Hydrogenation catalyst based on modified carbon nanofibers

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Abstract. The aim of this work was to study the palladium-carboxylated carbon nanofibers (CNF) as a catalyst for the hydrogenation of nitrobenzene model reaction. It is shown that the efficiency of the catalyst obtained more than 6 times higher than that of the industrial counterpart (Pd/C).

Development and reduce the cost of production of carbon nanomaterials (CNM), expands the range of applications. Surface modification of functional groups of CNM offers new opportunities to use them, for example, as a carrier for catalysts of different chemical processes [4,5,7,8].

Used in the carbon nanofibers (CNF) were obtained in the Vladimir State University, the pyrolysis of propane-butane mixture in a copper-nickel catalyst at a temperature of 500 °C. Specific surface area of the material used was 124 m$^2$/g, and the CNF content in the material - about 90%. CNF have a coaxial-conical shape (Fig. 1).

Fig. 1 Photos palladium carboxylated SAM CNF Phenom™ G2.

Initially, the CNF do not exhibit catalytic activity and are not binding transition metals. In order to be secure metal to CNF is necessary to modify their surface functional groups [1,2]. Functionalization of CNF was carried out by treatment with concentrated sulfuric acid at 70 °C with vigorous stirring for 24 hours. Then the material was filtered, washed successively with water, ethanol, and dried in air to air-dry state.

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The resulting material was characterized by IR- and X-ray photoelectron spectroscopy. The IR spectra of CNF signal appears in the 1713 cm\(^{-1}\), indicating the presence of carboxyl groups in the samples [3]. In the XPS spectra of C 1s peak can be seen in the area of 285 eV, indicating that carbon is sp\(^3\) hybridization, which is typical for two-dimensional grids of graphite, graphene and nanotubes [6]. In the 288 eV peak is recorded indicating the presence of carboxyl groups on the surface of the CNF (Fig. 2).

To fix the palladium-modified CNF placed in a 2% solution of PdCl\(_2\) in 1n HCl and stirred with a magnetic stirrer for 60 min at 20 °C. The material was then filtered, washed successively with water, ethanol, and dried in air to air-dry state. The number of entrenched palladium was determined by XPS (Fig. 3, Table 1.). As can be seen from the data, initially assigned as a palladium Pd (II) and Pd (0), and their ratio close to 1:1. Simultaneously, the sample contains chlorine.
Further activation was carried out, for which the material was placed in ethanol (25 mL) and treated with 10 mg of NaBH₄ in hydrogen at a temperature of 45 °C for 60 min. After that, it was filtered, washed successively with water, ethanol, and dried in air to air-dry state. Activation of catalyst is necessary in order that would remove the chlorine from the sample. Analysis of the activated material by XPS shows that the relation Pd-Cl, most likely, not, however, the total number of Pd decreased and the ratio of Pd (II) and Pd (0) was 1.8:1. Apparently, this is due to the fact that the sample is oxidized in air. This is evidenced by the peak of 529 eV at the O 1s line in XPS spectrum of
CNF after activation (Fig. 4). The same peaks in the region 534 eV and 532 eV confirm the presence of carboxyl groups in the sample.

Hydrogenation reaction was carried out as follows: in the reactor under a layer of solvent (ethanol, 25 ml) was placed portion of the catalyst (Pd/CNF, 40 mg) and NaBH₄ (10 mg) and stirred under hydrogen at 45 °C for 10 min. Then, in a hydrogen contributed 1 mmol of nitrobenzene hydrogenation and reacted with molecular hydrogen at \( T=45 \, ^\circ \text{C} \), \( P_{H_2}=0.1 \, \text{MPa} \). In the triple repetition of the reaction we received palladium catalyst fixed on the surface of carboxylated carbon nanofibers showed showed stability by giving the same results.

According to the analysis of reaction products, made with a gas-liquid chromatography, nitrobenzene reacted completely. By-products were found. Hydrogenation products of the aromatic ring and incomplete recovery of the nitro group were found.

In Table. 2 shows the efficiency of palladium-carboxylated carbon nanofibers as catalyst hydrogenation of nitrobenzene in comparison with the commercial (industrial) Pd/C.
The effectiveness of Pd / CNF and Pd / C in the hydrogenation of nitrobenzene

| catalyst  | The content of Pd wt.% | The reaction rate 10-4 mol/(l*s) | TN mol/(g*atom Pd*min) |
|-----------|------------------------|----------------------------------|------------------------|
| Pd/C      | 1                      | 1.02                             | 4.0                    |
| Pd/YHB    | 1.5                    | 8.60                             | 23.4                   |

Thus, the palladium catalyst attached to the carboxylated carbon nanofibers is almost 6 times more effective than Pd/C.

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