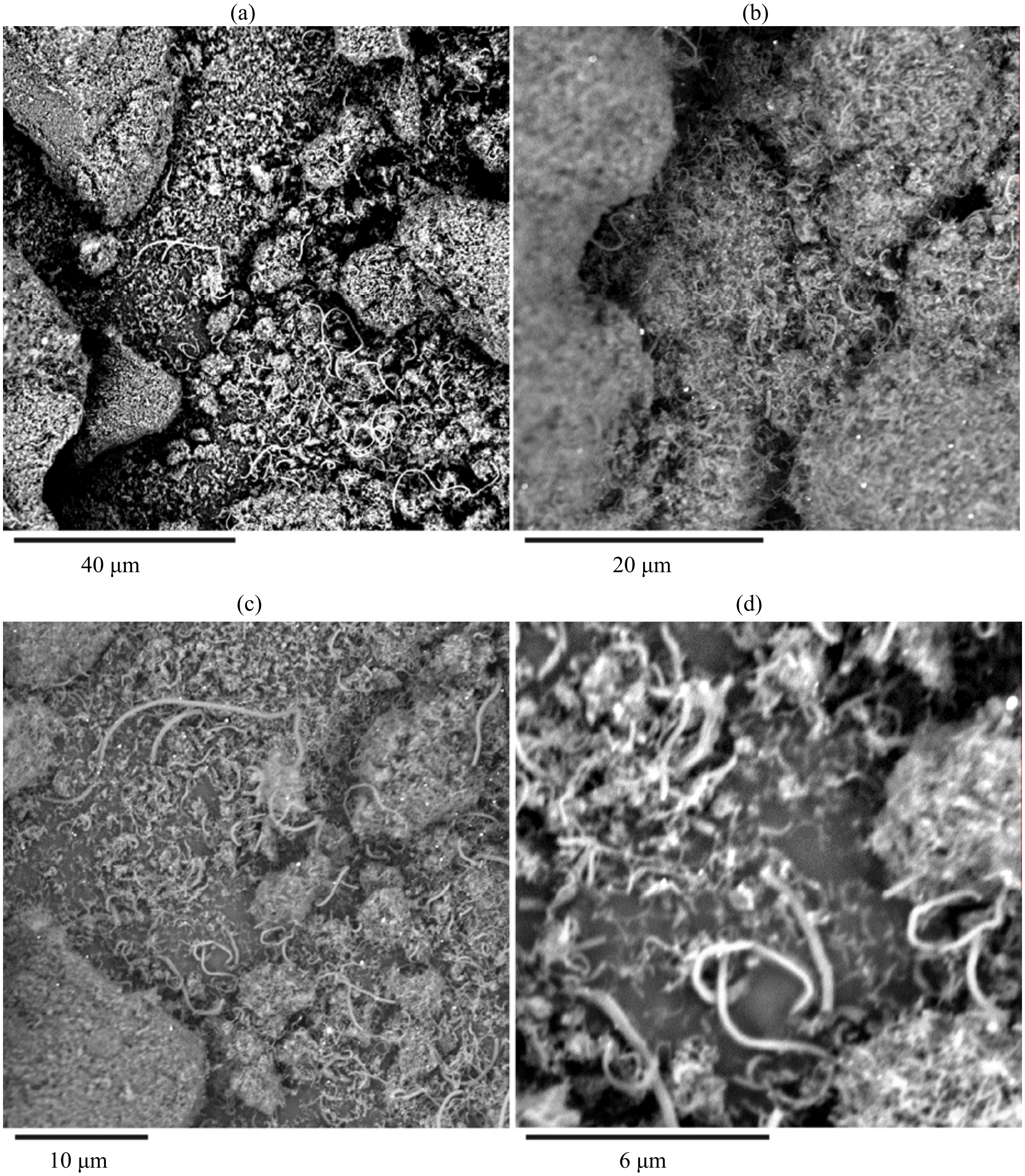

Fig. 1. Scanning electron microscopy image of the carbon nanofibers: (a) ×2950, (b) ×6300, (c) ×7100, and (d) ×21500.

fixed palladium was confirmed by the appearance of a small peak at 40 eV in the diffraction pattern (Fig. 3). Amount (wt %) of palladium fixed was estimated by XPS.

Total Pd content	Pd^{2+}	Pd^0	Pd^{2+}/Pd^0
1.55	0.83	0.72	1.15
1.48	0.95	0.53	1.79
1.38	0.85	0.53	1.60

As seen from the above data, the total amount of the metal in the carbon nanofibers is about 1.5 wt %, the palladium is fixed initially in the form of Pd(II) (338 eV) and Pd(0) (335 eV), and their ratio is close to 1:1. Simultaneously, the sample contains chlorine as indicated by the signal at 198 eV.

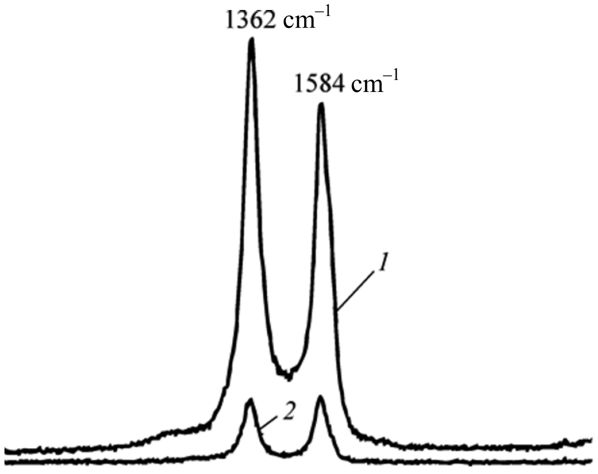

Fig. 2. Raman spectra of the modified carbon nanofibers (*1*) and carbon nanofibers without treating with acid (*2*).

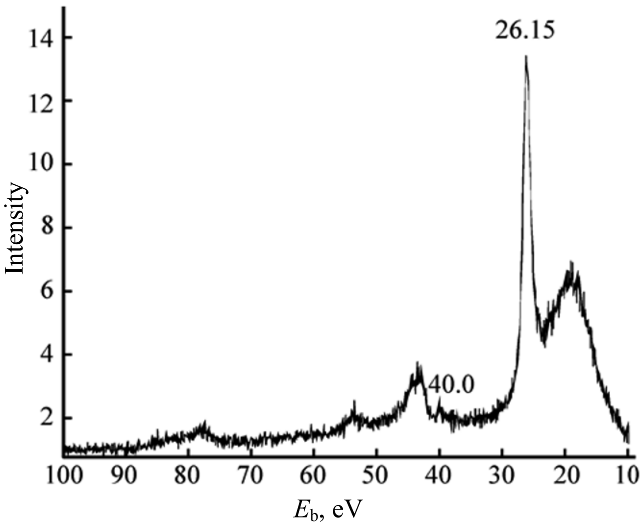

Fig. 3. XRD pattern of palladium-containing carboxylated carbon nanofibers.

The obtained material was activated before using as a hydrogenation catalyst. The material was placed into a reactor, equipped with a stirrer and a jacket for heating, under a layer of ethanol (25 ml) and treated with 10 mg of $NaBH_4$ in a hydrogen atmosphere at 45°C for 60 min. It was then filtered off, washed successively with water, ethanol and dried in air. The XPS analysis of the obtained material at this stage indicates that the Pd–Cl bonds are absent, since there is no signal in the region of 198 eV. However, the total content of Pd somewhat decreases (presumably due to losses during the activation), and the ratio of Pd(II):Pd(0) is 1.79, which can be explained by the palladium oxidation in air (appearance of a peak at 529 eV on O1*s* line corresponding to the Pd–O bond).

The hydrogenation reaction was carried out as follows: into a reactor under a layer of solvent (ethanol, 25 ml) was placed 40 mg of a catalyst (Pd/carbon nanofibers) and $NaBH_4$ (10 mg); the mixture was stirred under a hydrogen atmosphere at 45°C for 10 min. Then 1 mmol of substrate was added, and its hydrogenation was carried out with molecular hydrogen at 45°C at the atmospheric pressure. According to GLC analysis of the reaction mixture [3], the conversion was complete. Byproducts were not detected. The results are shown in the table. XPS analysis of the catalyst samples after hydrogenation revealed that the content of Pd^{2+} decreases slightly, and the ratio of Pd (II):Pd(0) becomes equal to 1.6. This can be explained by loss of the palladium in the reaction, separation and washing of the catalyst.

The rate of hydrogenation of 1-hexene is almost 3 times higher than that of cyclohexene (see the table). This can be explained by the fact that the terminal

Data on hydrogenation of organic compounds in the presence of palladium-containing carbon nanofibers (CNF)[a]

Substrate	Cartalyst	Reaction rate 10^{-5} mol min^{-1} [b]	TN, mol g-at^{-1} Pd min^{-1}
Allyl alcohol	Pd/CNF	20.0	35.5
Acrylic acid	Pd/CNF	17.0	30.0
Hexene-1	Pd/CNF	18.0	32.0
Cyclohexene	Pd/CNF	6.5	12.0
Nitrobenzene	Pd/CNF	17.0	30.0
Nitrobenzene	Pd/C	1.5	4.0
p-Nitrophenol	Pd/CNF	15.0	27.0
p-Nitrobenzoic acid	Pd/CNF	8.5	15.0

[a] Conditions: Pd/CNF (40 mg), ethanol (25 ml), substrate (1 mmol), atmospheric pressure, 45°C. [b] The error in the measurement of the reaction rate was no more than 13%.

double bond is sterically more accessible than the internal. The presence of functional groups in the case of hydrogenation of acrylic acid and allyl alcohol does not influence the reaction rate, and it is comparable with the rate of hydrogenation of 1-hexene (see the table), apparently due to the fact that in these cases we are dealing with the reduction of the terminal bond >C=C<.

It should be noted that the hydrogenation of nitrobenzene takes place almost at the same rate as the terminal double bond (see the table). This circumstance requires further studying because usually nitro compounds are hydrogenated with lower rates than olefins. Apparently, in the case of such catalysts different mechanisms of activation of hydrogen and hydrogenation are realized compared with the commonly used commercial catalyst Pd/C.

The rate of hydrogenation of the nitro group in the molecule of nitrobenzene is almost two times higher than that of *p*-nitrobenzoic acid. The rates of hydrogenation of nitrobenzene and *p*-nitrophenol are virtually similar (see the table). This effect can be explained by the different effect of carboxy and hydroxy groups on the electron density in the substrate molecules.

The developed catalyst was compared with a commercially available industrial analog Pd/C with a palladium content of 1%. Hydrogenation of nitrobenzene was used as a model reaction. Under identical conditions, the reaction rate and catalyst efficiency (turnover number, TN) on a Pd/C catalyst was below by factors 11 and 7, respectively (see the table).

Thus, the carboxylated palladium-containing carbon nanofibers are of interest as catalysts for liquid-phase hydrogenation of organic compounds of different structure.

EXPERIMENTAL

In the work the following instruments were used: Perkin-Elmer Spectrum 100 Fourier spectrometer (USA), atomic force microscope with confocal Raman/fluorescence microscopy and spectroscopy (NanoLaboratory Integra Spectra), and X-ray powder diffractometer DRON-1 using X-ray tube with a copper anode. Surface analysis of the samples was performed by X-ray photoelectron spectroscopy (XPS) on a LAS-3000 instrument (Riber) equipped with a hemispherical analyzer with retarding potential OPX-150. For excitation of photoelectrons was used X-ray irradiation of an aluminum anode (AlK_a 1486.6 eV) with tube voltage of 12 kV and an emission current of 20 mA. The vacuum in the chamber was 5×10^{-9} Torr. The calibration of the photoelectron peaks was performed by the carbon C1*s* line with the binding energy of 285 eV.

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