ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 6, pp. 1106–1112. © Pleiades Publishing, Ltd., 2009.
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Platinum Nanoparticles on Fullerene Black as Effective Catalysts of Hydrogenation

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Received June 19, 2008

Abstract—Fixation of platinum from H_2PtCl_6 on fullerene black through non-conjugate double bonds or hydroxyl groups created on their base in the presence of an organic base with postreduction by formate ions allows platinum particles of size 3–4 nm to be obtained. These compositions catalyze 1-decene and nitrobenzene hydrogenation and exceed in activity the traditional catalyst Pt/C with platinum particle size of 70–80 nm. The average size of the fixed platinum particles affects the catalytic activity stronger than the specific surface area and the electron conduction of the carrying agent.

DOI: 10.1134/S1070363209060127

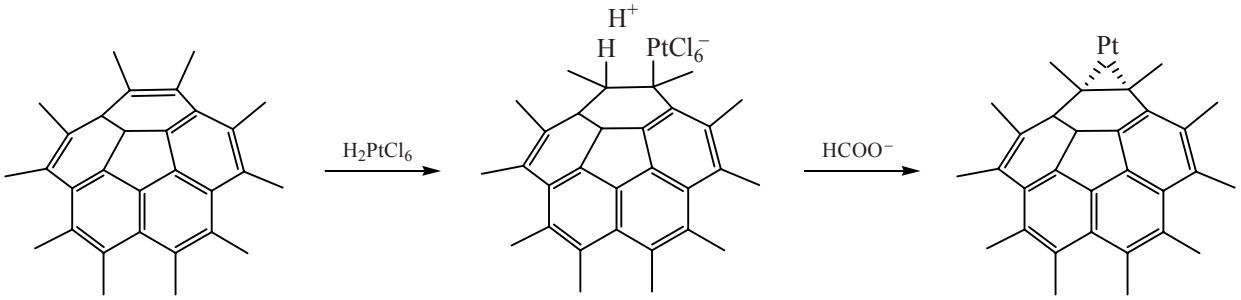
High efficiency of hydrogenation catalysts on the carbon carrying agents is connected usually with the developed surfaces of the carrying agents, their electron conduction caused by the presence of developed system of conjugated bonds in their structure, and a possibility to serve as electron carriers [1]. Fullerene black, which is prepared by graphite vaporization [2], unlike this latter is roentgen-amorphous, its specific surface area considerably (more than tenfold) exceeds the specific surface area of graphite, and its bulk weight is lower by a factor of 3–50 than that of graphite. In the present work we have obtained platinum catalysts with fullerene black as a carrying agent, and have studied their catalytic properties in the liquid-phase hydrogenation of alkenes and aromatic nitro-compounds, using 1-decene and nitrobenzene as examples.

As it was shown earlier [3, 4], carbon atoms in the fullerene black structure are connected with each other by alternating non-conjugated single and double bonds. These bonds are present in the solid insoluble substance, therefore we can consider a "concentration" of double bonds accessible to various reagents. Wagner's reaction shows the presence of one double bond per 3–5 carbon atoms, and the Br_2 addition, of one double bond per 7–8 carbon atoms. The classical method of the determination of double bonds by hydrogenation is inapplicable, as the action of hydrogen at temperatures ≥700°C results in the hydrogenolysis with the formation of methane, ethane, and ethene [3].

Alkenes are known to react with acid reagents (X is a halogen). This reaction makes it possible to provide a platinum bond with fullerene black without preliminary making any functional groups, using the reaction of available double bonds with the acid H_2PtCl_6 (Scheme 1). Available data do not allow us to estimate accessibility of double bonds for H_2PtCl_6 and to prognosticate a type of platinum coordination. At the accessibility of each second double bond and coordination of one platinum atom to a double bond, the concentration of fixed platinum can exceed 60 wt % {[195/(2×5×12 + 195)]100% = 61.9%}.

It is easy to see that such platinum fixation demands precursors of the acid nature. At the same time, the addition of an organic base (in particular, amine) facilitates platinum fixation on a carrying agent. The reason of it is not clear and requires the further study, but it is known that platinum compounds form various amine complexes with amines. In addition amines form charge-transfer complexes with fullerene and fullerene black, as fullerenes and fullerene black are electron-deficient, and amines contain a lone electron pair. Pseudo-homogeneous (microcolloidal) catalysts are known, in which a zero-valent metal is kept from sedimentation by stabilizers, for example, amines [5, 6]. Metals were fixed on fullerene black by treating it with metal complexes stabilized by conjugated ligands [7], which, if it was necessary, were reduced by hydrogen, carbon oxide, or sodium borohydride in an organic solvent (benzene,

Scheme 1.



toluene, xylene, ethylbenzene, chloro- and dichlorophenylbenzene, mono-, di-, tri- or tetrachloromethane or tetrahydrofuran) in anaerobic conditions, though it is known that fullerene black does not sorb metal ions [8]. When nanocluster soot was used as the carrying agent palladium was precipitated from tetraaquapalladium(II) perchlorate [9].

When the addition product, in which Pt^{4+} is connected with fullerene black by covalent bonds, was further treated by a reducing agent, for example, by formate ions, platinum was reduced up to Pt(0). We cannot say how zero-valent metal is bound with fullerene black, however it is clear that the reduction of platinum not bound with the carrying agent gives a mixture including Pt(0) and the carrying agent. The mixture of ingredients strongly differing in density cannot be homogeneous and undergos to a gravity separation.

After fixing platinum with the use of double bonds, fullerene black did not sorb oxygen (Fig. 1), and the products of carbon oxidation (CO, *m/e* 28, and CO_2, *m/e* 44), as well as nitrogen (*m/e* 28), were absent. Sorbed water was removed at 115°C.

The second possibility of platinum fixation is also connected with the presence of multiple bonds in the fullerene black structure, but with preliminary formation of hydroxyl groups. Earlier we have shown a possibility of fullerene black bromination following a nucleophilic addition [3] with the formation of a dibromo derivative. Its following treatment by an alkali makes it possible to introduce one OH group per 6–7 carbon atoms (Scheme 2) and to obtain a hydroxy derivative of fullerene black. The main products of its thermolysis in argon atmosphere (Fig. 2) are water, *m/e* 18, 17, desorbed at 110°C, and carbon dioxide, *m/e* 44, appearing at 280 and 570°C.

Fullerene black and its hydroxy derivative substantially differ from each other by thermolysis products [10]. The thermolysis of fullerene black in argon medium at 160°C yields carbon monoxide CO, *m/e* 28, from which dioxide CO_2, *m/e* 44, is formed as a result of the further oxidation at 160, 300, and 550°C. The evolution of significant amounts of water, *m/e* 17, 18, at ~100°C (Fig. 2) points out the hydrophylic nature of the fullerene black hydroxy derivative. Probably, at 220-260°C the fragments with *m/e* 17, 18, are products of the thermal dehydration of the hydroxy derivative, and CO_2, *m/e* 44, (a unique product of carbon oxidation at 274 and 574°C) is the decarboxylation product (Fig. 2). The hydroxy derivative, unlike fullerene black, does not sorb oxygen.

The reaction of $PtCl_4^{2-}$ or $PtCl_6^{2-}$ with OH groups gives HCl (Scheme 2), therefore, to shift the equilibrium, it is necessary to add a base (for example, amine, Am) to the reaction mixture.

According to the elemental analysis, the hydroxy derivative of fullerene black contains one OH group

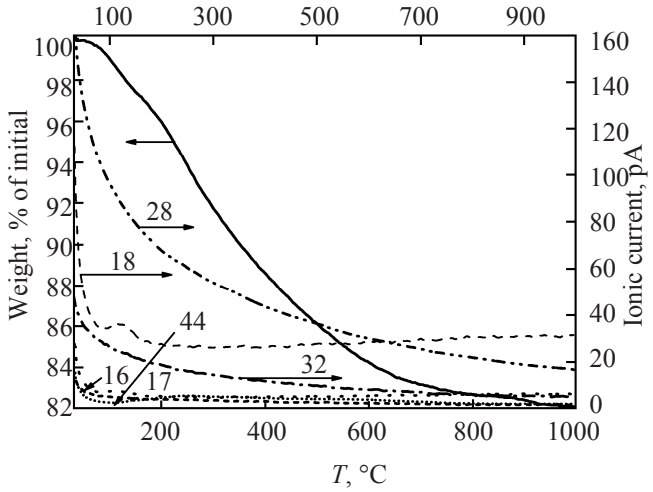
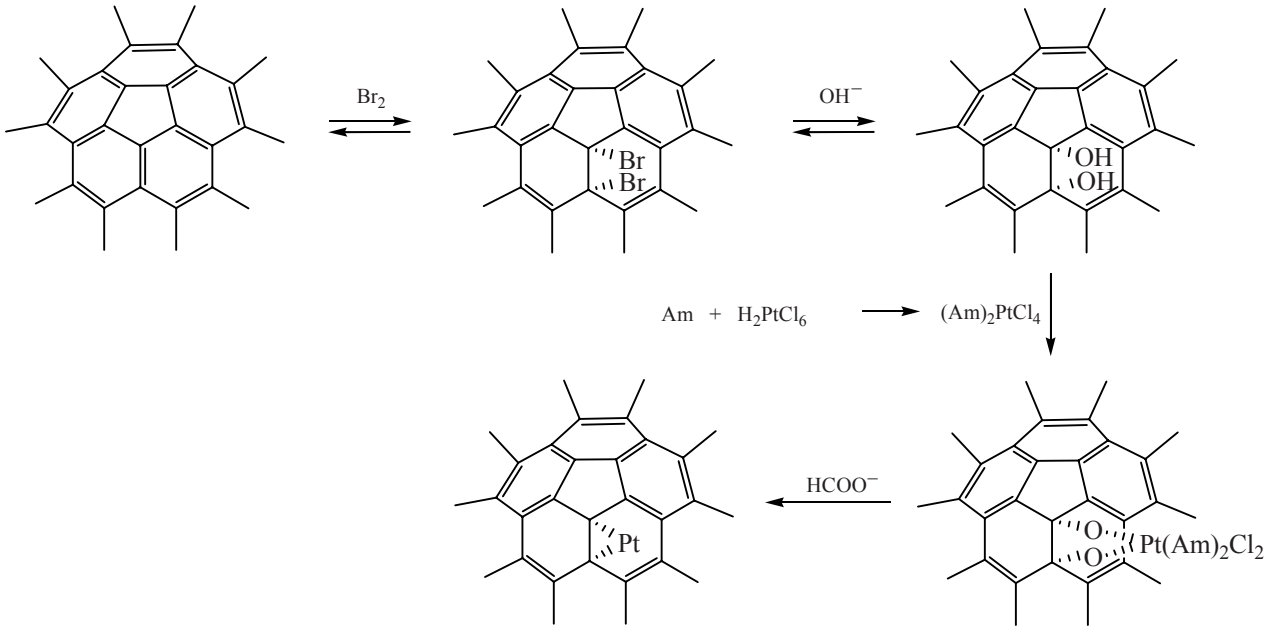


Fig. 1. Thermogram of the composition 12.8% Pt-fullerene black in an argon flow, combined with the mass spectrometric analysis of gaseous thermolysis products. Numbers above curves indicate *m/e* values.

Scheme 2.



per 6–7 carbon atoms. Even at the formation of a chelate complex (two hydroxyl groups per one platinum atom) it is possible to fix 49% of platinum {[195/(7×2×12 + 2×17 + 195)] 100 = 49.1%}.

After platinum fixation, the hydroxy derivative of fullerene black also does not sorb oxygen (Fig. 3). Water is practically absent from the products of the thermolysis of the composition based on the hydroxy derivative of fullerene black containing 12.1% Pt, but insignificant amounts of carbon dioxide are evolved at 240 and 595°C. After platinum precipitation, ionic currents of water (*m/e* 17, 18), though are exhibited at 80°C, become much weaker than in the thermolysis of the hydroxy derivative at 106°C; CO_2 appears in the thermolysis products at the same temperatures, but in greater amounts. The appearance of extremely small amounts of water, *m/e* 17, 18, in the thermolysis products of the hydroxy derivative with attached platinum additionally confirms the assumption that hydroxy groups participate in the platinum fixation (Scheme 2).

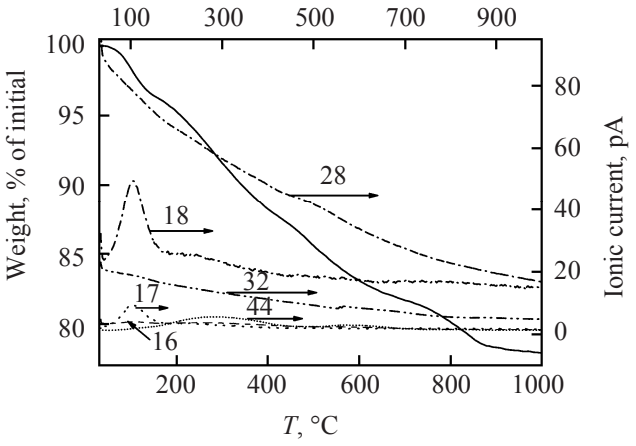


Fig. 2. Thermogram of the hydroxy derivative of fullerene black in an argon flow, combined with the mass spectrometric analysis of gaseous thermolysis products. Numbers above curves indicate *m/e* values.

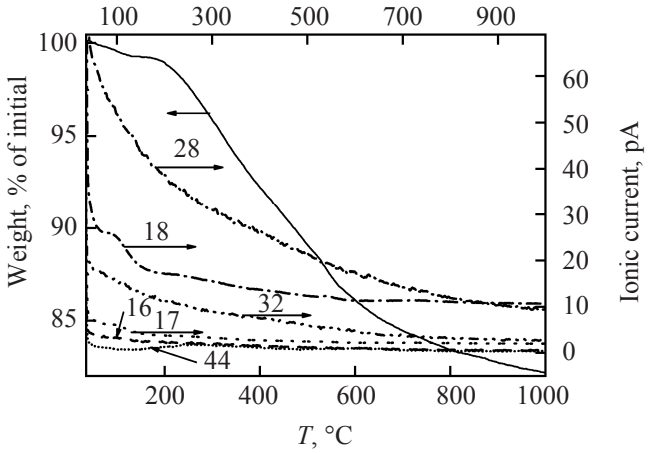


Fig. 3. Thermogram of the composition 12.1% Pt with the fullerene black hydroxy derivative in argon flow combined with the mass spectral analysis of gaseous thermolysis products. Numbers above curves indicate *m/e* values.

Comparing Figs. 1 and 3, it is necessary to point out appreciable similarity of platinum-containing compositions based on fullerene black and its hydroxy derivative, despite of the considerable difference between the carrying agents. The thermolysis of the com-position 12.8% Pt, fullerene black at 115°C yields water, *m/e* 18, and at 270 and 610°C, CO_2, *m/e* 44. The thermolysis of the second composition yields such products at lower temperatures (80, 240, and 595°C, respectively). In the both cases amounts of water and CO_2 are insignificant.

Thus, platinum from the solutions containing $PtCl_4^{2-}$ or $PtCl_6^{2-}$ ions can be attached to fullerene black at C=C bonds or through OH groups formed on their basis. It is not difficult to see that such interaction provides the strongest platinum fixation by covalent bonds. Platinum-containing anions and Pt compounds forming weak bridging –O–O– or only donor–acceptor bonds with hydroxyl groups are unsuitable for these purposes.

Using Pt(IV) or Pt(II) fixed on fullerene black and reducing them by formate ions $CHOO^-$, we have obtained metal platinum particles with average size 3.5 nm in the composition based on the hydroxy derivative of fullerene black and 3.2 nm in the composition based on fullerene black. Platinum particle size in the traditional catalyst 10% Pt/C is 70–80 nm (Fig. 4). Similar particle sizes of platinum particles were detected by electron microscopy (Fig. 5).

The diffraction pattern of the composition of Pt with fullerene black (Fig. 6) contains, apart from amorphous halos, two rings from a finely crystalline phase, which are designated in the electron diffraction pattern.

Indexing the electron diffraction pattern yields the following experimental values of interplanar distances: 0.140 and 0.119 nm. Parameters of the platinum cubic lattice are: d_{111} 0.226; d_{220} 0.139; d_{113} 0.118 nm. Two of these three interplanar distances are observed in the electron diffraction pattern, and the ring (111) is hidden in the amorphous halo.

Platinum fixed on fullerene black considerably reduces the temperature of its oxidation beginning, acting as a catalyst (Fig. 7, curves *1* and *2*). The introduction of hydroxyl groups in fullerene black also reduces the oxidation temperature (Fig. 7, curves *1* and *3*).

To estimate catalytic activity of the resulting samples of platinum-containing compositions, we used the hydrogenation reactions of nitrobenzene in 2-

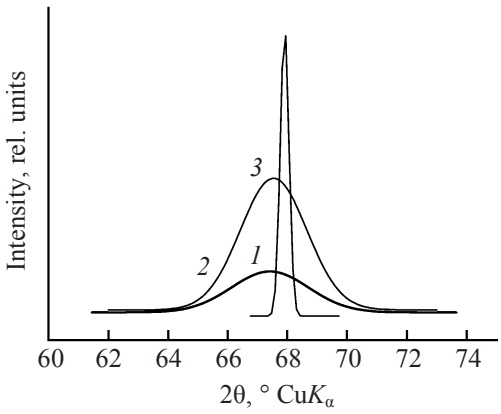


Fig. 4. Line Pt (220) in diffractograms of the samples of the compositions: (*1*) Pt + fullerene black, (*2*) Pt + hydroxy derivative of fullerene black, and (*3*) Pt/C.

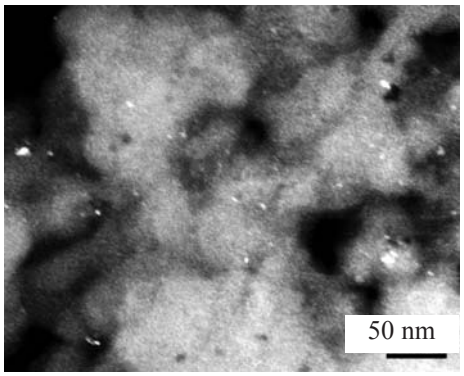


Fig. 5. Darkfield micrograph of a Pt + fullerene black composition.

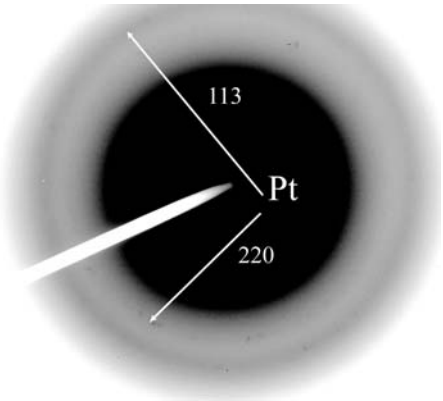


Fig. 6. Electron diffraction pattern of a composition Pt + fullerene black.

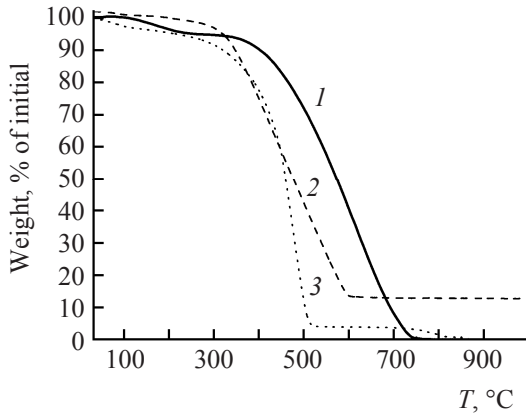


Fig. 7. Oxidative thermograms of samples: (*1*) fullerene black, (*2*) composition Pt + fullerene black, and (*3*) fullerene black hydroxy derivative.

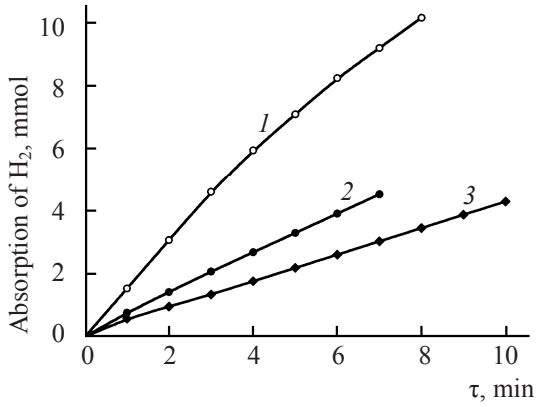


Fig. 8. Initial sections of hydrogen absorption curves for the hydrogenation of individual 1-decene on catalysts: (*1*) 12.8 and (*2*) 5.25% of Pt on fullerene black and (*3*) Pt/C at 45°C.

propanol and of 1-decene (in pure state and in 2-propanol) at atmospheric pressure of hydrogen and temperature of 45°C.

In hydrogenation of individual 1-decene (initial concentration 5.14 M) catalysts based on fullerene black, irrespective of a platinum content, exhibit a higher activity (Fig. 8) than the traditional Pt/C catalyst (10% Pt on AG-3 coal).

Carrying agent	Fullerene black		Coal AG-3
Pt content, wt %	5.25	12.8	10.0
Specific activity, mol H_2/mol Pt min	94.9	77.8	37.5

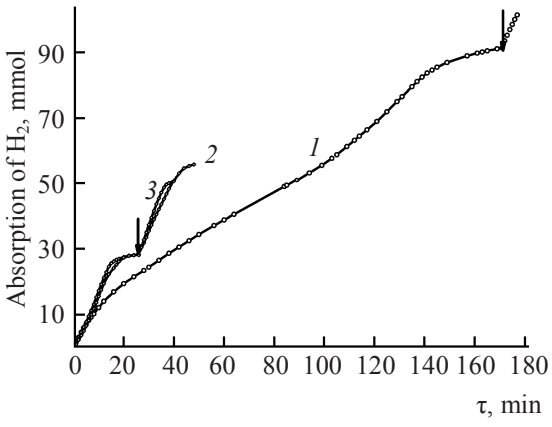


Fig. 9. Curves of hydrogen absorption for the hydrogenation of (*1*) individual 1-decene on the catalyst 12.8% Pt + fullerene black and of 1-decene solution in 2-propanol on the catalysts (*2*) 12.8% Pt + fullerene black and (*3*) 12.1% Pt + fullerene black hydroxy derivative. The moment of adding a new portion of 1-decene is noted by arrows.

During hydrogenation of individual 1-decene after the absorption of ~20% of a rated amount of hydrogen the specific activity sharply decreases from 94.9 up to 24.3 mol H_2/mol Pt min (Fig. 9).

The hydrogenation of a new portion of 1-decene after termination of individual 1-decene hydrogenation [i.e. the hydrogenation of 1-decene (initial concentrations 2.57 M) in formed decane] results in a rise in specific activity, for example, for the catalyst based on fullerene black (12.8% Pt) from 94.9 up to 107 mol H_2/mol Pt min.

Low hydrogenation rate of individual 1-decene, as compared to the 1-decene hydrogenation with accumulation of a product (decane), and a decrease in the hydrogenation rate after absorption of ~20% of rated hydrogen amount, probablly, are connected in this case with a deficit of protons [11]. Accelerating action of the proton-donor solvent is more noticeable in the case of 1-decene hydrogenation in 2-propanol (Fig. 9). According to Fig. 9, specific activities of catalysts based on fullerene black (12.8% Pt) and its hydroxy derivative (12.1% Pt) are practically equal and come to 83.5 mol H_2/mol Pt·min at the initial 1-decene concentration in 2-propanol of 1.028 M. Specific activities remain constant up to the absorption of ~90% of a rated amount of hydrogen. In the hydrogenation of the second portion of 1-decene with decrease in its concentration up to 0.734 M the specific activity increases up to 166.7 mol H_2/mol Pt min and remains constant up to the absorption of ~90% of a rated amount of hydrogen.

In the case of nitrobenzene hydrogenation the reaction order with respect to it is pseudo-zero, and

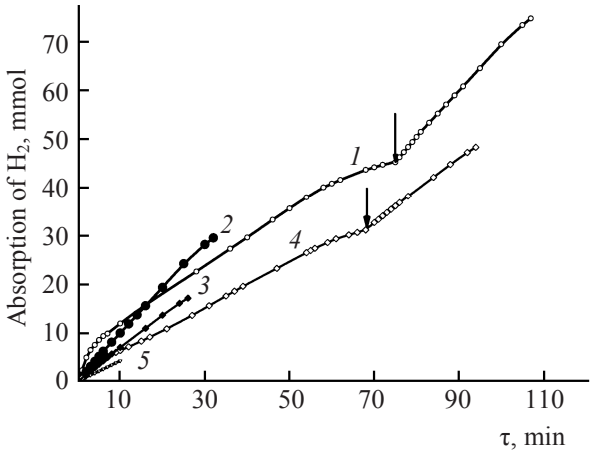


Fig. 10. Curves of hydrogen absorption for the hydrogenation of nitrobenzene in 2-propanol over the catalysts 12.8% Pt + fullerene black, 12.1% Pt + fullerene black hydroxy derivative (*1, 4*) common for two portions, (*2, 3*) for the second portion of nitrobenzene, respectively) and (*5*) 10% Pt/C at 45°C. The moment of adding a new portion of nitrobenzene is noted by arrows.

specific activities of 52.7 and 40 mol H_2/mol Pt min for the same catalysts do not vary as the initial concentration of nitrobenzene is varied (Fig. 10). The specific activity of the 10% Pt/C catalyst (28.7 mol H_2/ mol Pt min) is lower than the activity of catalysts based on fullerene black.

The hydrogenation of the C=C double bond and nitro group is usually considered as structurally insensitive reaction, and the hydrogenation rate should not depend on platinum particle sizes. Nevertheless, the specific activities of catalysts based on fullerene black and its hydroxy derivative with particle sizes 3.2–3.5 nm are rather close to each other and exceed the specific activity of catalyst Pt/C (10% Pt on AG-3 coal) with platinum particle sizes of 70–80 nm.

EXPERIMENTAL

The X-ray patterns were recorded on a DRON-3 instrument. Average sizes of platinum particles were calculated by Selyakov-Scherer equation for the Pt (220) line. The thermograms were recorded on a STA-409 PC Luxx thermoanalyzer combined with a QMS-403 C (NETZSCH, Germany) mass-spectrometer. Values of *m/e* are given in atomic weight units.

Fullerene black was obtained from fullerene-containing soot synthesized by electric-arc graphite vaporization under special conditions providing its high specific surface area and reactivity [2].

Hydroxy-derivative of fullerene black. To 10.0 g of fullerene black a solution 4.0 ml of bromine in 150 ml of carbon tetrachloride was surged and boiled for 28 h. A solid reaction product was filtered, washed out with ethanol and water, then 100 ml of 30% NaOH was added and boiled for 8 h, filtered, washed out with water up to a neutral reaction, and dried. Yield 9.611 g. Found, %: C 82.70; H 1.00. $C_{6.89}OH$.

Platinum fixation was carried out from an aqueous solution, using $H_2PtCl_6 \cdot xH_2O$ (≈40% Pt) as a mother compound. To a suspension of 0.500 g of fullerene black and 0.5 ml of pyridine in 100 ml of water a solution of 0.200 g of $H_2PtCl_6 \cdot xH_2O$ in 50 ml of water was added within 3 h with stirring. After termination of the reagent addition the reaction mixture was boiled for 0.5 h, then 10 ml of formic acid was added, a solution of 10 g of sodium carbonate was surged slowly, and the mixture was held for 12 h. The precipitate was filtered, washed out with water up to a neutral reaction, and dried. Yield 0.511 g. Found, %: C 78.70; H 0.50; solid residue (Pt) 12.81.

Catalytic hydrogenation was carried out in a temperature-controlled vessel with intensive shaking (≥600 min^{-1}), under atmospheric pressure of hydrogen, temperature 45°C. Individual 1-decene or its solution in 2-propanol (20 vol %) was hydrogenated. A weighted sample of the catalyst in all cases was 0.030 g. In all cases, unless otherwise specified, specific catalytic activity was calculated by initial sections of hydrogen absorption curves when the conversion did not exceed 1–2%. The second portion of 1-decene (5 ml) was introduced in a hydrogen flow after a noticeable (more than 10-fold) decrease in the rate of hydrogen absorption.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 08-03-01117).

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