ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2020, Vol. 65, No. 10, pp. 1623–1629. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Zhurnal Neorganicheskoi Khimii, 2020, Vol. 65, No. 10, pp. 1426–1433.

INORGANIC MATERIALS AND NANOMATERIALS

Synthesis of Pd, Pt, and Pd–Pt Nanoparticles on Carbon Nanotubes under Hydrothermal Autoclave Conditions

R. V. Borisov[a, b, *], **O. V. Belousov**[a, b], **and A. M. Zhizhaev**[a]

[a] *Institute of Chemistry and Chemical Technologies, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
[b] *Siberian Federal University, Krasnoyarsk, 660041 Russia*
**e-mail: roma_boris@list.ru*

Received April 24, 2020; revised May 14, 2020; accepted May 27, 2020

Abstract—Pd/CNT, Pt/CNT, and Pd–Pt/CNT composites having various metal contents were prepared via ammoniate thermolysis under autoclave conditions at 180°C, and were characterized. The morphology of the thus-manufactured items was comprehensively studied by scanning electron microscopy (SEM). Metallic palladium had particles sizes in the range within 20–120 nm, and platinum in the range within 20–150 nm. X-ray powder diffraction showed that the joint reduction of palladium(II) and platinum(II) ammine complexes on carbon nanotubes under autoclave conditions yielded a Pd–Pt solid solution phase. When Pd/CNT composites were brought in contact with hydrochloric acid solutions of H_2PtCl_6 under hydrothermal conditions at 130°C, a Pd–Pt solid solution phase was also formed on carbon nanotubes.

Keywords: palladium, platinum, bimetallic nanoparticles, hydrothermal synthesis, thermolysis, carbon nanotubes

DOI: 10.1134/S0036023620100034

INTRODUCTION

Functional composite materials containing noble metal nanoparticles are widely used in electronics, the hydrogen energy industry, medicine, and other fields [1–3]. Palladium and platinum particles on various substrates are used in catalytic processes [4–6] and in fuel cells [7]. Supports for active metals that have recently found the greatest application are chemically and thermally resistant porous carbon materials such as sibunite [8], SMK-3 [9], graphene [10], and carbon nanotubes [11, 12].

Palladium or platinum monometallic disperse particles anchored to carbon supports are conventionally used in catalytic processes [13], but catalysts comprising two or more metals have the highest activities and selectivities [14, 15]. For example, the transition from a palladium-on-sibunite catalyst to a gold–palladium bimetallic catalyst significantly increased furfurol hydrogenation rates due to the synergistic effect of the two metals [14].

There is a whole variety of synthetic methods used to prepare monometallic and bimetallic particles, in particular, on carbon substrates [16–22]. The main approaches to the chemical synthesis of bimetallic nanoparticles can be reduced to a consecutive or simultaneous reduction of metal complex salts from solution, as a rule, with reducing agents and stabilizers [19]. The most popular method involves impregnation followed by reduction to the metal in a hydrogen environment [16–18]. Martin-Martinez et al. [18] used this method to manufacture a Pd–Pt/C (0.5 wt % Pd, 0.9 wt % Pt) bimetallic catalyst, which was active in hydrodechlorination processes. Zheng et al. [20] advanced a sonochemical method to prepare Pd/C and Pd–Pt/C catalysts of various compositions. In recent years, the layer-by-layer vapor deposition of metal nanoparticles onto a substrate the have been used very actively [14, 21, 22]; the underlying idea is the decomposition of organometal compounds. This method can produce both palladium monometallic particles sized 6–10 nm on carbon [14] and core–shell Pd–Pt bimetallic particles [22]. A very interesting method for preparing palladium–gold bimetallic solid solutions is via the decomposition of double complex salts in a gas phase [23]. The thermolysis of relevant metal ammine complexes in alkaline media under autoclave conditions was used to coat ruthenium, palladium, platinum, and chromium on oxide and carbon supports [24–28]. The thus-produced palladium and platinum monometallic particles [24, 27] may be modified by a second metal by means of the contact reduction of noble metals from solutions [29, 30]. Belousova et al. [29] studied the formation of Pd–Au and Au–Pt bimetallic particles having complex structure under autoclave conditions. Borisov et al. [30] prepared Au–Pd/C composites.

One goal of this work was to study the formation of nanosized platinum and palladium particles on carbon nanotubes (CNTs) via the thermolysis of their ammine complexes at 180°C. The other goal was to study the behavior of Pd/CNT composites in contact with H_2PtCl_6 solutions at 130°C.

EXPERIMENTAL

The chemicals used were palladium(II) chloride (pure grade), $H_2[PtCl_6]$ (pure grade), hydrochloric acid (specialty grade 20-4), aqueous ammonia (specialty grade 23-5), potassium hydroxide (reagent grade), and gaseous argon (top grade). Working solutions were prepared by diluting calculated reagent aliquots with distilled water. The tetramminepalladium(II) chloride and tetrammineplatinum(II) chloride to be used were prepared by routine methods [30].

The support used was Taunit, a commercially available carbon nanotube material [31]; its specific surface area was 151 m^2/g. Experiments were performed in 30-mL titanium autoclaves equipped with Teflon inserts and in 45-mL quartz autoclaves as described elsewhere [27, 29, 30].

Palladium and platinum fine particles were formed on CNTs in autoclaves at 180°C. The carbonaceous material and the required amount of tetramminepalladium(II) chloride or tetrammineplatinum(II) chloride were placed in a Teflon reactor, flooded with 20 mL of 0.05 M KOH, then air was removed by purging argon, and the system pressurized. Stirring at 25°C was for 120 min, after which the autoclave was placed in a thermostat preheated to 180°C to be held there for 240 min under constant vertical stirring. After the experiment was over, the autoclave was disassembled, the liquid phase was sampled to be analyzed, and the solid was repeatedly washed with distilled water and then dried at 100°C.

Palladium–platinum particles were synthesized via contact exchange under hydrothermal conditions. A quartz autoclave was charged with a certain portion of hydrochloric solution (1 M) having a set H_2PtCl_6 concentration. A Pd/CNT composite weight was placed in a Teflon cup on the inner surface of the autoclave lid. Argon was bubbled through the solution for 1 h. Bubbling and autoclave pressurizing were performed in a box filled with an inert gas. Then, the autoclave was vertically positioned in the shaft hole of an air thermostat preheated to 130°C. After the reactor was heated (which took 40 min), stirring was switched on in order for the solid and solution were in contact only at the set temperature. After being thermostated for 15–240 min, the autoclave was cooled. A solution aliquot was sampled to be analyzed, and the deposit was washed with distilled water until the chloride ion test was negative and then dried at 100°C. The amounts of metals in the composite were derived from the results of atomic-absorption analysis of solutions before and after the reaction.

X-ray diffraction patterns were recorded in the 2θ angle range from 5° to 90° in 0.02° steps on a Proto AXRD (Proto Manufacturing) benchtop diffractometer using CuK_α radiation with an accumulation time per point of 3 s. The morphologic features of prepared particles were studied by scanning electron microscopy (SEM) on a TM3000 (Hitachi) microscope equipped with a Quantax 70 (Bruker) microanalytical unity and on an S5500 (Hitachi) microscope. Energy dispersive X-ray microanalysis was used to assess the uniformity of particle distribution over the support and the particle morphology.

Nitrogen adsorption isotherms for the studied materials were recorded on an ASAP-2420 (Micromeritics) analyzer at 77 K. The textural characteristics were calculated by the BJH and BET methods.

The chemical elements in solutions were determined by atomic absorption spectroscopy on an AAnalyst-400 (PerkinElmer) atomic absorption spectrometer.

RESULTS AND DISCUSSION

Manufacturing of Pd/CNT, Pt/CNT, and Pd–Pt/CNT Materials via Ammoniate Thermolysis in Alkaline Solutions

At 170°C or higher temperatures, alkaline aqueous solutions of tetramminepalladium(II) chloride and tetrammineplatinum(II) chloride are reduced to fine-grained metal powders [24, 27, 30]. The thermolysis of palladium and platinum complexes in alkaline aqueous solutions follows the following equations:

$$\begin{gathered}3[Pd(NH_3)_4]Cl_2 + 6KOH \\ \rightarrow 3Pd + N_2 + 10NH_3 + 6H_2O + 6KCl.\end{gathered} \tag{1}$$

$$\begin{gathered}3[Pt(NH_3)_4]Cl_2 \cdot H_2O + 6KOH \\ \rightarrow 3Pt + N_2 + 10NH_3 + 9H_2O + 6KCl.\end{gathered} \tag{2}$$

When a carbonaceous material is added to the reactor, ammine complexes are reduced on its surface to form nanosized particles, as shown in [27, 30]. We used this method to prepare Pd/CNT and Pt/CNT composites (Table 1). The quantitative reduction of ammoniates makes offers an easy way to vary the amount of metal on the support. The simultaneous reduction of platinum(II) and palladium(II) to metal particles provided their production on a carbon support in the tailored molar ratio (Table 1). The specific area decreased insignificantly (S_{in} = 151 g/cm^3) when the metals were applied to the carbonaceous material; the decrease corresponds to the contribution to the total weight of the sample made by metals, which have low specific surfaces relative to CNTs.

The electron-microscopic studies of Pd/CNT, Pt/CNT, and Pd–Pt/CNT composites in all cases detected metallic particles bound to carbon nanotubes. The Pd/CNT (4.8 wt % Pd) material contained metal particles sized from 20 to 120 nm; the larger particles consisted of smaller fragments sized 8–12 nm (Fig. 1a).

Platinum was distributed over carbon nanotubes less uniformly in the form of particles sized 20–200 nm; these particles, as palladium particles, were built of finer particles sized 5–10 nm (Figs. 1b–1d). In addition to spherical globules, platy platinum particles were observed (Fig. 1d). X-ray powder diffraction proved the formation of palladium and platinum metal phases on carbon supports. The diffraction patterns (Fig. 2) featured peaks corresponding to the metals. The peak broadening calculated by full-profile X-ray diffraction analysis correlates with the particle sizes of the produced particles. Along with the metal peaks, the diffraction patterns featured peaks of the carbon material (at $2\theta = 26°$ and 43°), in agreement with published data [31, 32].

The simultaneous autoclave reduction of platinum and palladium complexes was shown to yield spherical particles sized 20–120 nm, consisting of finer spheres (Fig. 3). The platinum and palladium were uniformly distributed over the carbon support as shown by energy dispersive X-ray microanalysis. The ammonic ratio Pd : Pt for sample **4** (Table 1) varied from spot to spot from 1 : 0.8 to 1 : 1.1. The X-ray diffraction pattern (Fig. 2), in addition to the carbon peaks, featured peaks corresponding to the palladium–platinum solid solutions phase ($Pd_{0.5}Pt_{0.5}$) with the unit cell parameter 3.905 Å. Changing the ratio of the initial complex salts, one can prepare functional materials comprising the tailored amounts of palladium and platinum. In sample **5** (Table 2), for example, the atomic ratio Pd : Pt was 1 : 0.7 and the particle distribution was uniform.

Table 1. Thermolysis products of complexes

Sample no.	Sample	Composition, wt %		S_{sp}, m^2/g
		Pd	Pt	
1	Pd/CNT	4.8	–	147
2	Pt/CNT	–	6.0	145
3	Pt/CNT	–	3.0	146
4	Pd–Pt/CNT	2.2	4.0	144
5	Pd–Pt/CNT	2.9	3.6	145

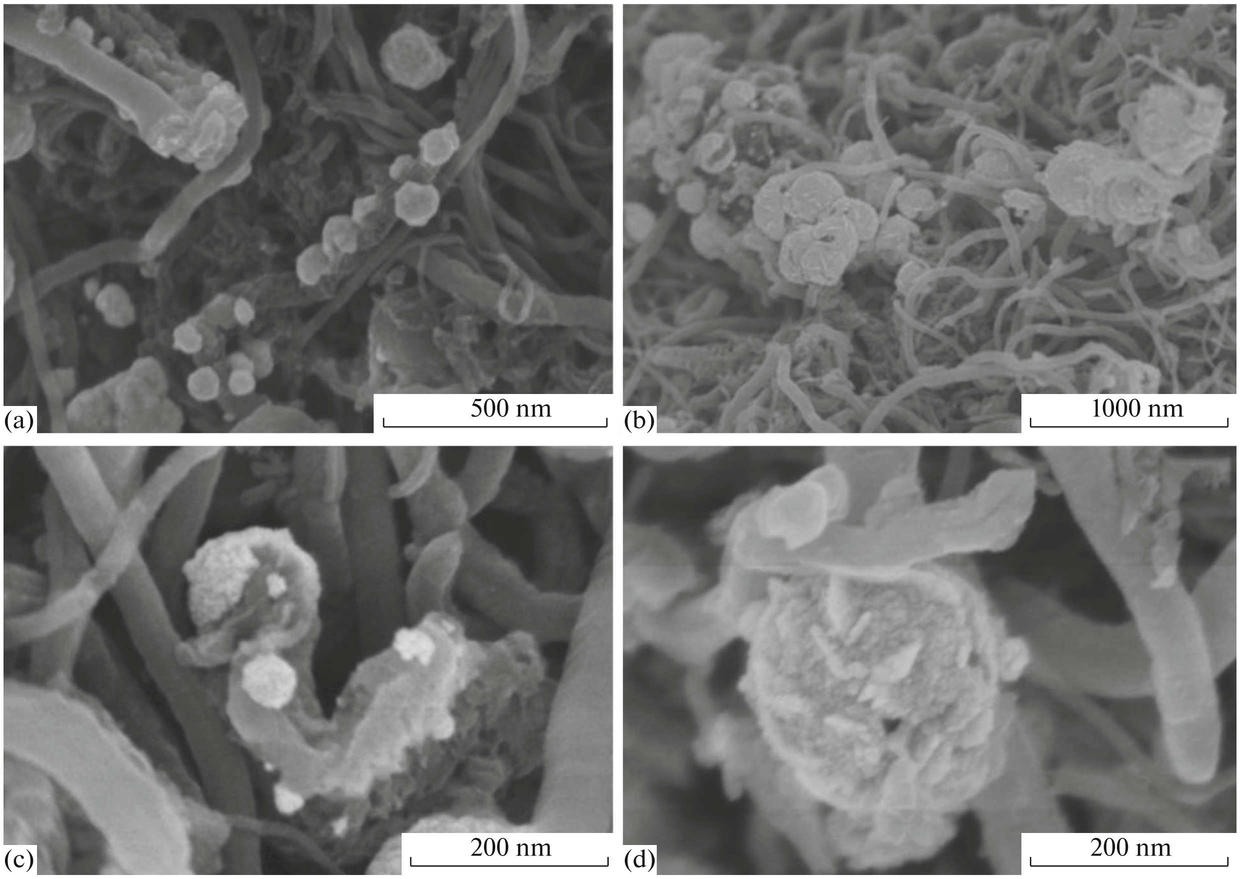

Fig. 1. SEM images of particles deposited on carbon nanotubes: (a) Pd/CNT, 4.8 wt % Pd, 240 min, 180°C; (b, d) Pt/CNT, 6.0 wt % Pt, 240 min, 180°C; and (c) Pt/CNT, 3.0 wt % Pt, 240 min, 180°C.

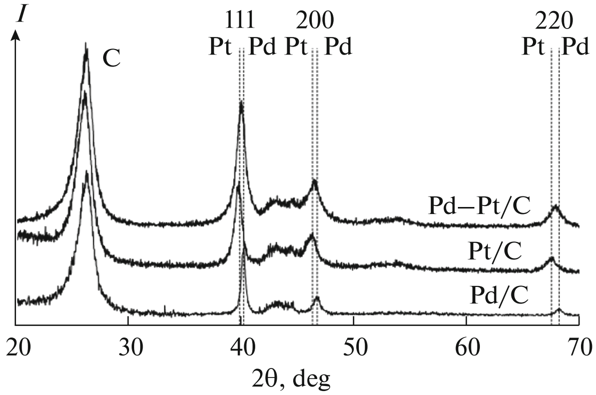

Fig. 2. Fragment of X-ray diffraction patterns of the products of Pd, Pt (6.0 wt %), and Pd–Pt particle deposition on carbon nanotubes via alkaline thermolysis.

Manufacturing of Pd–Pt/CNT Materials via Cementation in Hydrochloric Acid Solutions

Another approach to the manufacturing of bimetallic particles can be the contact reduction of the metal from solution by a second, more electropositive, metal [29, 30].

We first discovered that, when carbon nanotubes were brought in contact with hydrochloric acid solutions of H_2PtCl_6 (c_{Pt} = 0.002 mol/L) and H_2PdCl_4 (c_{Pd} = 0.002 mol/L) for 240 min, the change in metal concentration in the solution at 180°C was less than 7%, and at 130°C less than 5%. This fact indicates low sorption and reduction abilities of carbon nanotubes toward $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ ions, unlike in $H[AuCl]_4$ solutions, from which gold(III) can be reduced at high temperatures in the form of metallic particles on a carbon support [33]. In addition, electron microscopy failed to detect metal particles, so we did not dwell on those processes and ignored them.

It was shown [34] that finely disperse palladium at high temperatures (>130°C) reacts with platinum(II) and platinum(IV) chloro complexes to yield Pd–Pt solid solutions. Platinum(IV) reduction by palladium proceeds in steps involving platinum(II) formation. The overall process can be written as

$$H_2PtCl_6 + 2Pd + 2HCl \rightarrow 2H_2PdCl_4 + Pt. \quad (3)$$

The reaction produces Pd–Pt bimetallic particles, which consist of a palladium core surrounded by a Pd–Pt solid solution phase; the composition of this phase can be purposefully changed by changing the molar ratio Pd/Pt [34]. Along with platinum(IV) reduction (Eq. (3)), metallic palladium is dissolved (Eq. (4)) due to being oxidized by the oxygen [30] contained in the vapor phase of the reactor or chemisorbed on the surface of the sample [35]:

$$2Pd + O_2 + 8HCl \rightarrow 2H_2PdCl_4 + 2H_2O. \quad (4)$$

Thanks to the high specific surface areas of Pd/CNT materials, the palladium solubility in hydrochloric acid media, associated with chemisorbed oxygen, can be higher than reported for palladium fine powders [35]. It was for this reason that we performed experiments at 130°C under an argon atmosphere to determine the palladium fraction that dissolved in the course of the experiment (Table 2; samples **1** and **2**). We found that 15% of the palladium was dissolved due to process (4), and this amount was independent of the time of the autoclave process.

When a palladium–carbon composite was brought in contact with a H_2PtCl_4 solution with the initial molar ratio Pd : Pt = 1 : 0.2, platinum(IV) was reduced and the palladium metal was dissolved by Eqs. (3) and (4). This process took 120 min, and a further increase in time had almost no effect on the composite (Table 2).

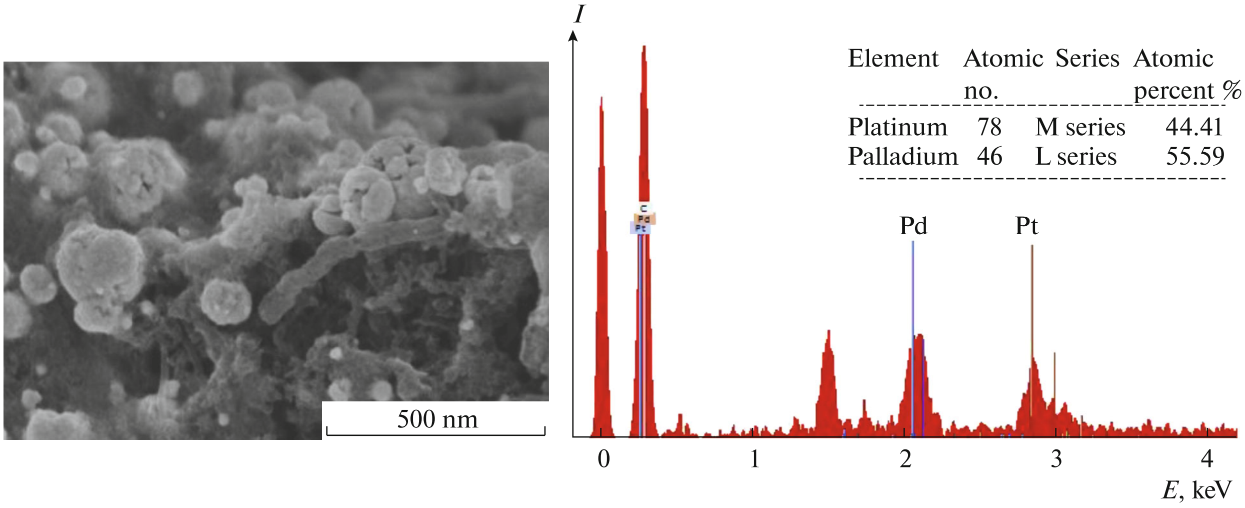

Fig. 3. SEM images of a Pd–Pt/CNT composite (sample **4**, Table 1) and the energy dispersive spectrum in the imaged area.

Table 2. Formation conditions and compositions of Pd–Pt/CNT composites (130°C, Ar atmosphere)

Sample no.	Batch mole ratio Pd : Pt	Autoclaving time, min	In the composite, wt %	
			Pd	Pt
1	1 : 0	30	4.1	–
2	1 : 0	240	4.1	–
3	1 : 0.2	30	2.9	1.1
4	1 : 0.2	60	2.2	1.6
5	1 : 0.2	120	2.3	1.7
6	1 : 0.2	240	2.3	1.7
7	1 : 0.5	240	2.2	1.8

Platinum ions remained in the solution even after 240-min exposure (Fig. 4), and cementation did not occur further, may be due to either the isolation of palladium or due to the disproportionation of the newly formed platinum(II) [34].

The X-ray diffraction patterns of Pd–Pt/CNT materials featured peaks from Pd–Pt solid solutions and poorly defined peaks from metallic palladium, the latter becoming almost inconspicuous as the synthesis time increased (Fig. 5). The uniform distribution of the metals over the carbon support as probed by energy dispersive X-ray microanalysis and the ratio of metals were unchanged from spot to spot, giving indirect evidence to solid solution formation.

Scanning electron microscopy showed that partial destruction and recrystallization of metal particles occurred around filamentary carbon nanotubes (Fig. 6). The spherical particles sized 40–100 nm consisted of finer particles. The destruction of spherical particles was related to palladium dissolution, and their growth was due to both the reduction of platinum ions on the palladium surface and to the recrystallization of palladium itself. The result was that the finest particles disappeared with the autoclave experiment time increasing from 30 to 240 min, while the large ones were coarsened (Fig. 6).

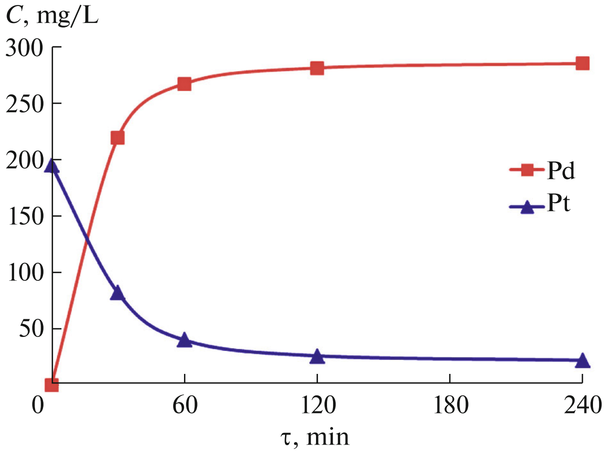

Fig. 4. Platinum(IV) reduction kinetics in contact with a Pd/CNT (4.8 wt %) composite and palladium metal dissolution kinetics (autoclave, 130°C, argon atmosphere).

The Pd : Pt molar ratio increasing to 1 : 0.5 did not give rise to the appearance of separately lying platinum(0) particles. A platinum(0) phase was not detected by X-ray diffraction; only some enrichment of the solid solution by platinum was observed. A considerable part of platinum remained in solution, and the composite only insignificantly deviated from the molar ratio 1 : 0.2. This fact may be regarded as evidence for the isolation of palladium by palladium–platinum solid solution and the impossibility of further proceeding of process (3).

CONCLUSIONS

We have shown that the thermolysis of ammoniates in alkaline solution offers a way to produce both palladium and platinum monometallic particles and Pt–Pd bimetallic solid solutions on carbon nanotubes. The reduction of hydrochloric H_2PtCl_6 solutions by Pd/CNT composites at 130°C in hydrothermal conditions was shown to yield Pd–Pt bimetallic particles on carbon nanotubes. The molar reagent ratio in the batch and the synthesis time were shown to influence the particle sizes and compositions of the produced metal phases.

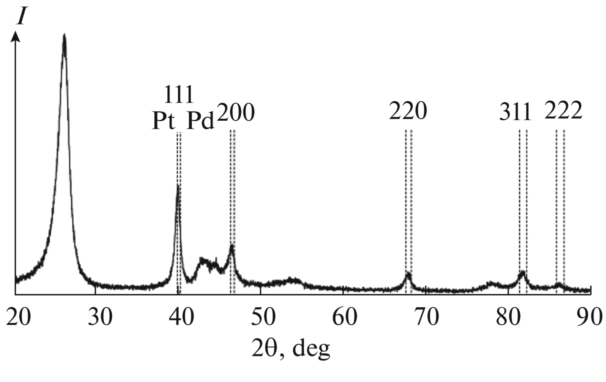

Fig. 5. Fragment of the X-ray diffraction pattern of a Pd–Pt/CNT sample (sample **5**, Table 2).

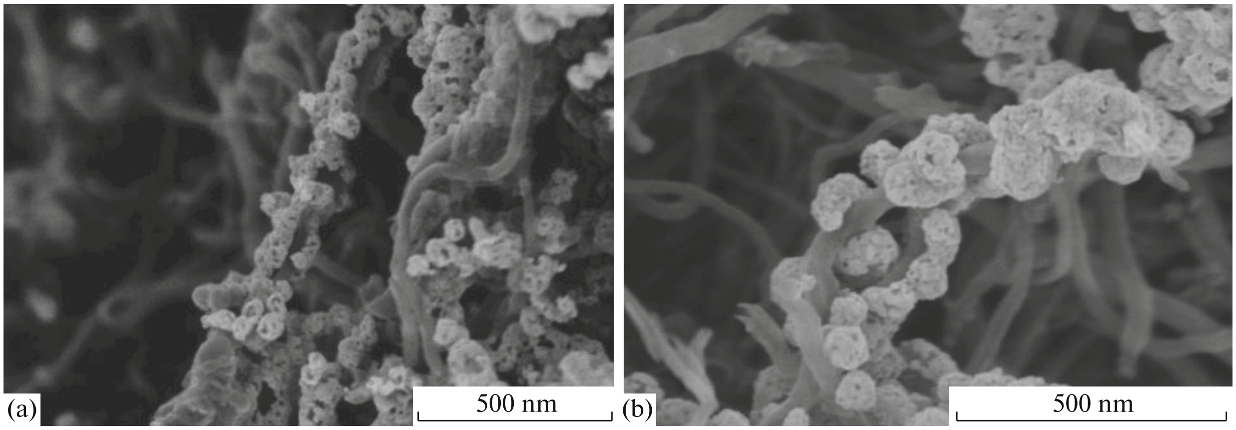

Fig. 6. SEM images of Pd–Pt particles on a carbon support manufactured at 130°C under autoclave conditions: (a) sample **3** and (b) sample **6** (Table 2).

The formation of Pd–Pt solid solutions was proved by X-ray powder diffraction.

FUNDING

This study used shared experimental facilities of the Krasnoyarsk Regional Scientific Center of the Siberian Branch of the Russian Academy of Sciences in part supported by the governmental assignment to the Institute of Chemistry and Chemical Technologies (project no. AAAA-A17-117021310220-0).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest to be disclosed in this paper.

REFERENCES

1. A. Chen and C. Ostrom, Chem. Rev. **115**, 11999 (2015). https://doi.org/10.1021/acs.chemrev.5b00324
2. S. Lankiang, M. Chiwata, S. Baranton, et al., Electrochim. Acta **182**, 131 (2015). https://doi.org/10.1016/j.electacta.2015.09.061
3. H. T. Nasrabadi, E. Abbasi, S. Davaran, et al., Artif. Sell. Nanomed. B **44**, 376 (2014). https://doi.org/10.3109/21691401.2014.953632
4. L. He, F. Weniger, H. Neumann, and M. Beller, Angew. Chem., Int. Ed. Engl. **55**, 12582 (2016). https://doi.org/10.1002/anie.201603198
5. F. Cai, D. Gao, R. Si, et al., Electrochem. Commun **76**, 1 (2017). https://doi.org/10.1016/j.elecom.2017.01.009
6. X. Xiao, H. Jeong, J. Song, et al., Chem. Commun. **55**, 11952 (2019). https://doi.org/10.1039/c9cc05915f
7. T. Bhowmik, M. K. Kundu, and S. Barman, Int. J. Hydrogen En. **42**, 212 (2017). https://doi.org/10.1016/j.ijhydene.2016.11.095
8. L. I. Godina, A. V. Tokarev, I. L. Simakova, et al., Catal. Today **301**, 78 (2018). https://doi.org/10.1016/j.cattod.2017.03.042
9. Z. Wang, W. Chen, Z. Han, et al., Nano Res. **7**, 1254 (2014). https://doi.org/10.1007/s12274-014-0488-x
10. Y. V. Ioni, V. V. Voronov, A. V. Naumkin, et al., Russ. J. Inorg. Chem. **60**, 709 (2015). https://doi.org/10.1134/S0036023615060066
11. S. Zhang, M. Qing, H. Zhang, et al., Electrochem. Commun. **11**, 2249 (2009). https://doi.org/10.1016/j.elecom.2009.10.001
12. P. K. Kalambate, Y. Li, Y. Shen, et al., Anal. Methods **11**, 443 (2019). https://doi.org/10.1039/C8AY02381F
13. A. T. Madsen, B. Rozmyslowicz, P. Maki-Arvela, et al., Top. Catal. **56**, 714 (2013). https://doi.org/10.1007/s11244-013-0030-5
14. O. V. Belousov, V. E. Tarabanko, R. V. Borisov, et al., React. Kinet. Mech. Catal. **127**, 25 (2019). https://doi.org/10.1007/s11144-018-1430-0
15. J. J. Musci, A. B. Merlo, and M. L. Casella, Catal. Today **296**, 43 (2017). https://doi.org/10.1016/j.cattod.2017.04.063
16. O. G. Ellert, M. V. Tsodikov, S. A. Nikolaev, et al., Russ. Chem. Rev. **83**, 718 (2014). https://doi.org/10.1070/RC2014v083n08ABEH004432
17. H. Li, G. Sun, Q. Jiang, et al., Electrochem. Commun. **9**, 1016 (2007). https://doi.org/10.1016/j.elecom.2007.01.032
18. M. Martin-Martinez, L. M. Gómez-Sainero, J. Palomar, et al., Catal. Lett. **146**, 2614 (2016). https://doi.org/10.1007/s10562-016-1895-2
19. A. Zaleska-Medynska, M. Marchelek, M. Diak, et al., Adv. Colloid Interface Sci. **229**, 80 (2016). https://doi.org/10.1016/j.cis.2015.12.008
20. H. Zheng, M. S. Matseke, and T. S. Munonde, Ultrason. Sonochem. **57**, 166 (2019). https://doi.org/10.1016/j.ultsonch.2019.05.023

21. B. J. O'Neill, D. H. K. Jackson, J. Lee, et al., ACS Catal. **5**, 1804 (2015). https://doi.org/10.1021/cs501862h
22. K. Cao, Q. Zhu, B. Shan, et al., Sci. Rep. **5**, 8470 (2015). https://doi.org/10.1038/srep08470
23. P. E. Plyusnin, I. A. Baidina, Y. V. Shubin, et al., Russ. J. Inorg. Chem. **52**, 371 (2007). https://doi.org/10.1134/S0036023607030138
24. O. V. Belousov, A. V. Sirotina, N. V. Belousova, et al., J. Sib. Fed. Univ. Eng. Technol. **7**, 138 (2014).
25. E. V. Fesik, T. M. Buslaeva, T. I. Mel'nikova, et al., Inorg. Mater. **54**, 1299 (2018). https://doi.org/10.1134/S0020168518120038
26. E. V. Fesik, T. M. Buslaeva, T. I. Mel'nikova, et al., Russ. J. Phys. Chem. A **93**, 1011 (2019). https://doi.org/10.1134/S0036024419060098
27. R. V. Borisov and O. V. Belousov, J. Sib. Fed. Univ. Chem. **7**, 331 (2014).
28. E. N. Tupikova, I. A. Platonov, and D. S. Khabarova, Kinet. Catal. **60**, 366 (2019). https://doi.org/10.1134/S0023158419030145
29. N. V. Belousova, A. V. Sirotina, O. V. Belousov, et al., Russ. J. Inorg. Chem. **57**, 15 (2012). https://doi.org/10.1134/S0036023612010044
30. R. V. Borisov, O. V. Belousov, A. M. Zhizhaev, et al., Russ. J. Inorg. Chem. **63**, 308 (2018). https://doi.org/10.1134/S0036023618030038
31. A. G. Tkachev, Perspektivn. Mater., No. 3, 5 (2007).
32. N. A. Yashtulov, M. V. Lebedeva, and S. M. Pestov, Fine Chem. Technol. **11** (5), 59 (2016).
33. R. V. Borisov, O. V. Belousov, and A. M. Zhizhaev, J. Sib. Fed. Univ. Chem. **12**, 494 (2019). https://doi.org/10.17516/1998-2836-0145
34. N. L. Kovalenko, O. V. Belousov, and L. I. Dorokhova, Russ. J. Inorg. Chem. **47**, 967 (2002).
35. O. V. Belousov, L. I. Dorokhova, L. A. Solov'ev, et al., Russ. J. Phys. Chem. A **81**, 1303 (2007). https://doi.org/10.1134/S0036024407080237

Translated by O. Fedorova