



THERMAL TRANSFORMATIONS IN COPPER/SODIUM-ORGANOSILOXANES OF A GLOBULAR STRUCTURE

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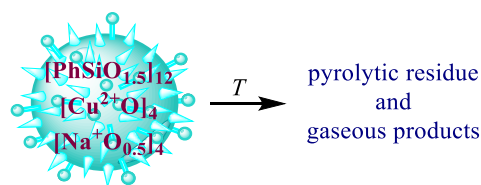
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Abstract

The thermal and thermo-oxidative transformations in cage-like metal-organosiloxanes of the general formula $[\text{RSiO}_{1.5}]_{12}[\text{CuO}]_4[\text{NaO}_{0.5}]_4$ (R= Ph, Me) were studied. It was established that their decomposition occurs in two stages and includes a number of solid-state reactions, leading to the abstraction of organic groups from the silicon atom, the partial or complete reduction of copper atoms, and the release of metallic and oxide phases.

Key words: cage-like metal-organosiloxanes, thermal destruction, ceramic precursors.



Introduction

Cage-like metal-organosiloxanes (CLMOs) [1] are of great scientific interest, since their structures suggest enormous potential for obtaining regular polymeric structures, which, upon their controlled pyrolytic decomposition, can serve as precursors of ceramic-like products [2]. Obviously, establishing the regularities of formation of pyrolytic metallasiloxane structures is an important task and implies a comprehensive study of the chemical and structural transformations that occur during the pyrolysis of these compounds, depending on their initial chemical composition and the configuration of siloxane bonds [3].

This work is devoted to the investigation of thermal transformations in Cu/Na-organosiloxanes of the general formula $[\text{RSiO}_{1.5}]_{12}[\text{CuO}]_4[\text{NaO}_{0.5}]_4 \cdot \text{solv.}$ (R= Ph, Me; Ph-CLMO and Me-CLMO, respectively) of a globular structure [4]. The synthesis of CLMOs was carried out according to the published procedure [5, 6].

Results and discussion

Figure 1 shows the TGA and DTA curves obtained during the thermal and thermo-oxidative destruction of the CLMOs. All the studied compounds contained coordinated solvent and water molecules. The first stage of the thermal and thermo-oxidative destruction, which followed the mass loss associated with the removal of the solvated solvent and water molecules, was a heterogeneous solid-phase reaction that results in the disintegration of the initial crystal lattice, while the particles of the amorphized product retain the shape of the initial crystals (Fig. 2). It occurred in the temperature range of 300–400 °C and led to the partial detachment of organic groups (~50%), the amorphization of the metallasiloxanes, and a change in the oxidation state of copper and silicon atoms. This stage was

accompanied by large exothermic effects (6–9 kJ/g, which approximately corresponds to the heat of complete combustion of 30–50% of the hydrocarbons formed). This indicates that the oxidation processes accompanied by the large mass losses and thermal effects are mainly secondary oxidation reactions of hydrocarbons formed as a result of the thermal abstraction of side organic groups.

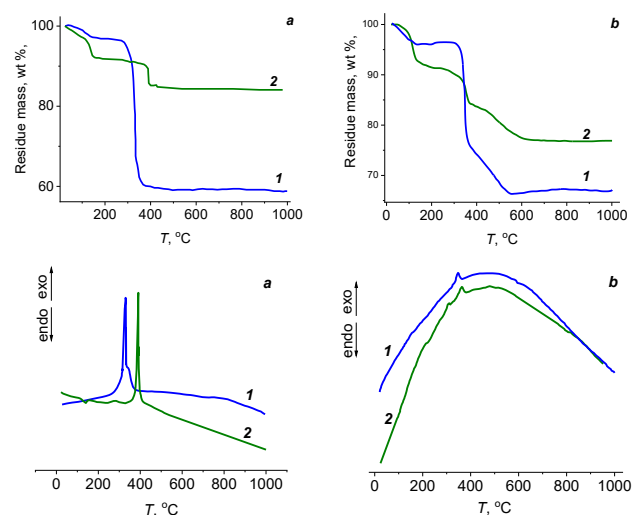


Figure 1. TGA (top) and DTA (bottom) curves for the Ph-CLMO (1) and Me-CLMO (2) in air (a) and in an argon atmosphere (b) at a heating rate of 5 °C/min.

It should be emphasized that the exothermic effects are observed both during the thermo-oxidative destruction in air and during the thermal destruction in an inert atmosphere. A possible reason for these exothermic reactions is the reduction of Cu^{2+} to Cu^+ and Cu^0 with the simultaneous oxidation of the silicon atom.

The second stage of the decomposition in the range of 550–800 °C comprised the completion of the abstraction of organic

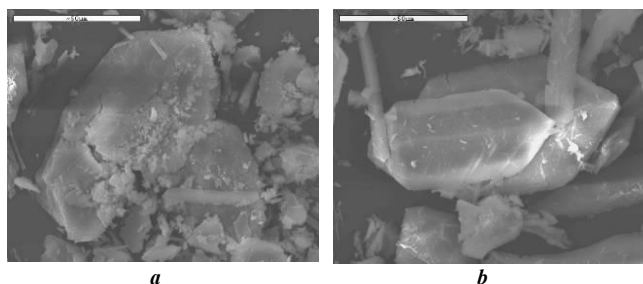


Figure 2. Micrographs of the initial Me-CLMO sample (*a*) and the sample heated at 400 °C under vacuum (*b*).

groups and redox reactions, as well as the release of metallic and metal oxide phases with a simultaneous increase in the sizes of their particles and improvement of the structure.

The investigation of the Ph-CLMO pyrolysis products by IR spectroscopy (Fig. 3) showed that at 400 °C the detachment of phenyl groups from the silicon atom occurs (the characteristic absorption bands of Si–Ph stretches at 1428 and 1129 cm^{-1} disappear). After heating to 1000 °C in air, the characteristic absorption bands of OH groups disappear and the absorption bands characteristic of silicon oxide arise.

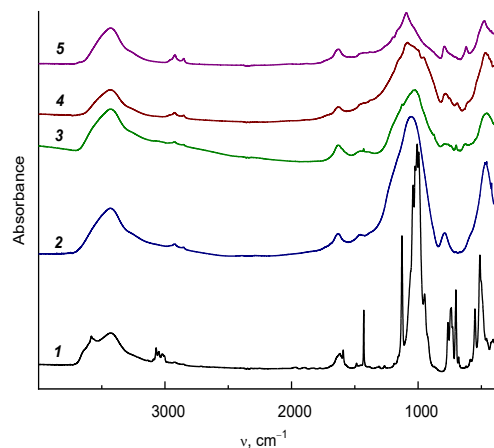


Figure 3. IR spectra for the initial Ph-CLMO (*1*), heated at 400 °C (*2*, *3*), 1000 °C (*4*), and 800 °C (*5*) under vacuum (*2*, *4*) and in air (*3*, *5*).

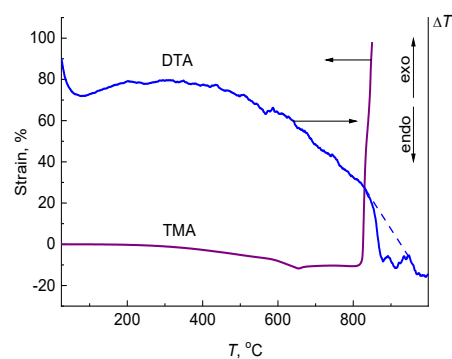


Figure 4. TMA and DTA curves of the pyrolytic residue of Ph-CLMO at the heating rate of 10 °C/min in air.

According to the results of TMA analysis, when heated in air at 820 °C, Ph-CLMO converts to a fluid state (Fig. 4). In the same temperature range, an endothermic peak appears in the DTA curve, indicating melting of the crystalline phase.

The reduction of copper to Cu^+ and Cu^0 during the pyrolysis of Ph-CLMO and Me-CLMO in an inert atmosphere or under

vacuum with the simultaneous oxidation of the silicon atom was confirmed by the XPS data (Table 1). Thus, these processes were manifested in the shift of the $\text{Cu}2p_{3/2}$, $\text{CuL}_3\text{M}_{45}\text{M}_{45}$, and $\text{Si}2p$ lines. At the same time, the thermal processing in air led to the formation of CuO and SiO_2 . The observed energies of the spectral peaks are in good agreement with the standard reference values [7].

Table 1. Energies of the Auger and photoelectron peaks for the metallasiloxanes with different histories

Sample	Energy, eV			
	Si2p	Cu2p _{3/2}	CuL ₃ M ₄₅ M ₄₅	Cu2p _{3/2} + CuL ₃ M ₄₅ M ₄₅
Me-CLMO initial	102.5	935.6	914.4	1850.0
Ph-CLMO initial	102.4	935.4	914.8	1850.2
Me-CLMO 410 °C vacuum	103.2	932.7	916.3	1849.0
Ph-CLMO 410 °C vacuum	103.2	932.8	916.4	1849.2
Me-CLMO 400 °C air	103.9	934.5	916.5	1851.0
Me-CLMO 1000 °C vacuum	103.2	932.7	918.1	1850.8
Me-CLMO 1000 °C air	103.9	933.8	917.6	1851.4
Ph-CLMO 1000 °C air	104.0	934.0	917.8	1851.6

The results of the XPS studies were confirmed by X-ray diffraction data, which indicated the formation of crystalline phases of copper oxides and neat copper under various conditions (Fig. 5). It should be noted that the reflexes for the crystalline phase of quartz are in the region of $2\theta = 20\text{--}30$ deg (the halo of the amorphous phase of quartz is also located there), and also that in a number of cases the reflexes of the copper and copper oxide phases are so broad that these phases can be conditionally considered amorphous.

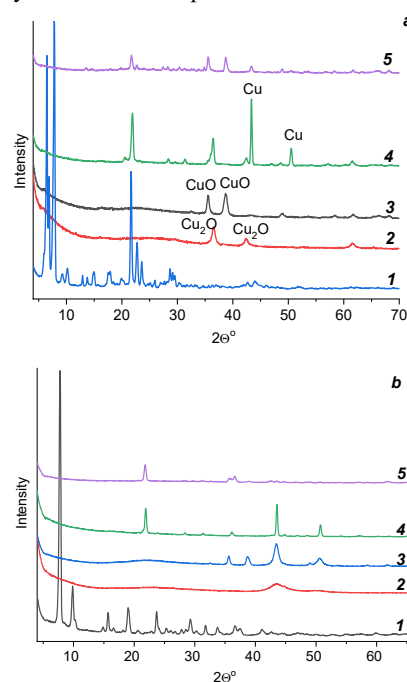


Figure 5. XRD patterns for Ph-CLMO (*a*) and Me-CLMO (*b*) of the initial samples (*1*) and those heated at 400 °C (*2*, *3*), 1000 °C (*4*, *6*), and 800 °C (*5*) under vacuum (*2*, *4*) and in air (*3*, *5*).

Conclusions

The performed investigations showed that the considered processes of thermal and thermo-oxidative destruction of metallasiloxanes lead to the formation of silicon oxide ceramic products with the embedded microphases of metals and their oxides. The substituents at the silicon atom are likely not to have a significant effect on the proceeding reactions and do not change significantly the compositions of the resulting products.

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