

VARIOUS  
TECHNOLOGICAL PROCESSES

## Decoration of Carbon Nanomaterial Powders with Dispersed Platinum Metal Particles

V. G. Isakova<sup>a,\*</sup>, I. V. Osipova<sup>a</sup>, A. I. Dudnik<sup>a</sup>, A. V. Cherepakhin<sup>a,b</sup>,  
N. V. Zharikova<sup>b</sup>, I. V. Nemtsev<sup>c</sup>, and M. N. Volochaev<sup>c</sup>

<sup>a</sup> Kirensky Institute of Physics, Separate Department of Federal Research Center Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia

<sup>b</sup> Siberian Federal University, Krasnoyarsk, 660041 Russia

<sup>c</sup> Federal Research Center Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia

\*e-mail: churilov@iph.krasn.ru

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**Abstract**—Carbon nanomaterials (fullerite, detonation nanodiamonds, Taunit, fullerene, fullerene-containing black) were decorated with platinum group metal nanoparticles in situ in one step by low-temperature combustion (~250–270°C) of a powdered mixture of platinum metal acetylacetonate [Pt-M(acac)<sub>n</sub>, Pt-M = Pt(II), Pd(II), Rh(III), Ir(III), acac = CH<sub>3</sub>COCHCOCH<sub>3</sub>, n is the oxidation state of Pt-M] with carbon nanomaterials in air. As shown by thermal analysis, the process is based on thermal oxidative degradation of the organometallic complex, catalyzed by carbon nanomaterials, with oxidation (combustion) of the organic moiety and release of the metal into the condensed phase. The thermal process in an open system occurs in the glowing mode (210–250°C); the size of the nanoparticles formed is 7–30 nm. Under the conditions restricting the air access to the reaction mixture and free outflow of gaseous products formed by oxidation of acac ligands, the nanoparticle size decreases to 3–10 nm. The particle size depends on the metal amount in the initial powder mixture and on the support morphology.

**Keywords:** carbon nanomaterials, platinum metal nanoparticles, in situ one-step method

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Nanostructured carbon materials (NCMs) with surface-deposited platinum metal nanoparticles attract growing attention because of the possibilities of using them in catalysis [1, 2], power units [3, 4], electrochemical probing [5, 6], and synthesis of materials for fuel cells [7–9]. On the other hand, the problem of preparing uniform fine platinum metal particles dispersed on a carbon support remains to be solved because of agglomeration of these particles in the course of the synthesis. However, because the particle growth and agglomeration are processes depending on the time of diffusion and migration over the support surface, short-time in situ one-step synthesis allows preparation of very fine (2–7 nm) nanoparticles [10].

One-step in situ methods for gas-phase thermolysis of Pt(acac)<sub>2</sub> have been successfully used recently for

preparing platinum nanoparticles deposited onto carbon supports of various types. Choi et al. [11] prepared Pt nanoparticles (2–7 nm) deposited onto a carbon material (VulcanXC-72R) by combustion of Pt(acac)<sub>2</sub> in a flame of a combustible solvent (xylene/acetone). Merche et al. [12] deposited Pt nanoparticles (~7 nm) onto carbon black by decomposing Pt(acac)<sub>2</sub> powder in the post discharge of atmospheric radiofrequency plasma combustion. Mercado-Zúñiga et al. [13] decorated carbon nanotubes by direct gas-phase thermolysis of Pt(acac)<sub>2</sub>. The mixture of Pt(acac)<sub>2</sub> with nanotubes was heated in a quartz tubular reactor first at 180 and then at 400°C. Wang et al. [14] decorated multiwalled carbon nanotubes with palladium nanoparticles by thermal decomposition of palladium acetylacetonate [Pd(acac)<sub>2</sub>] in refluxing xylene. As reported by Isakova et al. [15–17],

direct heating of powdered mixtures of platinum metal acetylacetonates with NCMs (detonation nanodiamonds, fullerite, fullerene-containing black) in air leads to the ignition at 170–180°C and low-temperature combustion in the glowing mode with the formation of metal or oxide particles. However, the mechanism of the thermal reaction in the Pt-M(acac)<sub>n</sub>/NCM system and the product morphology were not studied in detail. In [18], we used the combustion of powdered mixtures of Pt(acac)<sub>2</sub> and Pd(acac)<sub>2</sub> with detonation nanodiamonds (DNDs) as an in situ one-step method for depositing Pt and Pd nanoparticles (7–10 nm) onto the DND powder. This study deals with in situ one-step synthesis of platinum metal (Pt, Pd, Ir, Rh) nanoparticles deposited onto detonation nanodiamonds, fullerite, fullerenol, Taunit, and fullerene-containing black by low-temperature combustion of powdered mixtures of platinum metal acetylacetonates with a carbon nanomaterial in air. Conditions were determined for decreasing the metal particle size by varying the deposition conditions.

## EXPERIMENTAL

A 0.2–0.3-g portion of a mixture of nanostructured carbon material and platinum metal acetylacetonate powders [Pt-M(acac)<sub>n</sub>/NCM] with 5 and 10 wt % metal content relative to NCM was ground in a mortar and heated in a crucible using two procedures. In the first procedure, the mixtures were heated in open air at a heater temperature of 250°C up to ignition of the powders (~180°C) with their subsequent glowing. In the second procedure, the mixtures were heated in an untightly closed crucible at ~220 and 250°C for ~20–30 min. Mixtures of Rh(acac)<sub>3</sub> and Ir(acac)<sub>3</sub> with NCM were heated at 250°C and introduced into a crucible preheated to 250°C.

Detonation nanodiamonds [TU (Technical Specification) 84-1124–87, Altai Federal Research and Production Center, Biisk, Altai krai, Russia] were annealed with sodium acetylacetonate and then kept in a boiling HCl solution for additional purification and disintegration of particle aggregates [18]. Fullerite was extracted with toluene from fullerene-containing black prepared by electric arc synthesis in carbon–helium plasma of high-frequency arc. Fullerenols were prepared by the previously described procedure [19]. Taunit (TU 2166-001-02069289–2007, Komsomolets Plant, Tambov, Russia) was modified to obtain –COOH groups

on the surface by treatment with concentrated nitric acid at 70°C for 10 h [20]. Platinum metal acetylacetonates were synthesized by the procedures described in [21].

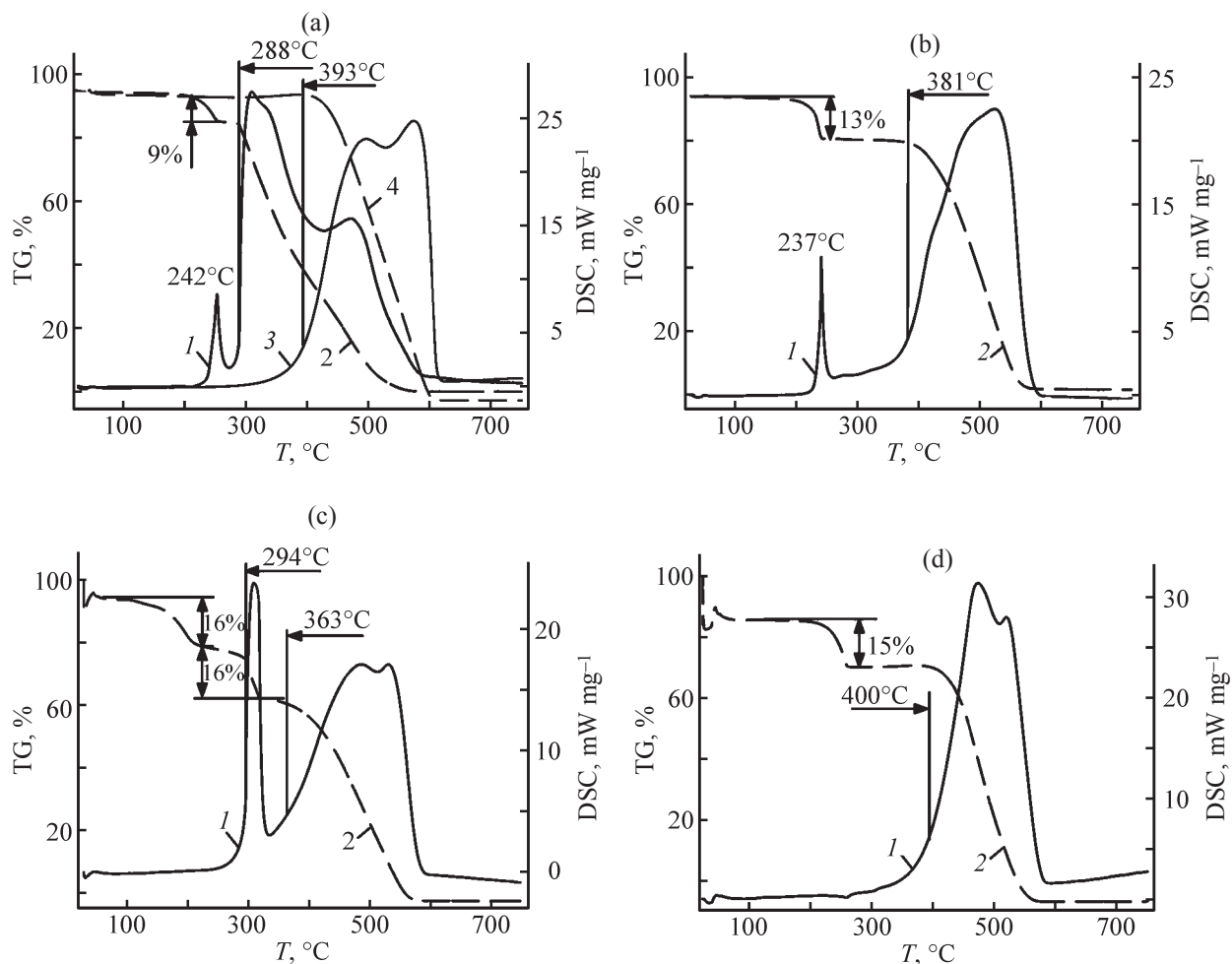
The structure of the solids obtained was studied by X-ray diffraction (XRD) with a DRON-4 diffractometer using CuK<sub>α</sub> radiation. Synchronous thermal analysis (STA) combining thermal gravimetric analysis (TG) with differential scanning calorimetry (DSC) was performed with an STA 449 C Jupiter device (Netzsch). The samples were heated in crucibles with untight lids at a rate of 10 deg min<sup>-1</sup> to 750°C in a flow (35 mL min<sup>-1</sup>) of a 1 : 5 oxygen–argon mixture. The weights of Pt(acac)<sub>2</sub>/fullerite, Pd(acac)<sub>2</sub>/fullerite, and Rh(acac)<sub>3</sub>/fullerite samples were 5 mg, and that of Ir(acac)<sub>3</sub>/fullerite sample (7 wt % metal), 2 mg. The images of the sample surface were obtained by scanning electron microscopy (SEM) with a Hitachi S-5500 microscope and by transmission electron microscopy (TEM) with an HT-7700 microscope.

## RESULTS AND DISCUSSION

Heating of Pt(acac)<sub>2</sub>/NCM, Pd(acac)<sub>2</sub>/NCM, and Rh(acac)<sub>3</sub>/NCM powdered mixtures in air leads to their ignition with the subsequent glowing. Ir(acac)<sub>3</sub>/NCM mixtures inflame. The ignition occurs at temperatures corresponding to vaporization of the free complexes but below the temperatures of their thermolysis in air [Pt(acac)<sub>2</sub>, 237°C; Pd(acac)<sub>2</sub>, 208°C; Rh(acac)<sub>3</sub>, 247°C; Ir(acac)<sub>3</sub>, 252°C] [22]. The exothermic behavior of the Pt-M(acac)<sub>n</sub>/NCM powdered mixture is a consequence of physicochemical transformations of the vapor phase of metal acetylacetonates on the solid surface of NCM particles. Red heat spots in the course of powder glowing are local. That is, there are small overheating areas (hot points) in which the exothermic reaction occurs, but the temperature of the mixture as a whole increases insignificantly (~250–270°C).

After the completion of the combustion of Pt-M(acac)<sub>n</sub>/NCM powdered mixtures, the weight loss determined by weighing corresponded, except the Ir(acac)<sub>3</sub>/NCM samples, to the weight of the acac ligands in the initial mixtures with a slight increase for the Pd(acac)<sub>2</sub>/NCM samples. This fact shows that Pt-M(acac)<sub>n</sub>/NCM mixtures decompose to metal particles without loss (oxidation) of nanocarbon.

To determine the nature of ignition and of the products formed, we studied the thermal behavior of

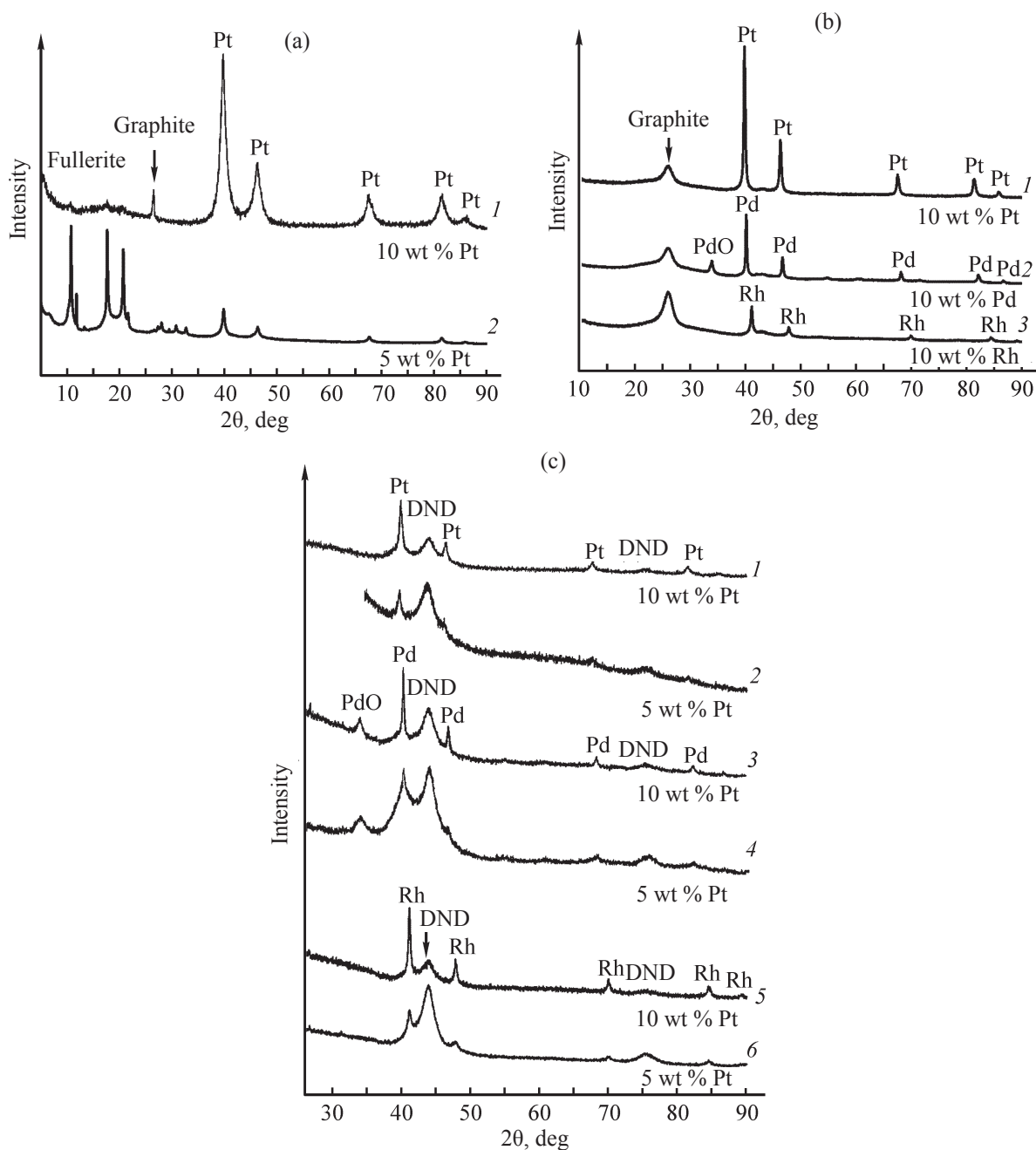


**Fig. 1.** DSC and TG curves of heating in an oxygen-containing medium. (a) Pt(acac)<sub>2</sub>/fullerite [(1) DSC and (2) TG] and fullerite [(3) DSC and (4) TG], (b) Pd(acac)<sub>2</sub>/fullerite [(1) DSC and (2) TG], (c) Rh(acac)<sub>3</sub>/fullerite [(1) DSC and (2) TG], and (d) Ir(acac)<sub>3</sub>/fullerite [(1) DSC and (2) TG].

powdered mixtures of Pt-M(acac)<sub>n</sub> with fullerite as a model system. For Pt(acac)<sub>2</sub>/fullerite and Pd(acac)<sub>2</sub>/fullerite samples, there are exothermic effects in the DSC curves with the onset at 210°C and peaks at 242 and 237°C, respectively, with small heat release (~0.9 and ~0.6 kJ g<sup>-1</sup>, respectively; Figs. 1a, 1b). These effects correspond to low-temperature combustion of the samples on their heating in air. The sample weight loss calculated from the TG curves in the temperature interval of these exothermic effects is close to the total weight of organic acac ligands, which suggests their oxidation and gasification with the subsequent formation of Pt/fullerite and Pd/fullerite composites. Rh(acac)<sub>3</sub> is more stable thermally and partially sublimates under the thermal analysis conditions; the exothermic effect for it is observed at higher temperatures (~240–320°C)

(Fig. 1c). However, the weight loss in the temperature region of the exothermic effect also corresponds to the loss of acac ligands and release of the metal. For the Ir(acac)<sub>3</sub>/fullerite sample, the weight loss in the interval 180–250°C is associated with complete sublimation of Ir(acac)<sub>3</sub> (Fig. 1d).

It is known that the weight loss of free volatile salts Pt-M(acac)<sub>n</sub> on heating in air corresponds to their vaporization up to the exothermic effect of the oxidation of acac ligands [20, 21], whereas the weight loss for the Pt(acac)<sub>2</sub>/fullerite and Pd(acac)<sub>2</sub>/fullerite mixtures in the experiment is associated directly with the ligand oxidation, suggesting the catalytic effect of the support on the thermal oxidative degradation of the platinum metal complex in the vapor phase (Figs. 1a, 1b). Above 290°C, a strong exothermic effect is observed in the DSC



**Fig. 2.** X-ray diffraction patterns of products formed by combustion of various mixtures in air. (a) Pt(acac)<sub>2</sub>/NCM [(1) fullerene-containing black and (2) fullerite], (b) Pt-M(acac)<sub>n</sub>/Taunit [(1) Pt(acac)<sub>2</sub>, (2) Pd(acac)<sub>2</sub>, and (3) Rh(acac)<sub>3</sub>], and (c) Pt-M(acac)<sub>n</sub>/DND [(1, 2) Pt(acac)<sub>2</sub>, (3, 4) Pd(acac)<sub>2</sub>, and (5, 6) Rh(acac)<sub>3</sub>].

curve for the Pt(acac)<sub>2</sub>/fullerite sample. This effect can be attributed to the fullerite combustion catalyzed by the already formed platinum particles. Fullerite itself is stable at these temperatures, and the exothermic effect of the fullerite combustion in the sample without Pt-M(acac)<sub>n</sub> starts only at 390°C (Fig. 1a). In mixtures of fullerite

with Pd(acac)<sub>2</sub>, the fullerite oxidation temperature does not decrease (Fig. 1b). Certain decrease in the fullerite oxidation temperature is recorded for the Rh(acac)<sub>3</sub>/fullerite mixture (Fig. 1c). Ir(acac)<sub>3</sub> is characterized by the highest thermal and chemical stability in the vapor phase among platinum metal acetylacetonates, but at

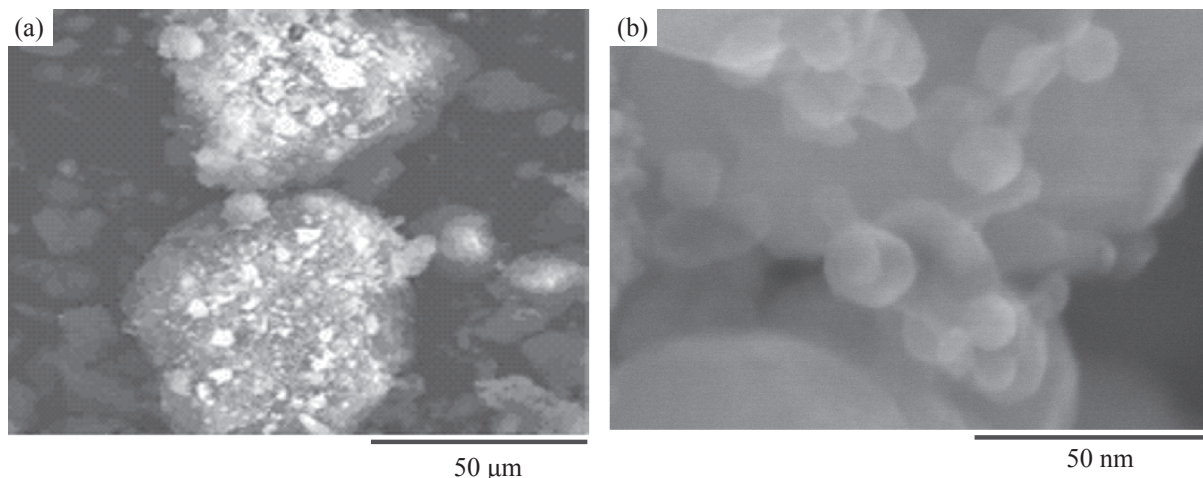


Fig. 3. SEM images of the surface of (a) Pd/DND<sub>com</sub> and (b) Pd/DND composites.

258°C the sample simultaneously sublimes, burns out, and decomposes with very intense heat release [22]. Therefore, for thermal analysis we took Ir(acac)<sub>3</sub>/fullerite mixtures with decreased Ir content, which did not allow conclusions on the character of the thermal reaction of the components (Fig. 1d). Thus, combustion of Pt-M(acac)<sub>n</sub>/NCM mixtures on heating in air is due to exothermic transformations of Pt-M(acac)<sub>n</sub> vapor on the NCM surface, when the released heat is accumulated in the system and prevails over the removed heat because of low thermal conductivity of the carbon material, which results in ignition of the mixture in the form of glowing.

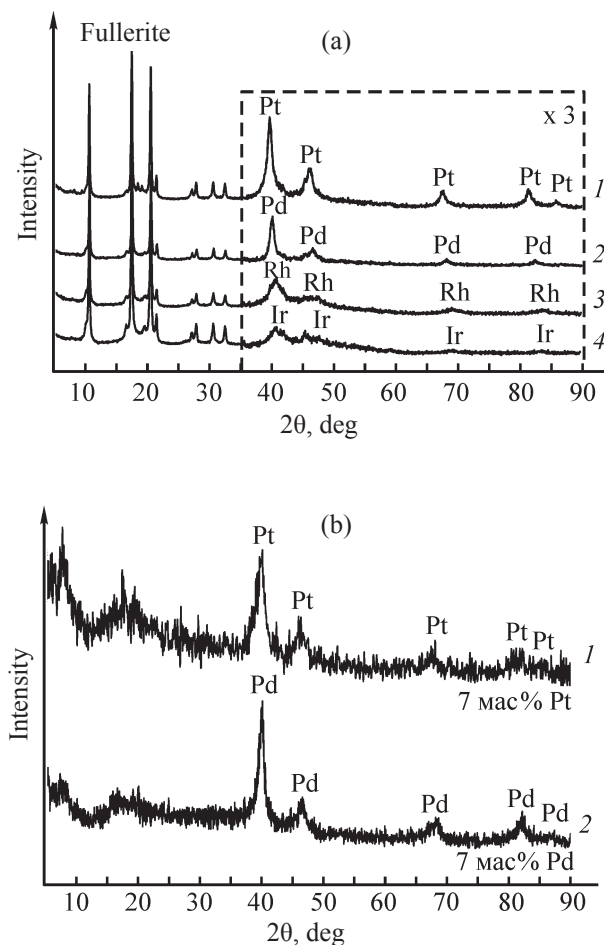
Figure 2 shows the X-ray diffraction patterns of reaction products obtained by heating Pt(acac)<sub>2</sub>/NCM, Pd(acac)<sub>2</sub>/NCM, and Rh(acac)<sub>3</sub>/NCM powdered mixtures in air in an open system. The reflections correspond to NCM [DND, 2θ 43.8° and 75.4°; fullerite, 2θ 10.7°, 17.6°, 20.6°, 21.5°, etc.; Taunit (graphite), 2θ 26.1°] and to the deposited metals (Pt, 2θ 39.8°, 46.2°, 67.5°, 81.4°, and 85.7°; Pd, 2θ 40.1°, 46.7°, 68.1°, 82.3°, and 86.6°; Rh, 2θ 40.7°, 47.4°, 69.4°, 83.7°, and 88.3°). The metal reflections correspond to the face-centered cubic lattice of platinum, rhodium, and palladium metal particles. Slight (~2%) oxidation of palladium is observed.

A decrease in the metal content of the mixture leads to broadening of metal particle reflections, which indicates that the platinum metal particles have smaller size at the lower metal amount on the support. The mean crystallite size in the metal particles of Pt-M/NCM composites, estimated by the Scherrer formula, is 7–15 nm at 5 wt %

metal content and 20–30 nm at 10 wt % metal content. In Pt-M/Taunit samples containing 10 wt % metal, the crystallite size in particles of the composites is 30–35 nm.

Thorough mixing of Pt-M(acac)<sub>n</sub> crystallites with NCM is used for ensuring rapid and direct contact of the vapor with the carbon surface on heating the samples to the vaporization temperature of the complex. Figure 3 shows how the morphology of palladium deposited onto DND powder varies with the support grain size. On coarse grains (~100 μm) of powders of the commercial sample (DND<sub>com</sub>), palladium deposited by thermal decomposition of Pd(acac)<sub>2</sub> has the form of coarse particles and films (Fig. 3a). The reduction of platinum metals is an autocatalytic reaction. For example, the deposited metal particle catalyzes further reaction of the metal reduction and formation of new particles, which leads to their agglomeration. On disintegrated DND grains (particle size ~100 nm), the number of sites for the sorption and reduction of Pd(acac)<sub>2</sub> increases; as a result, ~10-nm particles are deposited (Fig. 3b). Thus, high dispersity of the support allows the size of the deposited particles to be decreased.

In heating of Pt-M(acac)<sub>n</sub>/NCM powdered mixtures in crucibles with untight lids, the air access to the mixture and the outflow of CO<sub>2</sub> and H<sub>2</sub>O vapor formed in the course of oxidation of acac ligands and deposition of the metal on NCM are restricted. Therefore, the pressure of CO<sub>2</sub> and H<sub>2</sub>O vapor under the conditions of their restricted outflow can prevent the diffusion of metal nuclei over the NCM surface and thus their agglomeration. The temperature of heating of Pt(acac)<sub>2</sub>/



**Fig. 4.** X-ray diffraction patterns of products formed by combustion of the mixtures under the conditions of restricted outflow of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapor. (a)  $\text{Pt-M}(\text{acac})_n/\text{fullerite}$  [(1)  $\text{Pt}(\text{acac})_2$ , (2)  $\text{Pd}(\text{acac})_2$ , (3)  $\text{Rh}(\text{acac})_3$ , and (4)  $\text{Ir}(\text{acac})_3$ ] and (b)  $\text{Pt-M}(\text{acac})_n/\text{fullerenol}$  [(1)  $\text{Pt}(\text{acac})_2$  and (2)  $\text{Pd}(\text{acac})_2$ ].

fullerite,  $\text{Pd}(\text{acac})_2/\text{fullerite}$ ,  $\text{Pt}(\text{acac})_2/\text{fullerenol}$ , and  $\text{Pd}(\text{acac})_2/\text{fullerenol}$  mixtures ( $210^\circ\text{C}$ ) corresponded to the onset temperature of the exothermic effect of the acac ligand oxidation (Figs. 1a, 1b). Heating of  $\text{Rh}(\text{acac})_3/\text{fullerite}$  and  $\text{Ir}(\text{acac})_3/\text{fullerite}$  mixtures at  $250^\circ\text{C}$  in crucibles preheated to  $250^\circ\text{C}$  allowed the sublimation loss of  $\text{Rh}(\text{acac})_3$  and  $\text{Ir}(\text{acac})_3$  to be prevented.

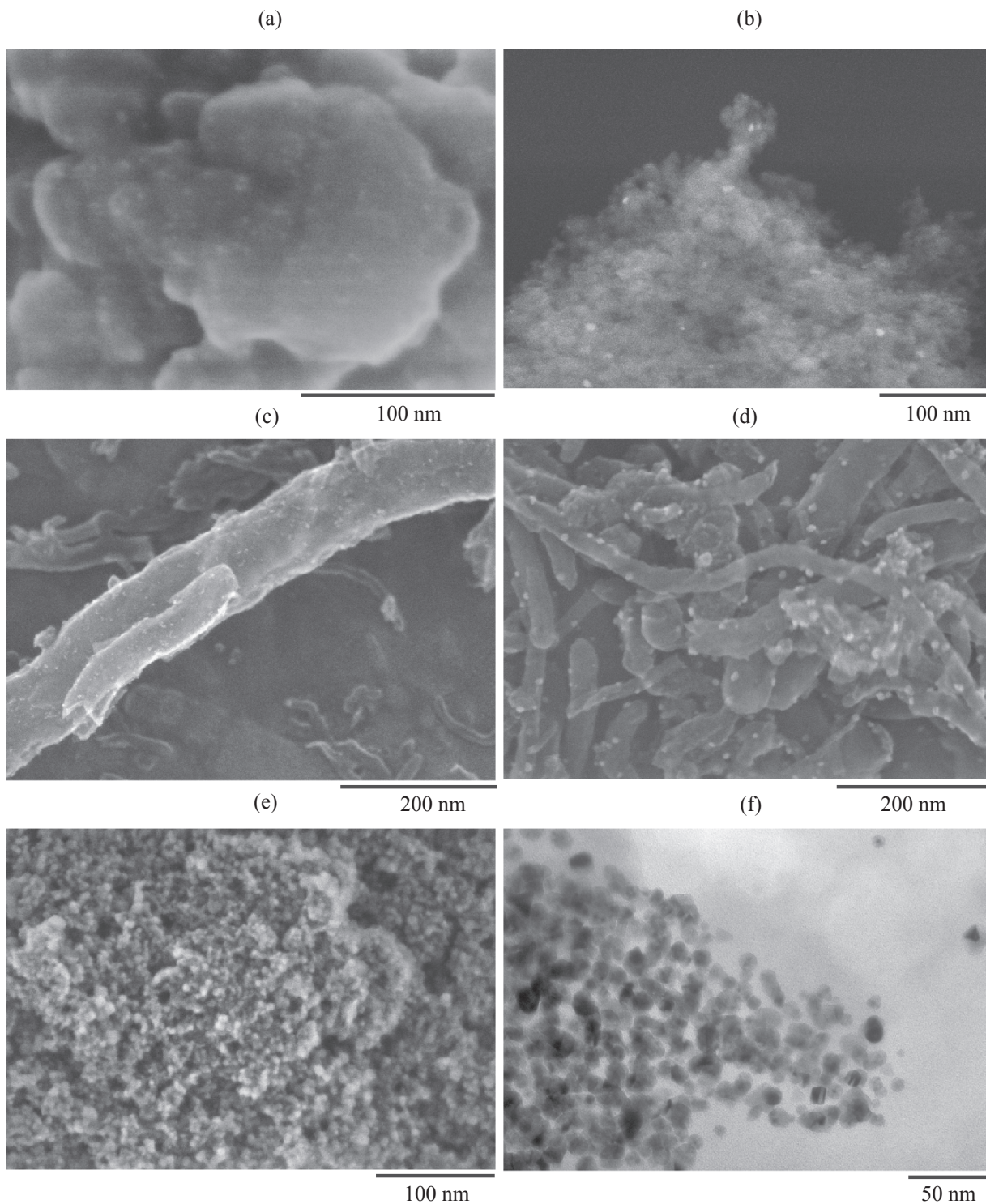
The X-ray diffraction patterns of the composites thus obtained contain reflections corresponding to fullerite and platinum metals (Fig. 4). Metal reflections correspond to the fcc structure, e.g., the Ir reflections with  $2\theta$   $40.7^\circ$ ,  $47.3^\circ$ ,  $69.2^\circ$ ,  $83.5^\circ$ , and  $88.1^\circ$ . The crystallite size of the metal deposited onto fullerite, estimated by the Scherrer formula, is 3–8 nm at 5 wt %

metal content. The mean size of metal crystallites on fullerenol is 6 nm at 7 wt % metal content. Thus, the metal particles have the smaller size than the particles obtained by combustion of  $\text{Pt-M}(\text{acac})_n/\text{NCM}$  in air in an open system.

Figure 5 shows the electron micrographs of the surface of NCM composites with the deposited metal nanoparticles. The metal particles are uniformly distributed over the NCM surface. The particle size is 3–7 nm at 5 wt % and 7–10 nm at 10 wt % metal content, being, on the average, smaller than the size of particles formed by  $\text{Pt-M}(\text{acac})_n/\text{NCM}$  combustion in open air. Thus, restriction of the outflow of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapor in the course of thermal combustion of  $\text{Pt-M}(\text{acac})_n/\text{NCM}$  mixtures is a steric factor preventing agglomeration of the metal particles formed.

## CONCLUSIONS

Platinum metal (Pt, Pd, Rh, Ir) nanoparticles supported on carbon nanomaterials (fullerite, detonation nanodiamonds, Taunit, fullerenol, fullerene-containing black) were prepared by an in situ one-step procedure involving low-temperature combustion ( $\sim 250\text{--}270^\circ\text{C}$ ) of the powdered  $\text{Pt-M}(\text{acac})_n/\text{carbon nanomaterial}$  mixture in air. As shown by thermal analysis methods, the process is based on thermal oxidative degradation of the organometallic complex, catalyzed by carbon nanomaterials, with oxidation (combustion) of the organic moiety and separation of the metal into the condensed phase. In an open system, the thermal process occurs in the low-temperature glowing mode ( $210\text{--}250^\circ\text{C}$ ), and the size of the nanoparticles formed is 7–30 nm. Under the conditions restricting the air access to the reaction mixture and free outflow of gaseous products formed by oxidation of acac ligands, the nanoparticle size decreases to 3–10 nm. Also, the size of the deposited particles depends on the metal loading in the initial powder mixture and on the support morphology. The use of thermal reactions of platinum metal acetylacetonates in a solid mixture with carbon nanomaterials allows decoration of carbon nanomaterials with platinum metal nanoparticles to be performed under mild conditions. No significant differences in the thermal behavior of  $\text{Pt-M}(\text{acac})_n/\text{carbon nanomaterial}$  mixtures are observed with variation of the sample weight (5 or 200 mg), which suggests the possibility of scaling the process.



**Fig. 5.** Electron micrographs of the surface of Pt-M/NCM composites prepared by heating the powdered mixtures in closed crucibles. Metal content, wt %: (a–c) 5 and (d–f) 10. (a–e) SEM and (f) TEM. (a) Pt/fullerite, (b) Ir/DND, (c) Ir/Taunit, (d) Pt/Taunit, (e) Pd/DND, and (f) Pd/fullerenol.

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