The Synthesis of Composites by the Thermolysis of the Salts of Carboxylic Acids

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Abstract

The present paper deals with thermal decomposition of the salts (both normal and acid) of transition metals with carboxylic acids: maleic, *ortho*-phthalic, and terephthalic. The residues after pyrolysis (up to 450 ºC) are composites including two structural components – an organic polymer matrix and spherical conglomerates from metal grains coated with polymer. Solid solutions of metal bimaleates have been synthesized, and their decomposition has been investigated. Some properties of the resulting composites have been studied qualitatively.

INTRODUCTION

The pyrolysis of organic compounds is widely used as a method of organic synthesis. As a rule, pyrolysis is accompanied by the formation of some amounts of polymers. Polymerization decreases the yield of the useful product and thus is undesirable. In the present study we considered the possibility to use polymer products of thermolysis as one of the components of composites. This fact determined the choice of initial compounds. We studied the salts of transition metals (Cu, Ni, Co, and Mn) with carboxylic acids containing double and aromatic carbon-carbon bonds. The presence of these bonds and the catalytic activity of transition metals were assumed to help forming polymer products of thermolysis. Possible schemes of the processes are as follows:

$$CH_2 = CH_2(COO)_2M$$
$$\rightarrow (CH \equiv CH) + M + CO_2 \qquad (1)$$
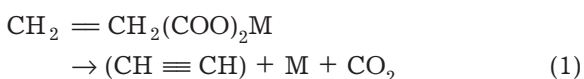
Acetylene and dehydrobenzene obtained during pyrolysis then polymerize.

Thermal decomposition of the carboxylates of transition metals has been thoroughly investigated; a detailed review is presented in [1]. Most thoroughly studied are only the simplest compounds (formiates and oxalates). The salts of saturated and aromatic carboxylic acids (in particular, maleates, phthalates, and terephthalates of transition metals) are investigated less thoroughly [2–7]. The major goal of these studies was the investigation of the mechanism of decomposition. It was stated that the decomposition of many metal carboxylates proceeds *via* the formation and growth of nuclei; the solid product is catalytically active with respect to the decomposition of the salt anion. The formation of a complicated mixture of gas-phase products was reported (carbon dioxide, hydrocarbons, aldehydes, ketones, acids and their anhydrides); however, less attention was paid to the composition of the solid organic residue. Only disperse carbon [2] and nickel carbide [8] were detected among the products of nickel maleate decomposition.

Among the investigations presented at the 7th European Symposium on Thermal Analysis and Calorimetry (ESTAC-7, 1998) there were many works dealing with thermal decomposition of

carboxylates, but only with saturated organic acids and hydroxy acids (for example, [9]).

We synthesized and investigated cobalt, nickel and manganese maleates and bimaleates, copper *o*-phthalate, *o*-biphthalate and terephthalate, as well as solid solutions: cobalt bimaleates − nickel bimaleates, and nickel bimaleates − manganese bimaleates with the salt molar ratio close to 1 : 1.

EXPERIMENTAL

Thermal decomposition was studied in helium flow in C-derivatograph (MOM, Hungary). Sample mass was 30−40 mg, heating rate 2 °C/min; a sample was held by a ceramic microcrucible; helium flow rate was 60 cm^3/min. Thermogravimetry of the compounds showed that their decomposition proceeds *via* several stages: a single- or two-stage detachment of crystal hydrate water, detachment of maleic
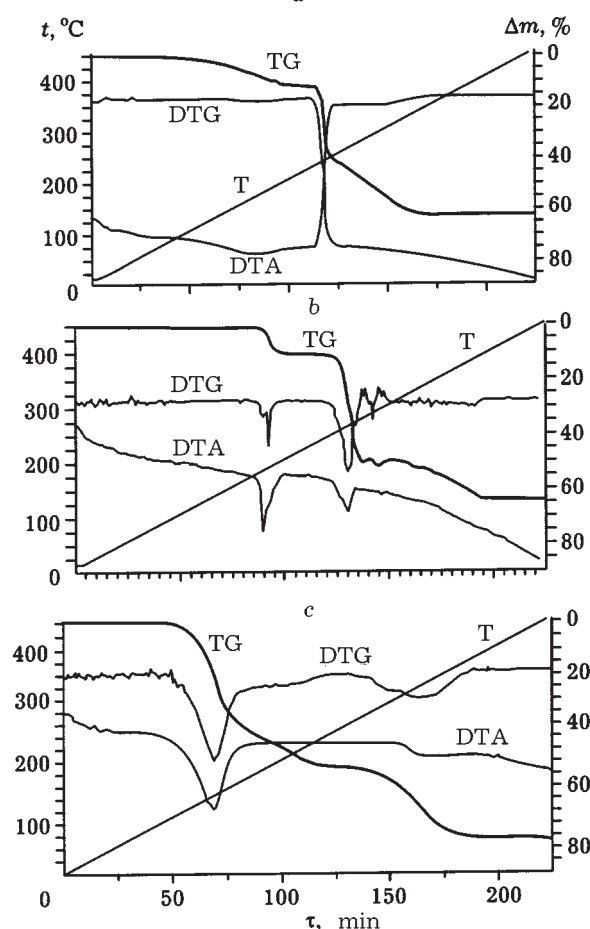
Fig. 1. Typical thermograms of dehydration and decomposition of salts: copper maleate (*a*), copper phthalate (*b*), and nickel bimaleate (*c*).
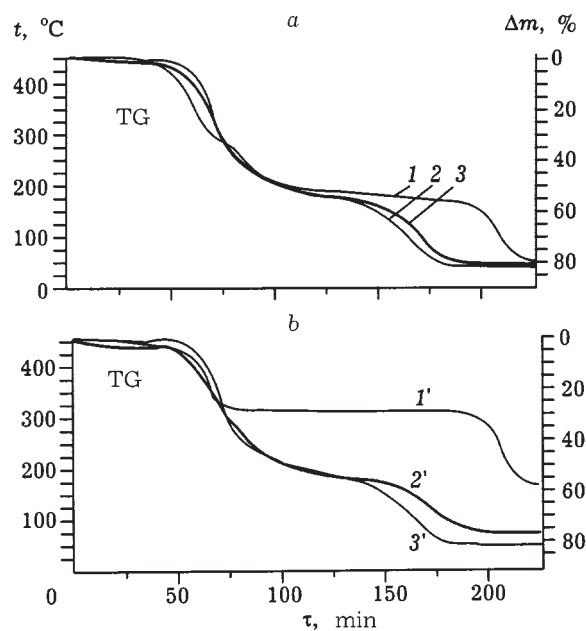
Fig. 2. Thermogravimetric curves of the decomposition of cobalt bimaleate (*1*), nickel bimaleate (*2*), and their solid solution (1 : 1) (*3*); manganese bimaleate (*1'*), nickel bimaleate (*3'*), and their solid solution (1 : 1) (*2'*).

acid or maleic anhydride (for the case of bimaleates); finally, the decomposition of the salt itself with the evolution of CO$_2$ and organic molecules. Figure 1 shows typical thermograms for several salts.

Studying bimaleates we found that the decomposition temperature of solid solutions is much lower than the decomposition temperature of the bimaleate that is thermally more stable among them both (Fig. 2).

In order to process thermoanalytical data, we used the integral method of non-isothermal kinetics (computer programme TA 1 B) [10, 11]. The selection of the best kinetic equation (among 13 different topochemical equations) was carried out using the linear dependence of log g (α) on $1/T$. The decomposition of salts is rather complicated process. For the major part of salts, thermal decomposition is an endothermic process described by the shrinking sphere equation: $d\alpha/d\tau = k(1 - \alpha)^{2/3}$.

The decomposition of copper and cobalt maleates is described by the Mampel equation: $\{f(\alpha) = (1 - \alpha)\}$. In this case, the formation of nuclei is the limiting stage. Kinetic parameters of the process are sharply different: for copper maleate, $E = 326$ kJ/mol, lg $A = 25.0$; for cobalt maleate, $E = 100$ kJ/mol, lg $A = 5.0$.

The decomposition of cobalt and manganese bimaleates is described by the shrinking sphere equation; kinetic parameters are close to each other ($E \approx 120$ kJ/mol, lg $A \approx 7$), though the resulting products are different: metal cobalt and manganese carbonate.

In all the cases (independently of the formal kinetic description of the macrokinetics of the slowest process stage), the solid residue after thermolysis is a composite of a metal (Cu, Ni, Co) or metal carbonate ($MnCO_3$) and an organic polymer.

The most interesting feature of the structure of composites was revealed by means of scanning electron microscopy. It was stated that the composite consists of two structural components: an organic polymer matrix and spherical conglomerates incorporating a metal and organic polymer and distributed over the matrix. Figures 3 and 4 show the photographs of the

Fig. 3. A photograph of the composite synthesized from copper maleate.
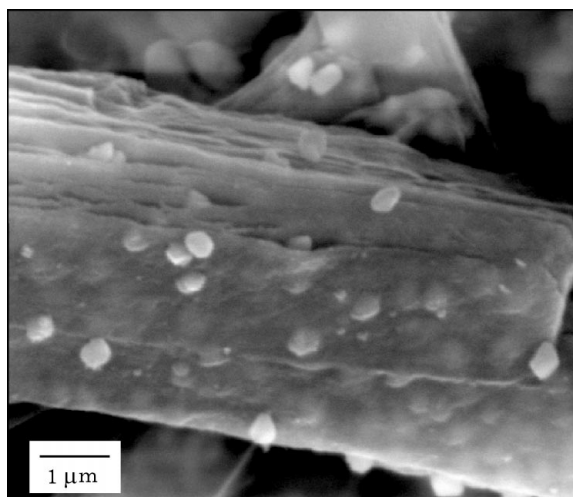
Fig. 4. A photograph of the composite synthesized from copper o-phthalate.

composites obtained from copper maleate and o-phthalate.

DISCUSSION OF RESULTS

Since composite particles conserve the shape and size of the crystals of initial salts (except for cobalt bimaleates that melts during thermolysis), the loss of a part of substance leads to the formation of open pores; as a result, a metal can be nearly completely (by 97 %) removed from the composite by treating it with nitric oxide or the iron (III) chloride solution. This does not cause the destruction of composite particles. Fluorination of the composite obtained from copper maleate can also be carried out without the destruction of particles by treating them with the BrF_3 solution in liquid bromine. Both the metal and the polymer matrix are fluorinated. It should be noted that the frequencies of the most intensive absorption bands corresponding to the C—F bond (1120 cm^{-1}) coincide in the IR spectra of the yellow fluorinated polymer and of fluorinated graphite CF_2. The removal of metal from the composite does not destroy large particles but is accompanied with the destruction of spherical conglomerates, only an organic shell remains (Fig. 5).

Physical properties of the composites were studied only qualitatively. Dielectric properties of the composites with copper (mass fraction of copper being ~ 70 %) are explained by the manner in which the metal is distributed over the polymer matrix. Cobalt- and nickel-containing composites exhibit electrical conductance which
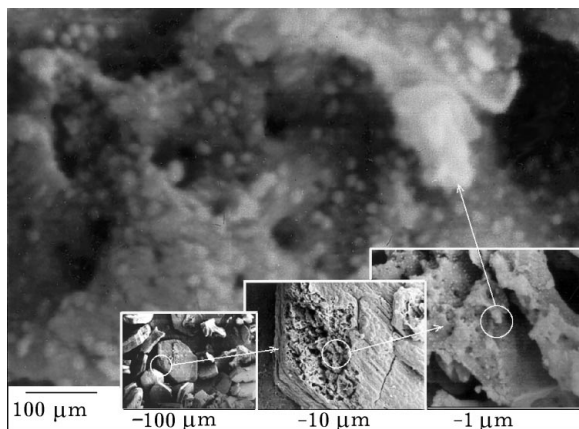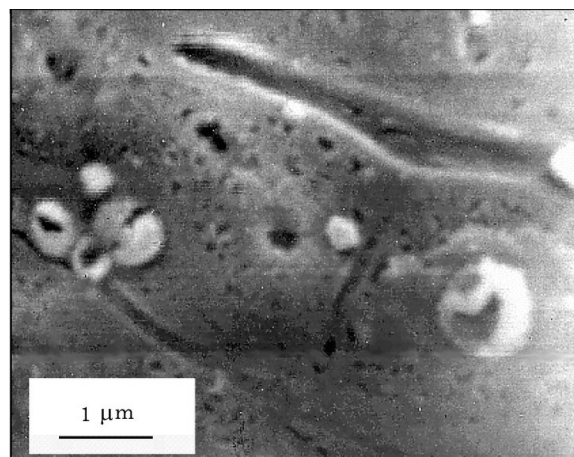

Fig. 5. A photograph of an empty polymer shell remaining after the removal of metal particles from the composite.

is likely to be due to the conductivity of the organic matrix itself. The mentioned metals are known to be catalysts of hydrogenation and dehydrogenation which can lead to the increase of carbon content of the polymer and thus to the increase of the polymer electrical conductivity. The composites obtained from Co and Ni salts (as well as by the decomposition of the solid solutions of Co-Ni and Mn-Ni bimaleates) exhibit ferromagnetic properties.

It can be assumed that two parallel processes take place during the formation of a composite: thermal polymerization of the organic products of thermolysis (resulting in the formation of the polymer matrix) and catalytic polymerization on the surface of metal particles (their size being ~ 50 Å, according to the data of X-ray diffraction). The formation of metal nuclei, their growth, agglomeration of metal particles with the simultaneous growth of a polymer layer on them (their possible rotation in the flow of gases evolved at the reaction front) lead to the round shape of metal-polymer conglomerates. Some particles are carried by the gas flow through the pores and deposited as a metal mirror on the reactor walls and on the surface of composite particles.

It should be noted that spherical conglomerates are weakly bound with the polymer matrix and can be isolated from it as a suspension by stirring with organic solvents, in particular acetonitrile. The composites with opal structure composed only of conglomerates can be obtained by drying this suspension. It can be assumed that these composites may possess a series of interesting properties.

The data obtained in the EPR investigation of the composite prepared from copper maleate are the evidence in favour of the proposed scheme of composite formation. EPR spectra before and after the removal of metal are sharply different from each other. This can be due to the screening of the polymer in conglomerates by metal particles. In the composite obtained from copper o-phthalate, the polymer component is soluble in organic solvents which allowed us to obtain the data on sharply different properties of the polymer (obtained by extraction with toluene) before and after the removal of metal from the composite. In the latter case, a substantial amount of the crystal substance is obtained from the extract after drying. The structure of this crystal substance has not been determined yet.

CONCLUSIONS

The investigation of general laws of thermal decomposition of the salts of transition metals with saturated and aromatic carboxylic acids is very promising due to the following two reasons:

1) a variety of organic carboxylic acids and a possibility to synthesize solid solutions of the salts of different metals allow to prepare composites with different properties;

2) different ordering of organic anions in the lattices of crystal salts can be useful in the synthesis of new organic polymers and individual monomer organic compounds.

REFERENCES

1 M. Brown, D. Dollimor and A. Galwey, Reactsii tverdykh tel, Mir, Moscow, 1983.
2 M. J. McGinn, B. R. Wheeler and A. K. Galwey, *Trans. Faraday Soc.*, 67 (1971) 1480.
3 M. J. McGinn, B. R. Wheeler and A. K. Galwey, *Ibid.*, 66 (1970) 1809.
4 A. K. Galwey, *J. Chem. Soc.*, (1965) 4235, 5433, 6188.
5 K. Taki, P. H. Kin and S. Namba, *Bull. Chem. Soc. Japan*, 43 (1970) 1450.
6 R. J. Acheson and A. K. Galwey, *J. Chem. Soc.*, (1968) 1125.
7 R. J. Acheson and A. K. Galwey, *J. Inorg. Nucl. Chem.*, 30 (1968) 2383.
8 A. K. Galwey and B. R. Wheeler, *J. Chem. Soc., Faraday Trans., I,* 70 (1974) 661.
9 L. Patron, O. Carp, I. Mandru and G. Grasa, *J. Thermal Anal. and Calorimetry*, 56 (1999) 597.
10 F. Satava and J. Sestak, *J. Thermal Anal.*, 8 (1975) 477.
11 V. A. Logvinenko, Termichesky analiz koordinatsionnykh soyedineniy i klatratov, Nauka, Novosibirsk, 1982.