

THERMAL ANALYSIS OF TRANSITION METAL SALTS OF CARBOXYLIC ACIDS The way for the synthesis of metal–polymer composites

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Abstract

The thermal decomposition of salts (both normal and acid) of transition metals with carboxylic acids (maleic, *ortho*-phthalic and terephthalic) was studied in inert atmosphere. The residues after pyrolysis (up to 450°C) are composites including two structural components: an organic polymer matrix and spherical conglomerates from metal grains coated with polymer. Thermal decomposition of solid solutions of metal bimaleates (Co–Ni, Fe–Ni, Zn–Ni) was investigated. Thermogravimetric data (obtained at different rates of linear heating) were processed with ‘Netzsch Thermokinetics’ computer program. Kinetic parameters were calculated only for the first decomposition step, and the process is described by Prout–Tompkins equation of n^{th} order with autocatalysis. Some properties of the resulting composites have been studied qualitatively.

Keywords: composites metal–polymer, coordination compounds, ‘model free’ kinetics, unsaturated carboxylic acids

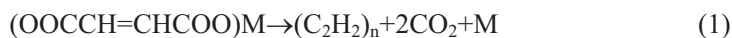
Introduction

Decomposition processes for various metals carboxylates under heating were studied widely during last decades, a detailed review is presented in [1]. The simplest compounds (formates and oxalates) were scrutinized, but the salts of aromatic and unsaturated carboxylic acids (maleates, phthalates, etc.) are not studied in depth. Usually found residua are metal oxides (in the air atmosphere), or pure metals (in the inert atmosphere); in the last-named cases it was stated, that the gas-phase products were carbon dioxide, hydrocarbons, aldehydes, ketones, acids (and acid anhydrides); metal carbides and dispersed carbon (in addition to metals) were found as solid products [2–3]. No special interest was shown in the composition and the structure of solid residua in the last publications, concerned to complexes with saturated, aromatic and unsaturated carboxylic acids [4–7].

Pyrolysis of organic compounds has found wide application as the method of organic synthesis although it is always accompanied by the formation of polymers. Such a

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polymerization reduces the yield of a useful product and is not desirable. In this work we show how to use these polymeric products as one of components of composites. We studied the decomposition of carboxylic acids salts of transition metals with double or aromatic carbon–carbon bonds in organic part. It is probable, that availability of such bonds as well as catalytic activity of transition metals should increase the yield of polymeric products formation. Possible reactions can be:



Experimental

We have synthesized and studied series of compounds: Co, Ni, Cu, Mn, Zn maleates, Fe, Co, Ni, Mn, Zn bimaleates, *ortho*-phthalates of Co, Ni, Cu, Cu *ortho*-biphthalate, Cu terephthalate, and solid solutions of bimaleates: Ni–Co, Ni–Mn, Ni–Cu, Ni–Zn (with the salt molar ratio close to 1:1). Some of these coordination compounds are crystalline hydrates.

Thermal decomposition was studied by means of Derivatograph-C and Derivatograph Q-1500-D (MOM, Hungary). Sample mass was 30–40 mg, a sample was held by ceramic micro-crucible; heating rates were within 2 and 15°C min, helium flow rate was 60 cm³ min⁻¹.

Thermogravimetric data were processed using the Netzsch Thermokinetics (version 2001.9d) computer program. We have studied only the kinetics of the pyrolysis processes (temperature interval >200°C). We have used ‘Model free’ approach and calculated the values of activation energy and preexponential factor by simultaneous processing of two thermogravimetric curves (obtained with two different rates of linear heating); used programs were ‘ASTM E698’ [8], ‘Friedman analysis’ [9] and ‘Ozawa–Flynn–Wall analysis’ [10–12]. Further we searched for the best kinetic description (from 16 topochemical equations: nucleation, diffusion, chemical reaction on the interface) by the Borchard–Daniels differential method (with linear regression utilization) [13–14]. We can choose the best kinetic description not only by the best correlation coefficients, but on the basis of kinetics parameters values, suitable for starting ‘Model free’ calculations.

Results and discussion

Thermal analysis of compounds has shown, that the decomposition proceeds in several steps: water elimination, elimination of maleic acid (or maleic anhydride – in case of bimaleates pyrolysis) and, at last, salts decomposition with elimination both of carbon dioxide, and various volatile small organic molecules. It was found that the initial temperatures of decomposition are related by the metal cation; for series Cu, Ni, Co, Fe, Zn, they are 250, 300, 350, 375, 375°C, accordingly. The decomposition temperature for solid solution of Co–Ni bimaleates depends upon the stability of the less stable Ni salt. The decomposition of Cu–Ni binary phthalates take place in two steps.

The solid residue after thermal treatment represents a composite, which consists from metal (for copper, nickel, cobalt) or metal carbonate (for manganese) and organic polymers. Scanning electron microscope investigation shows that the composite consists of two structural components: an organic polymeric matrix and spherical conglomerates (involving metal particles and organic polymer), disorderly distributed in this matrix. These conglomerates exhibit dimensions 0.2–1 μm , the particles size is $\approx 50 \text{ \AA}$ (according to X-ray diffraction data). The matrix (e.g., in 'terephthalate' composite) has lamellar texture and the layers transparency testifies to the netlike structure (Fig. 1).

So as the composite grains hold the shape and size of initial salts crystals, the elimination of obtained gaseous parts of substance results in formation of a lot of open pores. Therefore the metal can be almost completely (up to 97%) removed from composite or by processing with a nitric acid, or by shaking of conglomerates suspension in organic solvents. 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. 2). The '*o*-phthalate' composite was segregated into two kinds of polymers and two kinds of crystal organic compounds.

It is possible to extract the conglomerates from the interlaminar spaces, with the production of the composite with opal structure.

Copper-contained composites have dielectric properties because of this distribution metal in the polymeric matrix. The conductivity of cobalt- and nickel-contained composites is, probably, connected with the conductivity of an organic matrix itself. It is known, that the mentioned metals are catalysts of hydrogenation and dehydrogenation reactions, which can result in the increase of carbon content in the polymer and the rise of its con-

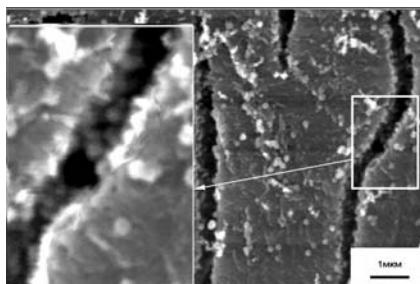


Fig. 1 Photomicrography of the composite, prepared from terephthalate of copper

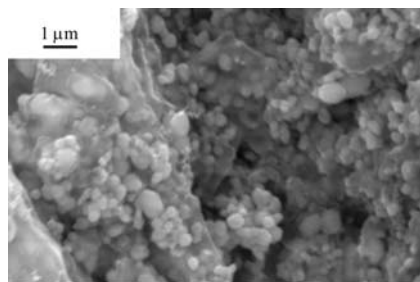


Fig. 2 Photomicrography of the composite, prepared from copper *o*-phthalate (after treating by organic solvent)

ductivity. The composites with cobalt and nickel (as well as composites synthesized from solid solutions cobalt–nickel bimaleates and nickel–manganese bimaleates) have ferromagnetic properties.

As it is possible to assume, two parallel processes are proceeding during the formation of the composite: thermal polymerization of organic products (with formation of a polymeric matrix) and catalytic polymerization on the surface of metal particles. The formation of metal nuclei, their growth according to complex topochemical laws, merging of metal particles and simultaneous outgrowth of a polymer layer on them, leads, as it is possible to assume, to spherical form of metal–polymer conglomerates. The biggest conglomerate spheres are observed in ‘*o*-phthalate’ composites, the smallest spheres – in ‘terephthalate’ composite.

Some volatile airborne particles are carried out by a current of gases through pores and are postponed in kind of a ‘metal’ mirror on reactor walls and on surface of grains of a composite. The study of the composite (formed from copper maleate) by the proton magnetic resonance method speaks in favor of this model of composites formation. PMR-spectra of a composite before and after metal removal are sharply distinguished which can be connected with the shielding of conglomerates polymer by metal particles.

The kinetic study shows that the decomposition processes (oxidation–reduction reactions) are complex, i.e. two- or three-step destruction. Ozawa–Flynn–Wall analysis [10–12] (in ‘Model free’ approach) shown that it is possible to isolate the first decomposition step with constant E and A . It was within the limits of $0.15 < \alpha < 0.45$ for Zn–Ni and Co–Ni bimaleates solid solutions, within the limits of $0.10 < \alpha < 0.45$ for Fe–Ni bimaleates solid solutions. So we have searched the best kinetic equation for the first decomposition steps for solid solutions of Co–Ni, Fe–Ni and Zn–Ni bimaleates by the Borchard–Daniels differential method [13–14]. The best kinetics description in all cases is Prout–Tompkins equation of n^{th} order with autocatalysis.

Co–Ni bimaleates solid solution. $E_a=120 \text{ kJ mol}^{-1}$, $\log A=7.6$.

Fe–Ni bimaleates solid solution. $E_a=274 \text{ kJ mol}^{-1}$, $\log A=21$.

Zn–Ni bimaleates solid solution. $E_a=111 \text{ kJ mol}^{-1}$, $\log A=6.5$.

We have studied single samples of compounds and so we did not calculate random errors; the estimated error of E_a and $\log A$ values is about 5–7%.

The formation of metal nuclei and their growth can explain the appearance of the topochemical Prout–Tompkins equation, involved the autocatalysis by metal particles.

Earlier we studied the thermal decomposition kinetics of the pure salt, bimaleate of Co. $E_a=120 \text{ kJ mol}^{-1}$, $\log A=7$ (the equation of contracted sphere) – chemical reaction on the interface) [15].

Conclusions

Thermal decomposition processes of salts of transition metals with unsaturated carboxylic and aromatic acids (such as maleates, phthalates) holds the greater promise for two reasons. The preparation of ‘metal–polymer’ composites with the most diversified properties is possible, so as there are large variety both of organic

carboxylic acids, and transition metals. The different ordered arrangement of organic anions in the salts crystal lattice can be useful for the synthesis of new organic polymers and individual organic monomer compounds in the process of salts thermal decomposition. The film of poly-conjugated polymer, extracted from the 'o-phthalic' composite, can be used for the production of memory cells.

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