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The thermal decomposition of crystalline and freeze-dried μ-oxo-acetato-complexes of manganese and iron

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Abstract

Mixed nuclear μ-oxo-acetato-complexes of Mn^{2+} and Fe^{3+} have been synthesized by means of two different synthetic paths (precipitation or freeze drying). These complexes are interesting because after the decomposition, a manganese ferrite with spinel structure is produced. That is why the decomposition process of both substances has been investigated by means of DTA, TG and mass spectroscopy and the results compared. Water, acetic acid, carbon dioxide and acetone are identified as decomposition products and assigned to the steps of the TG graph. Quantification of the decomposition products using wet analysis methods enables a complete decomposition mechanism to be worked out.

INTRODUCTION

We have investigated the preparation and decomposition of μ-oxo-carboxylates $[Fe_2^{3+}M^{2+}O(CH_3COO)_6(H_2O)_3] \cdot nH_2O$ (M = Zn, Mn) (**A**) from the viewpoint of the synthesis of Mn–Zn ferrites with spinel structure.

These compounds were first mentioned by Weinland and Holtmeier [1]. They have a central oxygen ion around which three transition metal ions are arranged in an equilateral triangle. The transition metal ions are connected with each other by two carboxylate groups [2]. As the metal ion stoichiometry of the spinel is already present in these compounds, they should be a good basis for the formation of the wanted spinel phase of a Mn–Zn ferrite. However, preparatively it is very difficult to achieve the exact 2:1 stoichiometry of the metal ions in (**A**). Therefore, we tried to make complex acetates of defined metal ion stoichiometry by means of freeze-drying suitable initial solutions. This has already been achieved for the analogous nickel compounds [3].

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In this paper a reaction scheme for the thermal decomposition of mixed μ-oxo-acetates of Mn^{2+} and Fe^{3+} is given based on a thermal analysis. In this connection, common features and differences in the decomposition behaviour of crystalline and freeze-dried amorphous samples are discussed.

PREPARATION

Following the slightly modified Weinland and Holtmeier method [1] and that of Blake et al. [4], a crystalline product was obtained: 0.31 mol of sodium acetate and 0.08 mol of manganese nitrate were dissolved in 70 ml water and 0.02 mol of ferric nitrate dissolved in 70 ml water were dropped in. After 1 h of stirring, the dark brown precipitate was filtered off, washed with water and air dried.

Upon analysing the metal ions it was found that for various solid products prepared according to this method, the $Fe^{3+}:Mn^{2+}$ ratio varied between 2:1 and about 2.2:1. The reason for this is that Mn^{2+} ions are preferentially washed out of the precipitate; this is favoured by the pH change and by the missing excess of acetate.

For the following investigations, a precipitate of $Fe^{3+}:Mn^{2+} = 2.04:1$ was selected which, after the C–H analysis, can be described approximately using the formula $[Fe_2MnO(CH_3COO)_6(H_2O)_3] \cdot 3H_2O$ (**B**). Incorporating freeze-drying, an amorphous light brown product of exact 2:1 metal ion stoichiometry is obtained via the following steps.

Iron powder is dissolved in a 50% aqueous solution of acetic acid in nitrogen atmosphere. Air is passed into the light green solution obtained. In this process, the solution turns red and a μ-oxo-acetato complex precipitates as a brown solid containing Fe^{2+} and Fe^{3+}. The solid is isolated as an intermediate.

For a solution which is to be freeze-dried, part of the solid is suspended in 0.8 M acetic acid and oxidized by H_2O_2. In the process, the solid is completely dissolved forming a deeply red solution with a concentration $c_{Fe^{3+}} \approx 0.75 \text{ mol l}^{-1}$. After the addition of the required quantity of manganese acetate the solution is frozen with liquid nitrogen and freeze-dried.

The product obtained was of the composition $[Fe_2MnO(CH_3COO)_5OH(H_2O)]$ (**C**). Compared with the product (**B**), the lower content of water and acetic acid can be explained by the low pressure (about 0.5 Pa) during the freeze-drying process.

DECOMPOSITION

To determine the mechanism of decomposition, a differential thermoanalyzer was used coupled with a mass spectrometer (Netzsch STA 409/QMS 125 (Balzers)-scimmer coupling system 403/5).

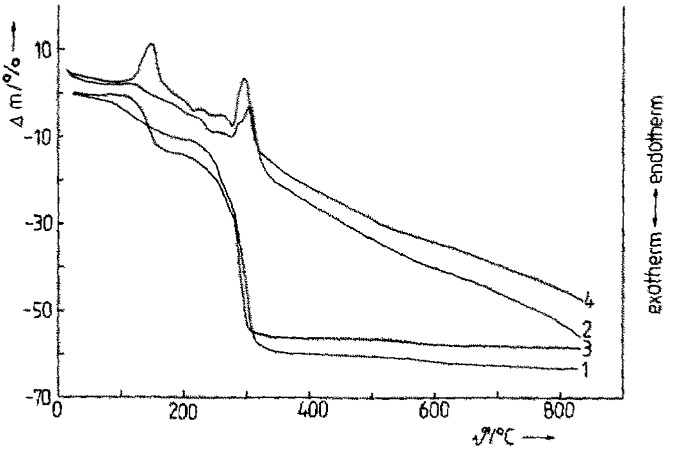

Fig. 1. Thermal analysis of the products (**B**) and (**C**). Heating rate, 5 K $\min^{-1}$; atmosphere, argon. Curve 1, TG product (**C**); curve 2, DTA product (**C**); curve 3, TG product (**B**); curve 4, DTA product (**B**).

Measurements were carried out under argon atmosphere after the equipment had repeatedly been evacuated. In the case of the crystalline product (**B**), this temporary pressure drop even results in liberating 3 mol of water of crystallization; however, the composition of the freeze-dried product (**C**) which had a lower water content was maintained.

In Fig. 1, the DTA and TG graphs of the substances (**B**) and (**C**) are compared. It can be seen that both substances show analogous decomposition behaviour. In the TG graph, there are two steps distinctly separate from each other; they are combined with sharp endothermic peaks in the DTA graph, where additional endothermic processes precede the decomposition step at about 300°C. However in the TG graph, no additional separate steps can be assigned to the additional endothermic processes mentioned.

When (**B**) and (**C**) are decomposed in air, an exothermic peak arises for the 300°C process as is also described in the literature [5, 6]. Additional endothermic water loss below 100°C reported in ref. 5 does not occur because of the evacuation already mentioned.

To elucidate the mechanism of decomposition, the gaseous decomposition products were analysed by mass spectroscopy. Besides water and acetic acid, acetone and carbon dioxide were also identified. By observing the intensities of the four mass numbers at increasing decomposition temperature, the gaseous products were assigned to the individual decomposition steps. In Fig. 2, the result of this measurement is shown for (**B**). It can be seen that during the decomposition, acetic acid is liberated in two steps (two maximum values) and carbon dioxide, acetone and water are liberated in one step only (one maximum value). In the lower

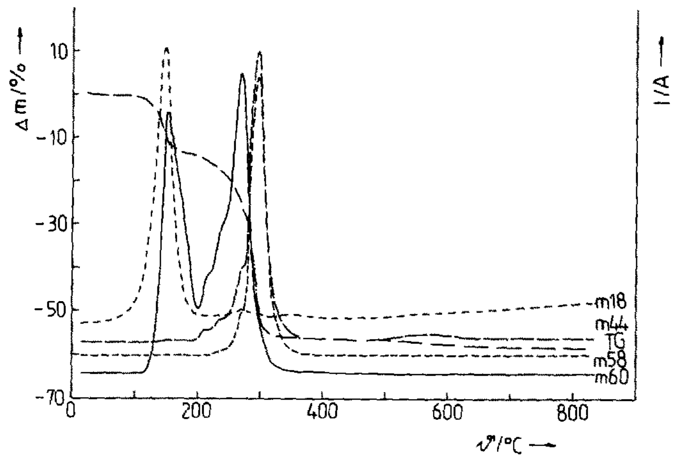

Fig. 2. Observation of several mass numbers during the decomposition of the product (**B**) in argon: m 18, H_2O; m 44, CO_2; m 58, acetone, m 60, acetic acid.

temperature range between 100 and 200°C, only acetic acid and water are split off. It can be seen that acetic acid is released at somewhat higher temperatures than water release takes place. The adequate mass loss nearly corresponds to the loss of 1 mole of acetic acid and 1 mole of water per formula unit. Hence, our results coincide with those of Yakubov et al. [5] who previously investigated this decomposition step for various (**A**) type compounds and who took as a basis

$$[Fe_2MO(CH_3COO)_6(H_2O)_3] \rightarrow$$
$$[Fe_2MO(CH_3COO)_5(OH)(H_2O)] + H_2O + CH_3COOH$$

Passing a minimum at 200°C, thermal hydrolysis continues at an increasing rate as the temperature increases, liberating acetic acid. At the same time, to a lesser extent, a further splitting off of water occurs. In the nearly water-free intermediate, finally beginning at 280°C, the decomposition prevails forming acetone and carbon dioxide which will be terminated at about 360°C. The small mass loss between 500 and 600°C correlates with low peak intensities for the mass numbers 28 (CO) and 44 (CO_2). It is probably caused by the oxidation of carbon traces originating from pyrolysis side reactions.

The qualitative decomposition steps explained for the crystalline (**B**) product are also found for the freeze-dried (**C**) product, only the liberation of water and acetic acid linked with the first step in the TG graph extend over a greater temperature range. Consistent with the composition of the freeze-dried sample resulting from the method of preparation, the total quantities of water and acetic acid released up to 200°C are somewhat lower.

Quantification of the mechanism of decomposition by means of the TG graph obtained is made more difficult because of the different rates of the individual steps. Therefore, for (**B**) the total quantities of acetic acid and carbon dioxide liberated were experimentally determined. The gaseous decomposition products were passed into carbonate-free sodium hydroxide solution using N_2. To determine acetic acid and hydrogen carbonate, an aliquot was titrated with hydrochloric acid with phenolphthalein; then, to determine carbon dioxide, an excess of hydrochloric acid was added; the mixture was heated and titrated again using sodium hydroxide. Hence, 1.5 mol of CO_2 and 3 mol of acetic acid were obtained per mol of (**B**).

CONCLUSIONS

The results of the investigations are summarized in the reaction scheme shown in Fig. 3, according to which, water not bound in the coordination sphere of the metal ions of compound (**B**) is released below 100°C in vacuum ($p < 0.5$ Pa) at room temperature.

In agreement with Yakubov et al. [5], the release of water and acetic acid in the temperature range 100–200°C should be an intramolecular process (eqn. (1)). According to Yakubov et al. [5], the electron density redistribution connected with the release of water from the manganese coordination sphere effects the protonation of an acetate ligand between two Fe^{3+} ions and its splitting off as acetic acid. The slight difference in the maximum values for the splitting off of water and acetic acid (Fig. 2) coincides with this assumption.

Processes connected with the decomposition steps (3) and (4), where acetic acid, water, acetone and carbon dioxide arise as gaseous products, are competition processes which acutally begin one after the other but proceed in parallel in a comparatively large temperature interval. These are intermolecular processes. As a result, a high molecular oxidic network

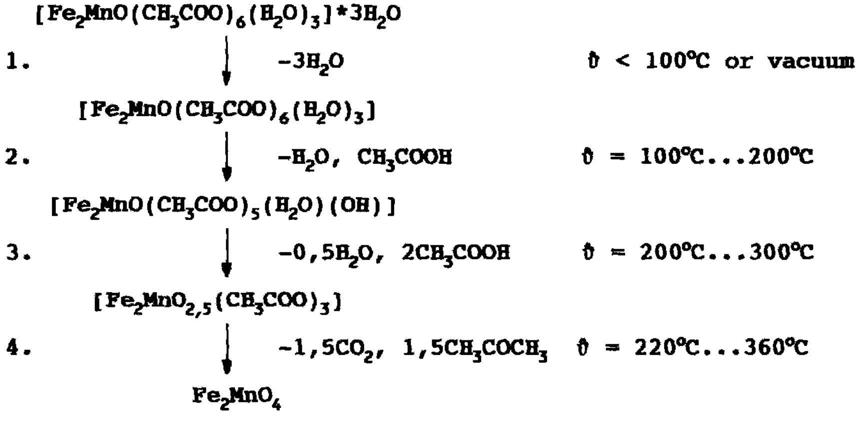

Fig. 3. Mechanism for the thermal decomposition of the product (**B**).

arises. Hence, the overall composition is characterized by the intermediate represented in brackets; this would be the result when the decomposition step (3) is accomplished in advance of the process (4).

It is clear that due to missing long-range-order and imperfect short-range-order in the freeze-dried product there is a comparatively large spectrum of activation energies for the splitting off of water and acetic acid. With the beginning of a cross-linkage of molecular species forming M–O–M bridges above 200°C intermediate decomposition states are obviously passed which are almost identical for a crystalline and freeze-dried initial product. Accordingly, under the same decomposition conditions, analogous final products are expected. Further investigations will be made to characterize the solids obtained.

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