ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 5, pp. 415–420. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © L.I. Yudanova, V.A. Logvinenko, N.F. Yudanov, N.A. Rudina, A.V. Ishchenko, P.P. Semyannikov, L.A. Sheludyakova, N.I. Alferova, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 5, pp. 309–314.

Thermolysis of Copper(II) Salts of Maleic Acid. Synthesis of Metal–Polymer Composites

L. I. Yudanova[a, *], **V. A. Logvinenko**[a], **N. F. Yudanov**[a], **N. A. Rudina**[b], **A. V. Ishchenko**[b], **P. P. Semyannikov**[a], **L. A. Sheludyakova**[a], **and N. I. Alferova**[a]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences,*
pr. akademika Lavrent'eva 5, Novosibirsk, 630090 Russia
** e-mail: judanova@niic.nsc.ru*

Received August 31, 2012

Abstract—The thermal decomposition of neutral ($[Cu(H_2O)(C_4H_2O_4)]$) and acidic ($[Cu(H_2O)_4](C_4H_3O_4)_2$) maleates can conventionally be divided into four stages: (1) dehydration, (2) polymerization, (3) isomerization of the maleate ion to the trans form with the simultaneous reduction $Cu(II) \to Cu(I)$, and (4) decarboxylation of copper(I) fumarate. The third and fourth stages of the decomposition of these salts coincide. The residue after the thermolysis of copper(II) maleates in a He flow is a composite consisting of aggregates from 50 nm to several microns in size. Spherical conglomerates (50–200 nm) containing many spherical Cu particles (5–10 nm) are incorporated into the organic polymer matrix of these aggregates.

DOI: 10.1134/S1070328413050102

INTRODUCTION

The thermolysis of transition metal salts of saturated and unsaturated mono- and dicarboxylic acids aimed at preparing highly dispersed metal-containing products are widely used in practice, for example, in catalysis or powder metallurgy [1–3].

Although the preparation of metal nanoparticles provides wide possibilities for researchers in choosing synthesis methods, the search for and development of new methods of preparing metal nanoparticles with a narrow size distribution remain topical. The stabilization of highly reactive species, depending on the stabilization method, is also an important problem.

The thermolysis of unsaturated mono- and dicarboxylic acid salts, in particular, transition metal acrylates and maleates, can produce metal nanoparticles and (or) their oxides with a smaller size than those obtained by the thermolysis of saturated acid salts, and these nanoparticles are stabilized by the polymer matrix [3–6].

The purpose of this work is to study the thermal decomposition of maleic acid salts of transition metals of the IV Period, particularly, of neutral and acidic copper(II) maleates, and to use the thermolysis of these salts as a method for the preparation of small (with a diameter not more than 10 nm) copper nanoparticles stabilized by the polymer matrix [7–9].

EXPERIMENTAL

Syntheses of neutral and acidic copper(II) maleates were carried out by crystallization from aqueous solutions. Crystalline hydrate $CuCl_2 \cdot 2H_2O$ (analytical grade), maleic anhydride $C_4H_2O_3$ or maleic acid $C_4H_4O_4$ (analytical grade), and sodium bicarbonate $NaHCO_3$ (reagent grade) were used as the starting reactants in the synthesis of neutral copper maleate. Copper(II) maleate was obtained in a small excess (compared to the stoichiometric value) of maleic (pH 3–4). Acidic copper(II) maleate was dissolved in a maleic acid excess on heating at pH 1–2 (copper maleate precipitates at pH 3–4). The yields of both neutral and acidic copper(II) maleates were 90–95%.

The thermal decomposition of neutral and acidic copper(II) maleates was studied under identical conditions in a helium flow (60 cm^3/min) on a C derivatograph (MOM, Hungary). Samples with the weight from 20 to 25 mg were placed in a chamber of the setup in ceramic microcrucibles, which were heated to 450°C with a rate of 2°C/min (the accuracy of temperature measurements was ±10°C, and the accuracy of mass loss determination was ±0.1% according to the passport of the instrument).

X-ray diffraction studies of neutral and acidic copper(II) maleates and products of their thermal decomposition at different stages of the process were carried out on DRON-UM1 and DRON-3M diffractometers (CuK_α radiation, Ni filter, ambient temperature).

The IR spectra of the studied copper(II) salts were recorded on a Scimitar FTS 2000 FT-IR spectrometer in the range from 400 to 4000 cm^{-1} (KBr pellets).

Gaseous products of the decomposition of copper(II) maleates were studied on a MI-1201 mass spectrometer. Weighed samples (2.0–2.5 mg) of the substance were placed in a chamber of the setup, and air was evacuated at ambient temperature to the pressure from 5×10^{-8} to 10^{-7} Torr. The gas phase composition was monitored with the temperature increase to ~350°C.

The copper content in maleates was determined by the atomic absorption method on a Z-8000 AA spectrophotometer. Analyses for carbon and hydrogen of the synthesized compounds and composites were carried out on a CHN analyzer (Euro EA 3000 series). The determination accuracy in the first and second methods was ±0.5 wt %. Elemental and X-ray analyses data showed that neutral ($[Cu(H_2O)(C_4H_2O_4)]$) and acidic ($[Cu(H_2O)_4](C_4H_3O_4)_2$) maleates were synthesized.

For $[Cu(H_2O)(C_4H_2O_4)]$

anal. calcd. (%):	C, 24.55;	H, 2.05;	Cu, 32.5.
Found (%):	C, 24.6;	H, 2.1;	Cu, 32.6.

For $[Cu(H_2O)_4](C_4H_3O_4)_2$

anal. calcd. (%):	C, 27.3;	H, 3.4;	Cu, 18.4.
Found (%):	C, 27.6;	H, 3.8;	Cu, 18.4.

Composites obtained by thermolysis were studied using scanning electron microscopy (SEM) on a JSM-6460LV electron microscope (JEOL, Japan) and high-resolution transmission electron microscopy (TEM) on a JEM-2010 electron microscope (JEOL, Japan) with an accelerating voltage of 200 keV and a lattice resolution of 1.4 Å. Data processing was performed using the DigitalMicrograph program (Gatan) by the Fourier analysis method, revealing the periodical motif of the crystal structure image.

Energy dispersive X-ray analysis (EDXA) of the elemental composition of the samples was carried out on a Phoenix spectrometer with a Si(Li) detector and an energy resolution of about 130 eV.

RESULTS AND DISCUSSION

Dark blue crystals of neutral copper(II) maleates were obtained from aqueous solutions. Like the earlier studied crystals of Co(II) and Ni(II) maleates, the crystals of neutral copper(II) maleate are monoclinic with somewhat different space group $P2_1$ ($Z = 2$). Blue crystals of acidic copper(II) maleate are also monoclinic (space group $I2/m$, $Z = 2$) [10], and their structure differs from that of acidic Fe(II), Co(II), and Ni(II) maleates.

Copper(II) maleate [10], as well as Co(II) [11] and Ni(II) maleates, represents a coordination polymer, whose main structural unit is a polyhedron with the copper ion in the center. An interesting feature of this structure is the formation of a seven-membered chelate including the metal ion linked with two oxygen atoms of the both carboxylate groups. Each maleate group is bound to three copper atoms to form hydrogen-bonded polymer layers.

In acidic copper(II) maleate [10], the copper atoms coordinated by H_2O molecules only form the chain of $[Cu(H_2O)_4]_n^{2n+}$, cations to which planar bimaleate anions are attached through hydrogen bonds. The intramolecular hydrogen bond in the anion is 2.409 Å. The Cu atom is localized in a distorted octahedron; the Cu–OH_2 bonds (bridging) being 1.952 and 2.682 Å, and Cu–OH_2 (terminal) is 1.933 Å.

Thus, acidic copper(II) maleate has a polymer chain structure. The multiple bond in copper(II) maleates is not involved in coordination, which is important for the subsequent polymerization transformations of the salts based on unsaturated dicarboxylic acids.

The thermal decomposition processes of neutral and acidic copper(II) maleates differ drastically from the decomposition of similar Fe(II), Co(II), and Ni(II) salts, although copper-containing composites are also the final products. The decomposition processes of the copper(II) salts can conventionally be divided into four stages. The first two stages of decomposition of the copper(II) compounds coincide with the same stages of the Fe(II), Co(II), and Ni(II) salts.

The first stage of dehydration with the removal of coordination water (as follows from the thermogravimetric data) from neutral maleate $[Cu(H_2O)(C_4H_2O_4)]$ proceeds as one step, whereas the first stage for acidic maleate $[Cu(H_2O)_4](C_4H_3O_4)_2$ includes three steps (Fig. 1). In the latter case, one H_2O molecule is detached in the first and second steps, and two H_2O molecules are detached in the third step. This sequence is well consistent with the structural characteristics of acidic copper(II) maleate [10], namely, with the copper–water oxygen distance.

At the end of this stage, the maleate samples were examined by chemical and IR spectroscopic analyses, which showed that no complete removal of H_2O (ν(OH) 3400 cm^{-1}) occurred. The diffraction patterns of the samples indicate that the products obtained at this stage are X-ray amorphous.

The studies by the thermal (Fig. 1) and mass spectrometric analyses show that, at the second stage of neutral Cu(II) maleate decomposition, the polymerization of the monomer formed by dehydration is accompanied by a small mass loss. The detachment of 50% of maleate anions of acidic copper(II) maleate occurs with the simultaneous polymerization of both the monomer formed and, most likely, the decomposition products. Polymer formation at the second stage of maleate decomposition was confirmed by the SEM study of the samples at the end of this stage. According to the mass spectrometric data, the decomposition of

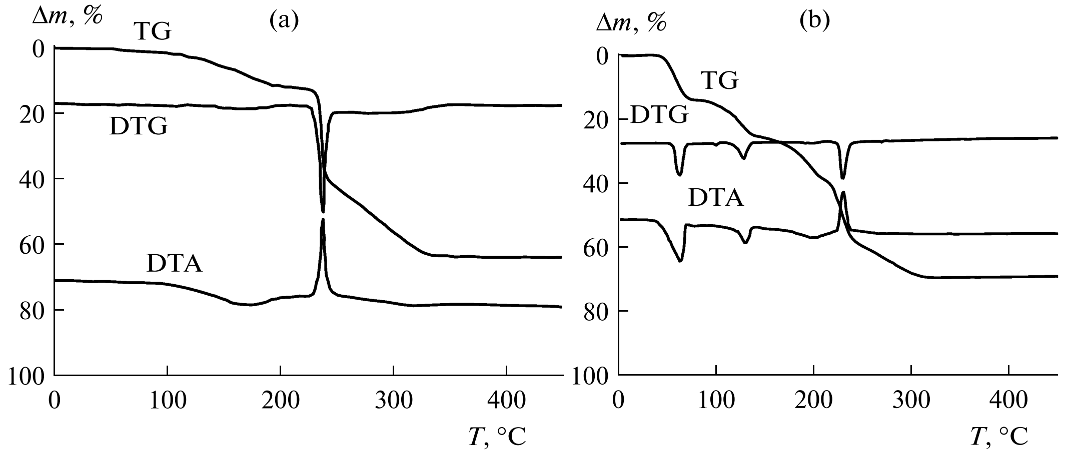

Fig. 1. Thermograms of the decomposition of (a) neutral and (b) acidic copper(II) maleates.

both neutral and acidic copper(II) maleates at the second stage is accompanied by the evolution of gaseous products: H_2O vapor, maleic anhydride $C_4H_2O_3$, acetylene C_2H_2, CO, CO_2, propanedionic aldehyde $CH_4(CO)_2$, and acetylenecarboxylic aldehyde C_2H_2CO.

The third and fourth stages of the decomposition of neutral and acidic copper(II) maleates coincide. At the third stage, the maleate ion isomerizes to the trans form with the simultaneous reduction of Cu(II) to Cu(I) and copper(I) fumarate formation. The fourth stage is the decomposition of copper(I) fumarate (in the course of this process univalent copper reduces to the metal, which is confirmed by X-ray diffraction) with the formation of a composite containing metallic copper. Spherical conglomerates containing copper nanoparticles are formed simultaneously. Several parallel processes occur at this stage: the decarboxylation of the salt, the polymerization of the organic thermolysis products, and the growth of metallic nuclei. Copper maleates decompose at the third and fourth stages with the evolution of the same gaseous products as at the second stage.

The exotherm in the DTA curves of copper maleate decomposition can be attributed to the formation of an intermediate (copper fumarate), which was confirmed by the elemental analysis results and IR spectra of this phase and is well consistent with published data. The thermal decomposition of neutral copper(II) maleate was studied by the isothermal kinetic method [12]. Intermediate solid phases were dissolved and studied by analytical methods and ^{1}H and ^{13}C NMR methods. The mechanism for copper maleate decomposition in the solid phase was proposed on the basis of the data obtained. Copper(I) fumarate was one of intermediates in this process. The quantitative determination of Cu^{2+} showed that the content of the bivalent copper salt decreased in the course of decomposition following the linear law and achieved 5 mol % at $\alpha = 0.5$ ($\alpha = m_0 - m_t/m_0 - m_f$; where α is the degree of conversion of the substance, m_t is the substance weight at an arbitrary time moment t (at temperature T), and m_0 and m_f are the substance weights at the beginning and end of the process, respectively).

In the IR absorption spectra of the decomposition products of copper(II) maleates, the bands undergo shifts compared to the spectra of the decomposition products of Co(II) and Ni(II) maleates. The band corresponding to the $\nu_s(COO^-)$ vibrations at 1400 cm^{-1} (maleate) shifts to the low-frequency region (1367 cm^{-1}) in the spectrum of fumarate, whereas the $\nu_{as}(COO^-)$ band at 1560 cm^{-1} (maleate) shifts to the high-frequency region (1593 cm^{-1}) in the spectrum of fumarate.

The onset temperatures for the stage of copper(II) maleate decomposition obey the regularities typical of Fe(II), Co(II), and Ni(II) maleates. The temperature of the first stage onset increases in the following series of acidic maleates: Cu < Fe < Co < Ni. The $M-O(H_2O)$ distance in this series decreases.

The onset temperature of the second decomposition stage also increases in the same series Cu ≤ Fe < Co < Ni. At the third stage, this regularity changes to an opposite one. The temperature of the decomposition onset at this stage decreases in the series of acidic maleates from Fe to Cu: Fe > Co > Ni > Cu, which coincides with a similar change in the onset temperatures of neutral maleate decomposition at the third stage: Co > Ni > Cu. The change in the character of the temperature dependence can be related to the rearrangement of the structure in acidic maleates with the formation of neutral salts of transition metals that occurs during the decomposition at the second stage. There is a qualitative (opposite) correlation of the presented temperature dependences with a change in the ionization electronegativity of the atoms: Cu (1.53) < Fe (1.79) < Co (1.85) < Ni (1.95) [3]. The low temperatures of the decomposition onsets of the third and

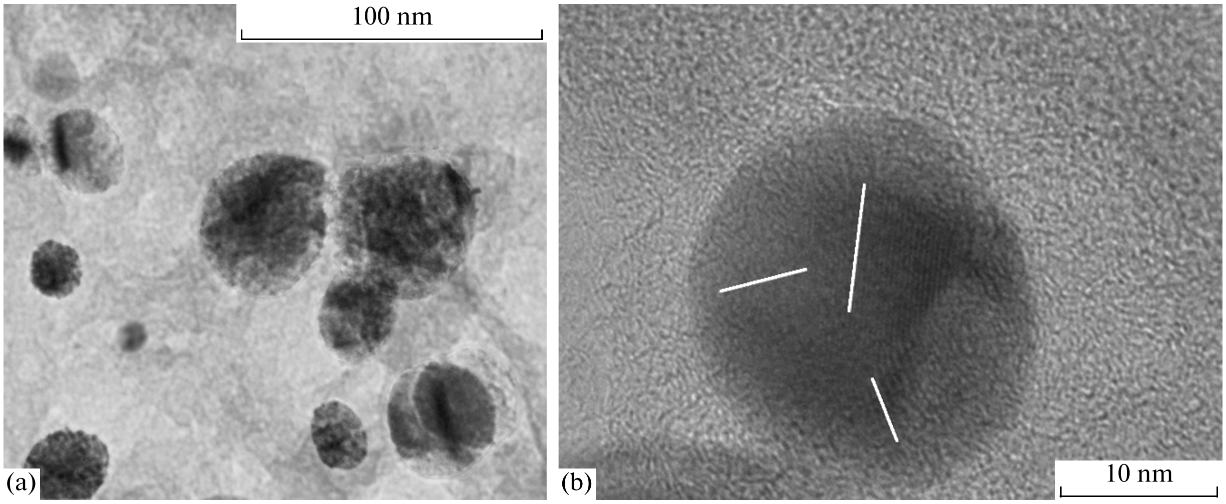

Fig. 2. TEM image of the composite obtained by the decomposition of (a) acidic copper(II) maleate and (b) the image of an individual copper particle.

fourth stages for copper(II) maleates (compared to Fe(II), Co(II), and Ni(II) maleates) can be explained, most likely, by comparing the filling of the energy levels of transition elements of the IV Period. In Cu one electron transfers from the external *s* sublevel to the internal *d* sublevel (Cu–[Ar]$3d^{10}4s^1$), due to which the *s* sublevel of Cu becomes less stable with respect to the *s* sublevels of Fe, Co, and Ni. It can be assumed that copper salts will be less stable than the salts of the same acids of other transition metals.

A residue of the substance after copper(II) maleate thermolysis in a He flow is a brown powder, being a composite consisting of copper, organic polymer, and amorphous carbon.

The elemental analyses of the composites obtained by the decomposition of neutral and acidic copper maleates showed the following (%): C, 14.95 and 30.1; H, 0.85 and 1.7; Cu, 84.2 and 68.2, respectively (i.e., in the both composites the C : H ratio is ~3 : 2, although the polymer content with respect to copper is higher in the acidic maleate). No oxygen was found in these samples.

The SEM and TEM methods showed that the composites prepared by the decomposition of copper(II) maleates, as well as the composites obtained by the decomposition of Fe(II), Co(II), and Ni(II) maleates, consisted of aggregates with the sizes from 50 nm to several microns. The aggregates of the copper-containing composites differ in structure from the composites with Fe, Co, and Ni. Spherical conglomerates (50–200 nm) containing many spherical copper particles 5–10 nm in size are incorporated into the organic polymer matrix (Fig. 2). In rare cases, graphene formations are observed on the surface of the copper particles.

The IR spectra of the composites obtained by the decomposition of copper(II) maleates are similar to those of the composites synthesized by the decomposition of Fe(II), Co(II), and Ni(II) maleates. The spectra of the composites synthesized by the decomposition of both neutral and acidic copper(II) maleates are identical and contain the following absorption bands (ν, cm^{-1}): 2920 ν(C–H), 1725 ν(C=O), 1591 ν(C=C), 1464, 1381 δ(C–H). Most likely, the solid residue of these composites includes a network structure with a system of conjugated multiple bonds $-HC=CH-(-CHCH-)_x-CH=CH-$ [5, 6] formed upon the polymerization of >C=C< fragments. The same network structure is observed in the composites synthesized by the decomposition of neutral and acidic Fe(II), Co(II), and Ni(II) maleates. The spectra of the composites exhibit weak absorption bands near 1725 cm^{-1} due to the oxidation of the carbon groups on the surface.

The X-ray diffraction method shows that metallic copper that crystallizes in the cubic crystal system (space group $Fm\bar{3}m$) ($a = 3.6150$ Å) is formed by the decomposition of copper(II) maleates.

It can be assumed that the process of composite formation includes two consecutive catalytic processes: the radical polymerization of the organic thermolysis products with the formation of the polymer matrix (maleic acid radicals were observed by mass spectrometry in the gaseous products at the second decomposition stage) and the catalytic polymerization of the thermolysis products on the metallic particle surface. The formation of metal nuclei, their growth, and coagulation of the metal particles with the simultaneous growth of a polymer layer on the particles (they could rotate in a current of gases evolved at the reaction front) result in a round shape of the metal-containing conglomerates. Some conglomerates are brought out with a gas flow and precipitate on the reactor walls and on the composite particle surface.

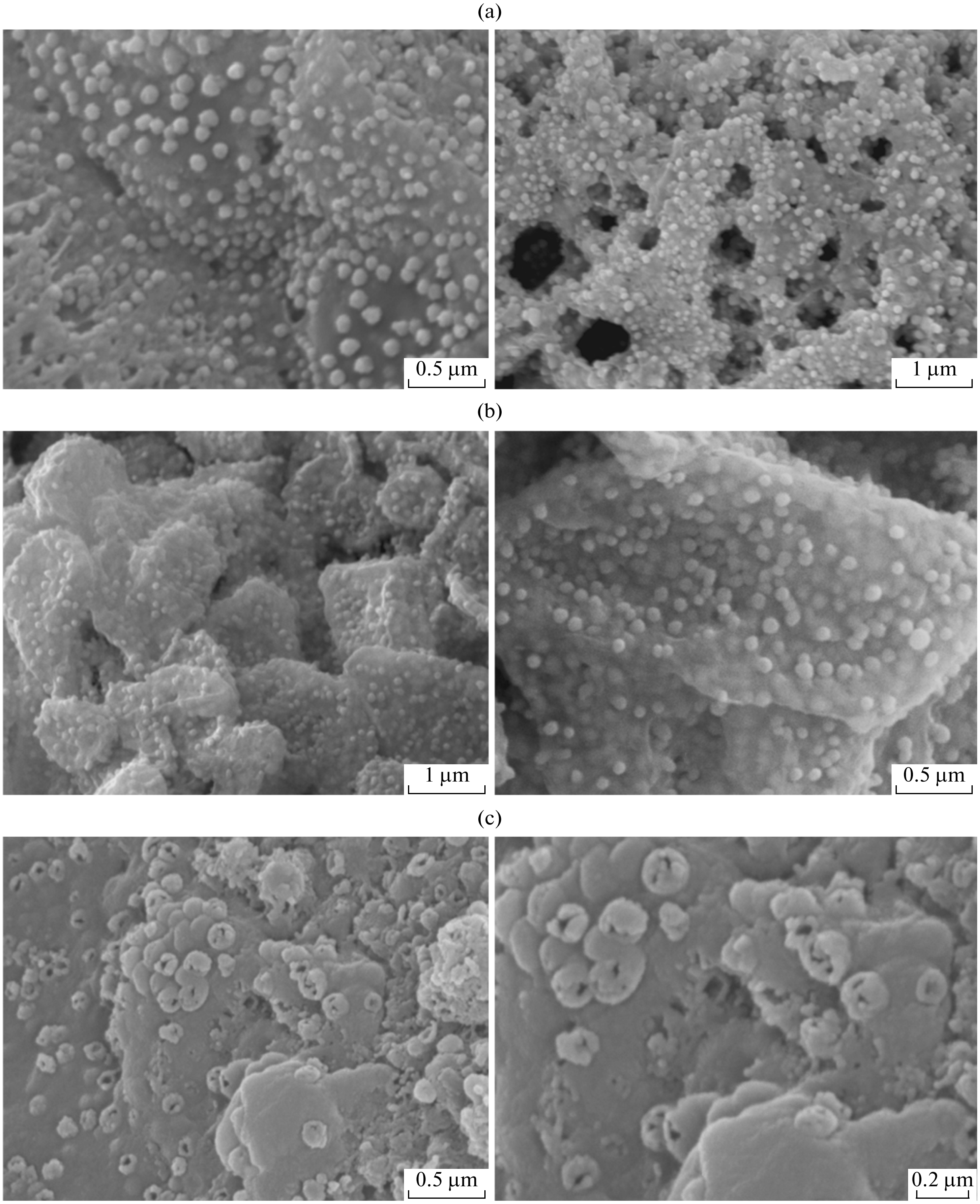

Fig. 3. Microimages of the composites obtained by the decomposition of (a) neutral and (b) acidic copper(II) maleates before and (c) after metal etching from the composite.

The high dispersity of copper in the composite and the presence of pores formed due to the loss of a portion of the substance in the course of thermolysis determine the high reactivity of copper in the composite. Copper can fairly rapidly be oxidized in air, and the X-ray diffraction study performed after the storage of the copper-containing composite in air for a week shows two phases: Cu and Cu_2O. A longer storage results in an almost complete oxidation of copper. The accessibility of the metallic (in the case of Cu) component to the chemical action is manifested in the possibility of the nearly complete (up to 99.7%) removal of this component from the composite by the treatment with HNO_3 or a solution of $FeCl_3$.

The removal of the metal from the composite does not lead to the decomposition of large particles of the polymer organic matrix but is accompanied by the destruction of spherical conglomerates, remaining organic residues of the shell (Fig. 3). The electronic microimages of the composite before and after etching of copper indicate that the metal particles are present in round conglomerates. After etching, only residues of the destroyed conglomerates are observed on the polymer surface. In addition, when the metal content is very high (84.2% in the composite synthesized by the decomposition of copper maleate), the dielectric properties of the copper-containing composite can be explained by the presence of the metal in the conglomerates.

ACKNOWLEDGMENTS

The authors are grateful to N.F. Beizel', A.P. Zubarev, and O.S. Koshcheeva for elemental analysis and to I.V. Korol'kov and V.V. Sokolov for X-ray diffraction studies.

REFERENCES

1. Morokhov, I.D., Trusov, L.I., and Chizhik, S.P., *Ul'tradispersnye metallicheskie sredy* (Ultradispersed Metallic Media), Moscow: Atomizdat, 1977.
2. Petrov, Yu.I., *Klastery i malye chastitsy* (Clusters and Small Particles), Moscow: Nauka, 1986.
3. Pomogailo, A.D., Rozenberg, A.S., and Uflyand, I.E., *Nanochastitsy metallov v polimerakh* (Metal Nanoparticles in Polymers), Moscow: Khimiya, 2000.
4. Shuvaev, A.T., Rozenberg, A.S., Dzhardimalieva, G.I., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1998, no. 8, p. 1505.
5. Rozenberg, A.S., Aleksandrova, E.I., Ivleva, N.P., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1998, no. 2, p. 265.
6. Pomogailo, A.D., Dzhardimalieva, G.I., Rozenberg, A.S., et al., *J. Nanopart. Res.*, 2003, vol. 5, p. 497.
7. Yudanova, L.I., Logvinenko, V.A., Sheludyakova, L.A., et al., *Russ. J. Inorg. Chem.*, 2008, vol. 53, no. 9, p. 1459.
8. Logvinenko, V.A., Yudanova, L.I., Yudanov, N.F., and Chekhova, G.N., *J. Therm. Anal. Calorim.*, 2003, vol. 74, p. 395.
9. Yudanova, L.I., Logvinenko, V.A., Semyannikov, P.P., et al., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 1, p. 22.
10. Prout, C.K., Carruthers, J.R., and Rossotti, F.J., *J. Chem. Soc., A*, 1971, p. 3342.
11. Porollo, N.P., Aliev, Z.G., Dzhardimalieva, G.I., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1997, no. 2, p. 375.
12. Carr, N.J. and Galwey, A.K., *J. Chem. Soc., Faraday Trans.*, 1988, vol. 84, no. 5, p. 1357.