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Platinum Nanoparticles on Carbon Nanomaterials with Graphene Structure as Hydrogenation Catalysts

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Abstract—Carbon nanomaterials with graphene structure (single- and multiwall nanotubes and nanofibers) after oxidizing by a mixture of sulfuric and nitric acids and presumable introducing of carboxyl groups can be used as carrying agents of hydrogenation catalysts. Platinum in a concentration which should not exceed 10 wt % can be fixed using H_2PtCl_6 as a precursor in presence of an organic base. Catalysts based on these nanomaterials with the average size of platinum particles 6–8 nm exceed in activity the Pt/C catalyst with the size of platinum particles 65–70 nm, but are inferior to catalysts based on fullerene black with the average size of platinum particles 3–4 nm.

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Carbon nanomaterials with graphene structures draw attention as potential carrying agents for catalysts or electrocatalysts. Principal causes of such attention are connected with the fact that they contain graphene structures in their constitution, which impair a high conductance (comparable with that of graphite) and satisfactory mechanical characteristics to the materials. A priori the conductance of a carrying agent is of great importance for catalysts of electron-transfer reactions [1], in particular, for the catalysts of hydrogenation, dehydrogenation, oxidation, etc.

In the present work we have prepared platinum-containing catalysts based on carbon nanomaterials with a graphene structure, in particular, single- (SNT) and multiwall nanotubes (MNT) and nanofibers (NF), and have studied their catalytic properties in the liquid-phase hydrogenation of organic compounds containing a double C=C bond or an aromatic nitro group.

Carbon nanomaterials with graphene structure, unlike fullerene black, are characterized by high temperatures of oxidation beginning (from 350°C) and by clearly pronounced graphite structure (Figs. 1 and 2). Of all materials studied in this work, only nanofibers NF 1 contain amorphous carbon which manifests itself as a characteristic halo (Fig. 2). The presence of amorphous carbon seems to be a reason for a higher specific surface area of NF 1 compared to NF 2. At the same time, nanofibers NF 1 containing amorphous carbon are oxidized more difficultly than NF 2 (Fig. 1).

We noted earlier [2] that it is difficult to introduce functional groups into carbon nanomaterials to the extent sufficient for the formation of covalent bonds with platinum. In fact, substitution reactions involving aromatic ring protons are impossible in this case because of the absence of protons and extremely small (of the order 10^{-4} g^{-1}) amount of broken bonds. The presence of mainly conjugated aromatic bonds, as differentiated from non-conjugated double bonds present in fullerenes or fullerene black, is the principal

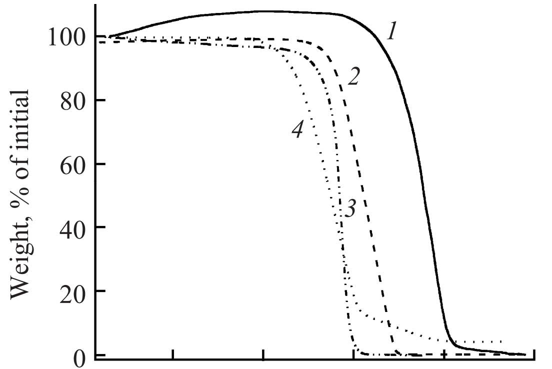

Fig. 1. Oxidative thermograms of carbon nanomaterials: (*1*) MNT, (*2*) NF 1, (*3*) NF 2, and (*4*) SNT.

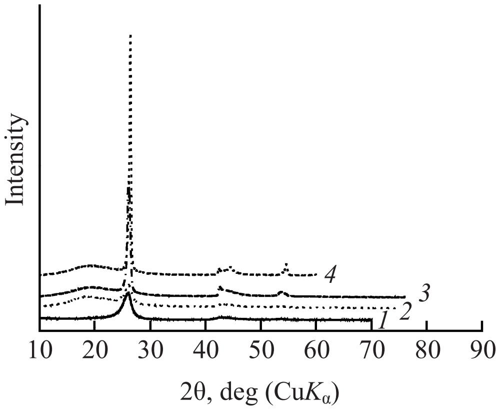

Fig. 2. Diffractograms of carbon nanomaterials: (*1*) NF 2, (*2*) NF 1, (*3*) MNT, and (*4*) graphite.

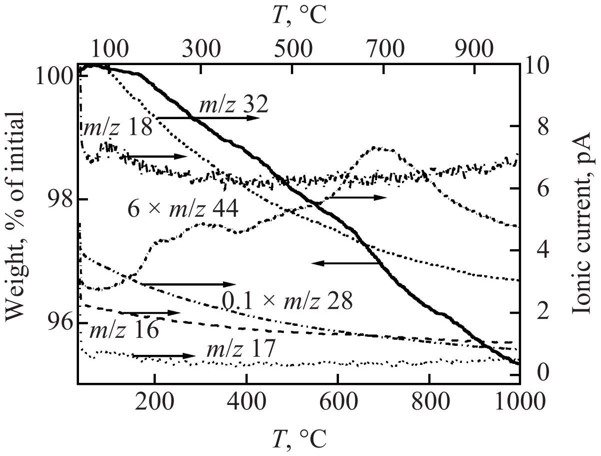

Fig. 3. Thermogram of oxidized nanofibers combined with mass-spectral analysis of gaseous products of NF 2 oxidation in argon atmosphere.

distinction of carbon nanomaterials with graphene structure from fullerene-like materials. The oxidation by sulfuric or nitric acid or by their mixtures (see, for example, [3–19]), or by a $K_2Cr_2O_7$ solution in sulfuric acid [20], or by hydrogen peroxide [21] widely used in the graphite functionalisation makes it possible to introduce carboxylic, anhydride, and lactone, phenolic and carbonyl, or quinoid groups into carbon nanomaterials, but results in destruction of a conjugation system in the site of adding these groups. As the amount of defects and ends with fullerene-like fragments in carbon materials with graphene structures is insignificant and aromatic structures are highly stable, it is clear that the amount of functional groups which can be introduced into these materials by a nondestructive oxidation is insignificant. In fact, the gross formula of these carbon nanomaterials after oxidation, calculated from the elemental analysis data, approaches $C_{27}O$. An additional oxidation of NF 1 after the catalyst removal by nitric acid does not change the gross formula. In view of unaffected internal carbon atoms, the gross formula points to a high concentration of surface functional groups in the nanomaterial. Nevertheless, when one platinum atom is coordinated with two oxygen atoms, it is possible to fix no more than $(195\times0.5\times100)/(27\times12 + 16 + 195\times0.5) = 22.28\%$ of platinum on these nanomaterials. Taking into account incomplete accessibility of functional groups and possible steric hindrances, this amount should be considered as being overestimated.

The amount of oxygen-containing groups in oxidized carbon nanomaterials with graphene structures is extremely small (no more than 6 wt %). In the course of thermal analysis the available functional groups are decomposed to evolve CO_2 (*m/z* 44) and water (Fig. 3). Oxygen (*m/z* 32 and 16) and CO are absent from the thermolysis products of carbon nanomaterials.

The comparison of the thermal analysis data of oxidized carbon materials with graphene structures points to the similar nature of functional groups introduced by the oxidation with nitric and/or sulfuric acids. Probably these are carboxylic groups as follows from the low temperatures of decarboxylation and the absence of water, except for physically sorbed water.

Reactions of carboxylic groups with $PtCl_6^{2-}$ were carried out with adding an organic base–amine (Am) that converts H_2PtCl_6 to $[Pt(Am)_2]Cl_4$ [22]. Conditions of the ligand substitution promote the formation of the only possible *cis*-fragment in the course of the complex formation of platinum with carboxylic groups of oxidized nanomaterials.

After platinum fixation with participation of carboxylic groups on oxidized nanomaterials and reducing by formiate ions, platinum particles of size 6–8 nm (Fig. 4) were obtained. The resulting products based on nanomaterials catalyze the hydrogenation of individual 1-decene (Fig. 5) and nitrobenzene in 2-propanol (Fig. 6). In the both cases the catalysts based on NF 1 are more active than catalysts based on other studied carbon nanomaterials including also the traditional catalyst of 10.0% Pt/C based on active carbon AC-3. Therewith no correlation between the catalytic activity and the specific surface area of the carrying agent was observed.

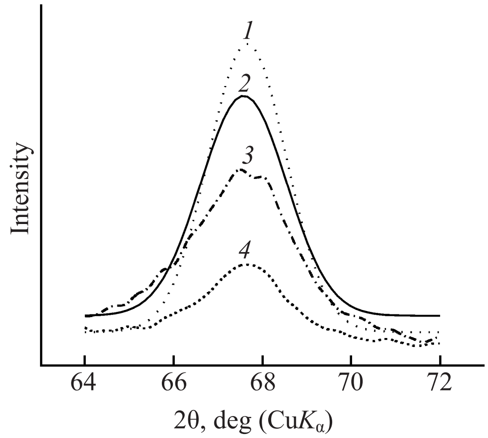

Fig. 4. Pt(220) line in diffractograms of catalysts: (*1*) 10.3% Pt/NF 1, (*2*) 12.6% Pt/NF 2, (*3*) 9.3% Pt/MNT, and (*4*) 11.4% Pt/SNT.

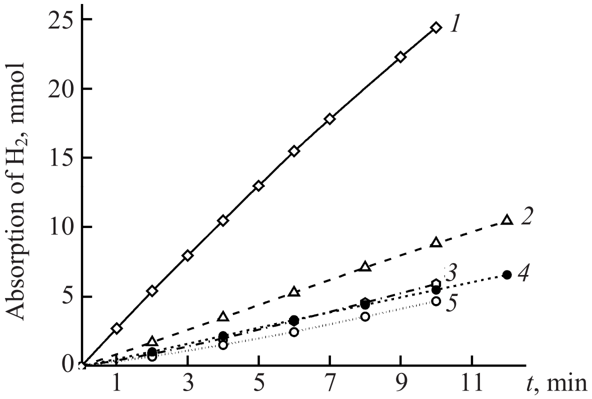

Fig. 5. Initial sections of hydrogen absorption curves for the hydrogenation of individual 1-decene over catalysts based on carbon nanomaterials: (*1*) 55.2% Pt/NF 1, (*2*) 10.3% Pt/NF 1, (*3*) 12.6% Pt/NF 2, (*4*) 9.3% Pt/MNT, and (*5*) 11.4% Pt/SNT.

When 1-decene is hydrogenated the rate of hydrogen adsorption for catalysts with a platinum content of 5-55% is not proportional to a platinum content on NF 1 (Fig. 7). The catalytic activity of 5.2% Pt/NF in the 1-decene hydrogenation is 105.43, whereas for the 55.2% Pt/NF 1 catalyst it is only 31.74 mol H_2/mol Pt·min (Fig. 5). Catalysts with high platinum contents are often deactivated, since a considerable part of platinum is precipitated on the walls of a reaction vessel.

Specific activities of catalysts based on NF 1 (for example, 14.45% Pt/NF 1) in the hydrogenation of 1-decene and nitrobenzene in 2-propanol are practically equal and comprise 45.87 mol H_2/mol Pt min (Figs. 8 and 9). It is not true for other carrying agents, i.e. normally the rate of hydrogen adsorption at the 1-decene hydrogenation is higher than in the case of nitrobenzene.

The catalysts containing platinum on carbon nanomaterials with graphene structure as carrying agents catalyze liquid-phase hydrogenation of alkenes and aromatic nitro compounds. The activity of such catalysts is not record-breaking high, but when the carrying agents are nanofibers obtained by the

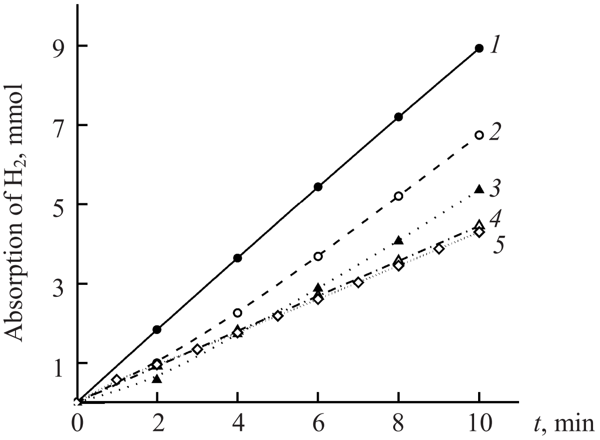

Fig. 6. Initial sections of hydrogen absorption curves for the hydrogenation of nitrobenzene in 2-propanol over catalysts based on carbon nanomaterials: (*1*) 10.3% Pt/NF 1, (*2*) 11.6% Pt/NF 2, (*3*) 11.4% Pt/SNT, (*4*) 9.3% Pt/MNT, and (*5*) 10.0% Pt/C.

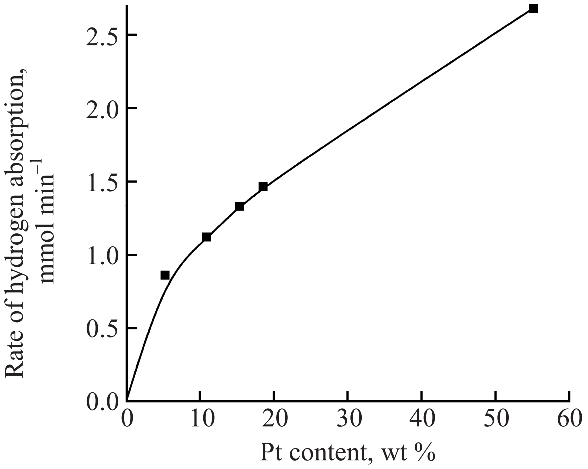

Fig. 7. Dependence of the rate of hydrogen absorption for the hydrogenation of individual 1-decene on the platinum content in Pt/NF 1 catalyst.

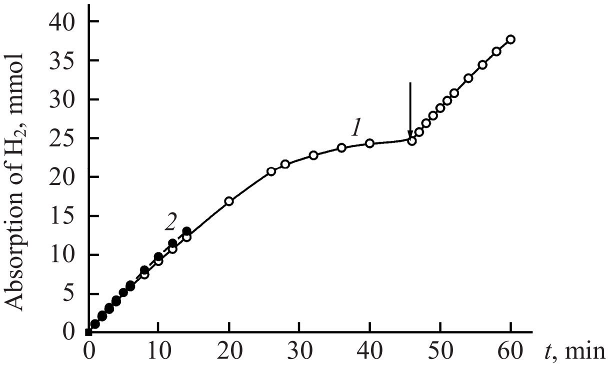

Fig. 8. Kinetic curve of hydrogen absorption for the hydrogenation of two [(*1*) total curve and (*2*) the second portion] portions of 1-decene in 2-propanol over 14.45% Pt/NF 1. The moment of the input of a fresh 1-decene portion is shown by an arrow.

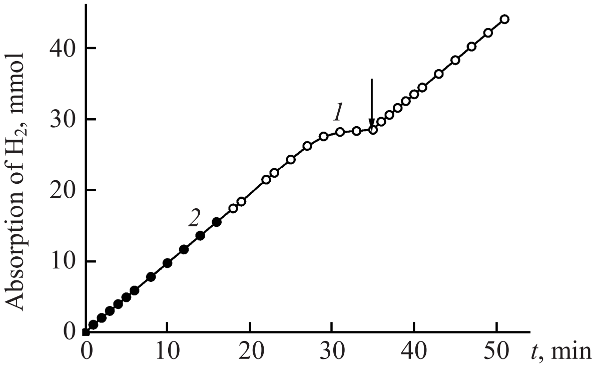

Fig. 9. Kinetic curve of hydrogen absorption for the hydrogenation of two [(*1*) total curve and (*2*) the second portion] portions of nitrobenzene in 2-propanol over 14.45% Pt/NF 1. The moment of input of a fresh nitrobenzene portion is shown by an arrow.

pyrolysis of the propane-butane fraction over a Ni/MgO catalyst, it surpasses the activity of the traditional catalyst: 10.0% Pt/C based on active carbon AC-3. Unlike catalysts on fullerene black, the hydrogenation of individual 1-decene for catalysts on NF 1 practically does not differ from the hydrogenation of 1-decene in 2-propanol. The catalysts are not poisoned by hydrogenation products (Figs. 8 and 9).

However catalysts based on NF 1 and AC-3 coal are inferior in activity to catalysts based on fullerene black, which have much lower conductance than graphite and a specific surface lower approximately by an order of magnitude than that of AC-3. Possibly the rather high activity of catalysts based on NF 1 is connected with a high content of amorphous carbon (likewise fullerene black), which is seen from Figs. 1 and 2.

Thus, no influence of conductance and specific surface area of the carrying agent on the activity of catalysts based on it was found, but, similarly to the use of fullerene black as the carrying agent, the activity of catalysts is defined by the size of platinum clusters.

EXPERIMENTAL

Multiwall nanotubes were obtained by electric arc graphite vaporization from a loose part of the cathode deposit, which was purified from amorphous carbon [23]. Single-wall nanotubes were synthesized under 500 torr pressure of helium and 130 A strength of current by the electric arc vaporization of a composite graphite rod of 6 mm in diameter containing a mixture of nickel and yttrium hydrides with a subsequent refining [23]. Carbon nanofibers NF 1 were obtained by a pyrolysis of the propane-butane fraction over the Ni/MgO catalyst with a subsequent removal of the catalyst by nitric acid. The resulting nanofibers NF 1 had a specific surface area of 130 $m^2 g^{-1}$. Carbon nanofibers NF 2 with a specific surface area of 59 $m^2 g^{-1}$ were obtained by a pyrolysis of a mixture of ethene with hydrogen (1:1.75 vol) in presence of argon (18 vol %) as a diluent over a powder of the $LaNi_5$ alloy at 700°C with a subsequent removal of the metals by hydrochloric acid.

A suspension of multiwall nanotubes in a mixture of concentrated nitric and sulfuric (1:1 vol) acids was subjected to an ultrasonic treatment at 40°C within 4 h. Single-wall nanotubes NF 1 and NF 2 were oxidized by concentrated nitric acid at a long-term (24–72 h) heating (70°C).

Platinum was deposited on oxidized carbon nanomaterials from an aqueous solution of chloroplatinic acid $H_2PtCl_6{\cdot}xH_2O$ (~40 wt % Pt). An ordinary procedure consisted in the dropwise addition of an $H_2PtCl_6{\cdot}xH_2O$ aqueous solution (concentration of approximately 1–4 g l^{-1}) under stirring and heating within 3–5 h to a suspension of an oxidized carbon nanomaterial in water (approximately 4–5 g l^{-1}) with 0.5 ml of pyridine added. Then the reaction mixture was boiled within 0.5–1 h, an aqueous solution of sodium carbonate was added, and 1 ml of formic acid was added dropwise. The mixture was held overnight, the prepitate was separated by filtration, washed with water up to a neutral reaction, and dried.

The elemental analysis was carried out by a semimicromethod. The X-ray patterns were recorded on a DRON-3 instrument. Average sizes of platinum particles were calculated by Selyakov–Scherrer's equation for the line Pt(220). Thermograms were recorded on an STA-409 PC Luxx thermoanalyzer combined with a QMS-403 C (NETZSCH corporation, Germany) mass-spectrometer. Catalytic hydrogenation was carried out in a temperature-controlled shaken ($\geq$600 min^{-1}) flask at atmospheric pressure of hydrogen and temperature of 45°C. 1-Decene was hydrogenated in a mass or in 2-propanol (5 ml of 1-decene per 20 ml of 2-propanol). A weighted sample of a catalyst in all cases was 0.03 g. Specific catalytic activity was calculated from initial sections when a conversion did not exceed 1–2%. The second portion of 1-decene (5 ml) was introduced in a hydrogen flow after noticeable (more than tenfold) decrease in the rate of hydrogen absorption.

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