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Preparation of Hydrogenation Catalysts Based on Platinum Nanoparticles Supported on Carbon Nanomaterials

S. D. Kushch, N. S. Kuyunko, and B. P. Tarasov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

e-mail: ksd@icp.ac.ru

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Abstract—Hydrogenation catalysts as platinum nanoparticles supported on carbon nanomaterials (single- and multi-walled nanotubes, nanofibers, and fullerene black) have been obtained by modifying the platinum precursor with an organic base. A support pretreatment procedure for producing carboxyl groups on the nanotube and nanofiber surface is suggested.

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In recent years, there has been increasing interest in carbon nanomaterials (CNMs) as supports for hydrogen activation catalysts and electrocatalysts. This is due to the unique properties of CNMs, primarily the nanometer-scale size of their particles and their compatibility with the membrane materials used in fuel cells. In addition, catalysts containing supported nanosized metal particles are expected to be highly active.

Fixation of metals through anchoring functional groups [1–4] is an important aspect of the problem of obtaining nanomaterial-supported catalysts.

Here, we report the preparation of platinum-based hydrogenation catalysts supported on various CNMs: single-walled nanotubes (SWNT); multi-walled nanotubes (MWNT); carbon nanofibers (CNF); and fullerene black (FB), which is the insoluble residue remaining after fullerene extraction from fullerene soot.

EXPERIMENTAL

MWNT, SWNT, and FB with a specific surface area of S_{BET} = 15, 300, and 290 m^2/g, respectively, were obtained by arc evaporation of graphite [5, 6]. CNFs were synthesized by catalytic pyrolysis of the propane–butane fraction (CNF1) and ethylene (CNF2) [7, 8] (S_{BET} = 130 and 60 m^2/g, respectively).

In order to produce functional groups capable of anchoring platinum on the support surface, SWNT, MWNR, and CNFs were pretreated with oxidizing acids. A MWNT suspension in a mixture of concentrated nitric and sulfuric acids (1 : 1 vol/vol) was ultrasonicated at 40°C for 4 h. SWNT, CNF1, and CNF2 were oxidized with concentrated nitric acid at 70°C for 24–72 h. Oxidized SWNT, MWNT, and CNF were filtered, washed with twice distilled water until neutral, and dried. FB was used without being pretreated.

For platinum anchoring, ~70 ml of an aqueous suspension of oxidized SWNT, MWNT, CNF, or untreated FB (CNM concentration of ≤5 g/l) was ultrasonicated for 20 min. Next, an $H_2PtCl_6 \cdot xH_2O$ solution (platinum concentration of up to 4 g/l) was added to the suspension over 2–3 h in the presence of 0.5 ml of pyridine under continuous stirring. The reaction mixture was boiled for 0.5–1 h.

For reduction of platinum, 10 ml of formic acid and a sodium carbonate solution (~10 g of the salt in 50 ml of water) were added to the reaction mixture. The mixture was left standing for 12 h, and the precipitate was then filtered, washed with twice distilled water until neutral, and dried.

Elemental analysis was carried out by semimicro methods. Specific surface areas were measured using the nitrogen adsorption technique (dynamic BET method, Quantasorb system, Quantachrome Instruments, United States). X-ray diffraction patterns we recorded on a DRON-3 diffractometer. The average particle size was derived from the Pt(220) line using the Selyakov–Scherrer equation. Thermal analysis was carried out on an STA-409 PC Luxx thermal analyzer couples with a QMS-403 C mass spectrometer (Netzsch, Germany). Hereafter, *m/e* values are expressed in atomic mass units.

Samples to be examined by transmission electron microscopy (TEM) were prepared by dispersing a powder in ethanol followed by spraying the suspension onto a copper grid coated with a collodion film. Measurements were carried out on a JEOL JEM-2000EX microscope at an accelerating voltage of 500 kV.

RESULTS AND DISCUSSION

Carbon nanotubes and nanofibers, which consist of rolled or flat graphene sheets with aromatic conjugated bonding, are fairly stable. Having no protons,

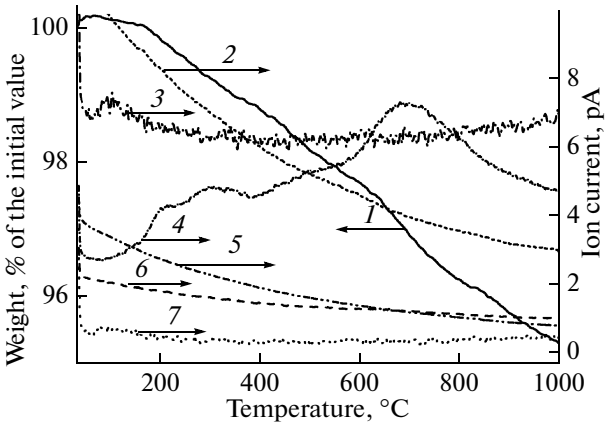

Fig. 1. (*1*) TG curve of oxidized MWNT in flowing argon. (*2*–*7*) Mass spectra of the gaseous products: m/e = (*2*) 32, (*3*) 18, (*4*) 44, (*5*) 28, (*6*) 16, and (*7*) 17. For convenience, the ionic current for $m/e = 44$ (curve *4*) is multiplied by a factor of 6, and that for $m/e = 28$ (curve *5*) is reduced by a factor of 10.

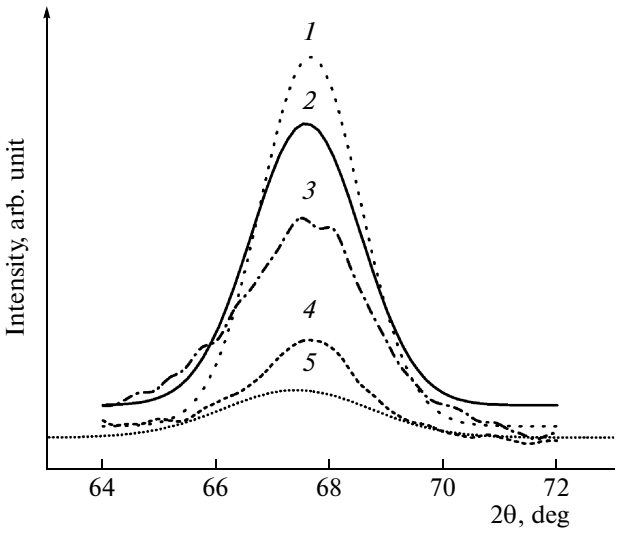

Fig. 2. X-ray diffraction patterns (Pt(200) line) from the catalysts (*1*) (10.3% Pt)/CNF1, (*2*) (12.6% Pt)/CNF2, (*3*) (9.3% Pt)/MWNT, (*4*) (11.4% Pt)/SWNT, and (*5*) (5.25% Pt)/FB.

they do not enter into substitution reactions. They are capable of forming complexes, but only oxidation makes them form covalent bonds. The oxidizer can be sulfuric or nitric acid or their mixture, a hydrogen peroxide + sulfuric acid mixture, or a sulfuric acid solution of permanganate or dichromate ions [4]. In our experiments, carbon materials with the highest oxygen content (not exceeding 6 wt %, however) were obtained by oxidizing the staring carbons with a sulfuric acid + nitric acid mixture (1 : 1 vol/vol) under ultrasonication for 4 h (MWNT) or by prolonged (24- to 72-h-long) heat treatment at 70°C in concentrated nitric acid (SWNT, CNF1, CNF2). It is likely that this treatment produces carboxyl groups all over the support surface.

This is suggested by the fact that the thermolysis of the oxidized materials mainly yields carbon dioxide ($m/e = 44$). Carbon monoxide ($m/e = 28$), which usually results from the thermolysis of introduced anhydride, lactone, phenol, carbonyl, and quinoid groups [4], is almost entirely absent (Fig. 1). The assumption that carbon dioxide results from carbon monoxide disproportionation is inconsistent with the shape of the weight loss curve (Fig. 1, curve *1*). The survey mass spectra of the gaseous products of the thermolysis of the oxidized materials indicate that, in the m/e = 1–300 range, there are no significant amounts of any products other than those indicated in Fig. 1. The thermoanalytical data for SWNT and CNF are similar to those presented in Fig. 1 for MWNT.

Chloroplatinic acid $H_2PtCl_6 \cdot xH_2O$, with its platinum-containing anion $PtCl_6^{2-}$, cannot react with the carboxyl groups of the functionalized support. Under the action of an organic base (e.g., pyridine), $H_2PtCl_6 \cdot xH_2O$ turns into dipyridineplatinum(IV) or tetrapyridineplatinum(IV) chlorides, which are limitedly soluble in water. In addition, the base favors hydrolysis yielding platinum hydroxo complexes, which are water-insoluble. Reacting with dipyridineplatinum(IV) and tetrapyridineplatinum(IV) chlorides, the carboxylated carbon material exchanges its protons for the resulting platinum-containing cations (e.g., $Pt(Py)_2^{4-}$). Excess pyridine binds the hydrochloric acid released in the ion exchange. After adding an aqueous $H_2PtCl_6 \cdot xH_2O$ solution to a stirred and heated suspension of oxidized nanocarbon in the presence of pyridine and boiling the reaction mixture for 0.5–1 h, no platinum is indeed detected in the mixture.

The reduction of the resulting material with the formate ion on the SWNT, MWNT, or CNF surface yields platinum particles with an average size of 6–8 nm (Fig. 2).

The composition prepared from SWNT, MWNT, and CNF that were not oxidized or treated with an organic base and the samples containing more than 18% platinum are unstable, releasing platinum metal under the action of gravity. These observations are quite consistent with the elemental analysis data for the maximum amount of platinum that can be bound to the oxidized SWNT, MWNT, or CNF surface under the assumption that one a platinum atom is coordinated with two carboxyl oxygen atoms (at most 22 wt %).

Because FB [6] with a particle size of 40–50 nm (Fig. 3a) has one nonconjugated double bond for each 3–5 carbon atoms, H_2PtCl_6 adds to FB like any other HX molecule. So-called anchoring hydroxyl groups can be produced in FB by hydroxylation or by bromination followed by alkaline hydrolysis [6]. Pyridine is

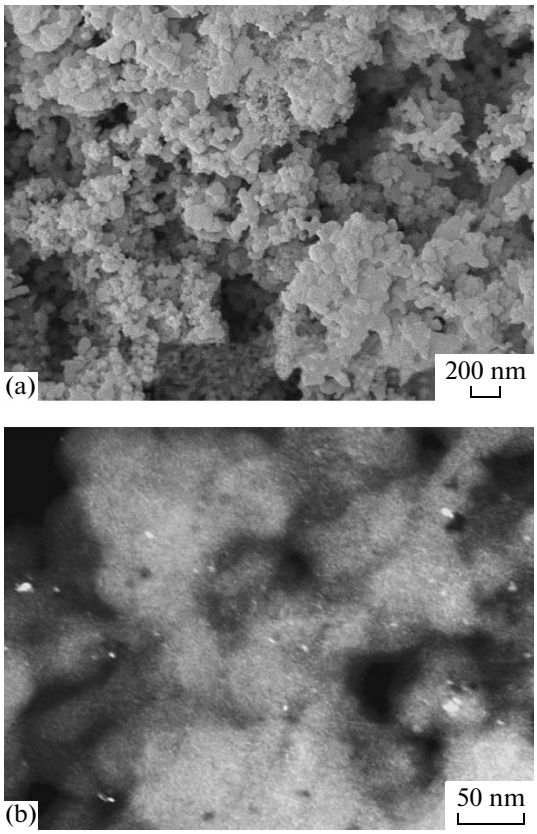

Fig. 3. TEM images of (a, light areas) FB and (b, dark areas) (5.25% Pt)/FB.

favorable for the interaction between FB and H_2PtCl_6 since, as in the case of carbon nanomaterials with a graphene structure, it facilitates platinum deposition because of the poor solubility of dipyridineplatinum(IV) and tetrapyridineplatinum(IV) chlorides. The reduction of the platinum addition product with the formate ion affords platinum particles with an average size of 4–5 nm (Fig. 2, curve *5*). This is confirmed by TEM data (Fig. 3b). Earlier, similar compositions with FB as the support were prepared using $Ru_x(CO)_y$ [9] or $Pd(NO_3)_2$ [10] as the precursor.

As was demonstrated by model experiments, these compositions can serve as dec-1-ene and nitrobenzene hydrogenation catalysts. The platinum nanoparticle catalysts supported on CNMs have a higher specific activity than the conventional catalyst Pt/C, in which the support is the activated carbon AG-3. The FB-based catalysts with a platinum particle size of 4–5 nm are more active than CNF1-based catalysts with a platinum particle size of 6–8 nm or the Pt/C catalyst with 70- to 80-nm platinum particles. In the case of nitrobenzene hydrogenation in propan-2-ol, the specific catalytic activity decreases in the order Pt/FB > Pt/CNF1 > Pt/AG-3 > Pt/SWNT > Pt/MWNT > Pt/CNF2 and is 52.8, 51.7, 37.4, 32.8, 32.3, and 27.8 (mol H_2) (mol Pt)$^{-1}$ min^{-1}, respectively [11]. Therefore, the activity of these catalysts is determined not by the specific surface area of the support, which decreases in the order AG-3 > FB > CNF1, and not by the electrical conductivity of the support, which decreases in the order CNF1 > AG-3 > FB, but by the size of the supported platinum particles.

Thus, for binding platinum to obtain hydrogenation catalysts supported on SWNT, MWNT, and CNF, the nanomaterials should be preoxidized. FB, which contains nonconjugated double bonds, generally needs no pretreatment before being used as the support. In some cases, it needs hydroxylation or bromination followed by the alkaline hydrolysis of the brominated derivative. By performing the reaction between a CNM prepared in one way or another and H_2PtCl_6 in the presence of an organic base and by reducing the resulting composition, it is possible to combine several ways of binding platinum [4]: the formation of a compound poorly soluble in water ($[Pt(Py)_2]Cl_4$ or $[Pt(Py)_4]Cl_4$), the exchange of carboxyl protons for platinum-containing cations, and the reduction of platinum compounds to platinum metal. This procedure affords active and stable hydrogenation catalysts.

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