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THE THERMAL DECOMPOSITION OF $Fe(NO_3)_3 \cdot 9H_2O$

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Abstract

Using thermogravimetric analyses as well as isothermal gravimetric measurements, the thermal stability of the iron(III) nitrate nanohydrate has been determined. Several decomposition stages are the result of melting, evaporation and hydrolysis processes occurring in the salt–water system in the temperature range of 20–400°C. Some of the intermediates and the final product (α-Fe_2O_3) are characterized by means of chemical analyses, X-ray diffraction patterns and IR spectra.

Keywords: dehydration, hydrates, hydrolysis, iron(III) nitrate, isothemal gravimetry, melting, thermal decomposition, thermogravimetry

Introduction

The thermal decomposition of inorganic crystalline salt hydrates belongs to an important class of reactions which are investigated for a variety of potential applications and also for better understanding of solid state reactions. Water in crystalline hydrates can vary between the weakly fixed water and the strongly retained structural hydroxyl groups.

There is a tendency to think of the mechanism of dehydration of salt hydrates as simple and of their thermoanalytical curves as easy to interpret in contrast, in most cases the process is a complicated system of several interacting chemical ard physical processes; it is usually more complicated than the decomposition of crystalline inorganic compounds leading to equilibrium' – as it has been written by Paulik [1].

The general objective of the study is attempting to correlate the nature of solid crystalline hydrates and their structural characteristics with their chemical pathways of dehydration and/or decomposition. Several studies of the dehydration of salts have been reported in the literature and very often divergent data for the same hydrates have been obtained. The cause of such phenomena seems to be interesting.

One of the dehydration categories is dehydration accompanied by hydrolysis. An example of this is the hydrate decomposition of iron(III), chromium and aluminium nitrates. In this case the crystallization water is often released in liquid form and the nitrate dissolves in its own water to reappear as a solid when it is already partially decomposed [2, 3].

This paper deals with investigations of thermal behaviour of $Fe(NO_3)_3 \cdot 9H_2O$.

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Experimental

Materials used in the present study were an analytical grade. Iron(III) nitrate nanohydrate (Fluka AG, Switzerland) was used without any further purification.

Thermogravimetric measurements (TG/DTG curves) were carried out using a Mettler Thermoanalyzer TA 4000 Systen. All experiments were performed up to 500°C in air at heating rates of 1.2, 3.0 and 12°C min^{-1} using an open platinum crucible.

The isothermal gravimetric experiments were based on heating of the parent salt and/or intermediates at fixed temperatures of 75, 105, 200 and 400°C during different periods (from several days to several weeks).

For the phase analyses of the products and the intermediates chemical analyses, X-ray powder diffraction (Philips Diffractometer X'Pert) and IR absorption (UR-20 Zeiss-Jena Spectrometer) using KBr pellets in the region 400–4000 cm^{-1} were used.

The amount of iron was determined gravimetrically as α-Fe_2O_3.

Results and discussion

The thermal stability and behaviour of nanohydrate of $Fe(NO_3)_3$ heated in air are described below on the basis of its thermal analysis and complementary measurements. It is obvious, that in the case of reactions leading to equilibrium, the temperature characteristics of decomposition depends, among other experimental conditions, on the heating rate used. Thus any values of initial and final decomposition temperatures are important and the chemical mechanism of the processes occurring are reported.

The TG/DTG curves for $Fe(NO_3)_3{\cdot}9H_2O$ are presented in Fig 1. They are recorded with 12.4 mg of initial mass of sample, at the heating rate of 3°C min^{-1}, chosen for illustration. One can see two distinct steps. The character of the first step indicates that the process (processes) occurs with a moderate rate in a broad temperature range, in contrast to a second one, which is rather strong and sharp (in a narrow range of temperature). The similar, two-stage decomposition is observed under quasi-isothermal – quasi-isobaric conditions [4]. The mass loss about 39% and 42% m/m, respectively, may at most to point at the presence of hygroscopic water in

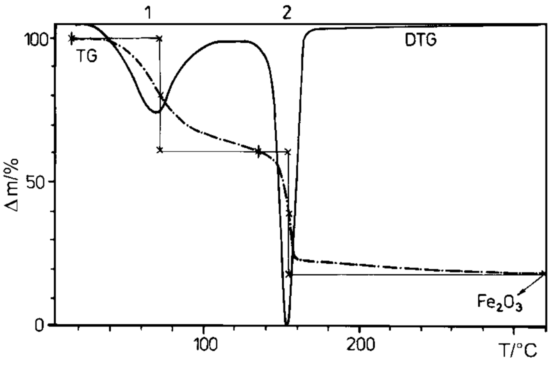

Fig. 1 The TG/DTG curves of $Fe(NO_3)_3{\cdot}9H_2O$ decomposition

the sample (5–8%), the absence of intermediate hydrates and unhydrous salt and the formation of Fe_2O_3 as a final product. Thus, the further interpretation of decomposition is impossible. Fortunately, the computerized processing of TG/DTG data, based on extending the temperature scale (which is not often in use), allow to derive benefit from registered experimental values of mass *vs.* temperature. The parts of TG/DTG curves are shown in Figs 2a and 2b. Namely, the second step, shown in Fig. l, is composed of several stages of decomposition, which could be separated (Fig. 2a). The Fe_2O_3 is a final product, as it is evidenced by TG curve. This oxide is forming very slowly as a result of thermal dehydroxylation of FeOOH. The stoichiometric hydroxide $Fe(OH)_3$ is not identified. Under conditions mentioned above, the two solids being the products of hydrolysis of iron nitrate are observed. These are hydroxo-species such as $Fe(OH)(NO_3)_2$ and $Fe(OH)_2NO_3$.

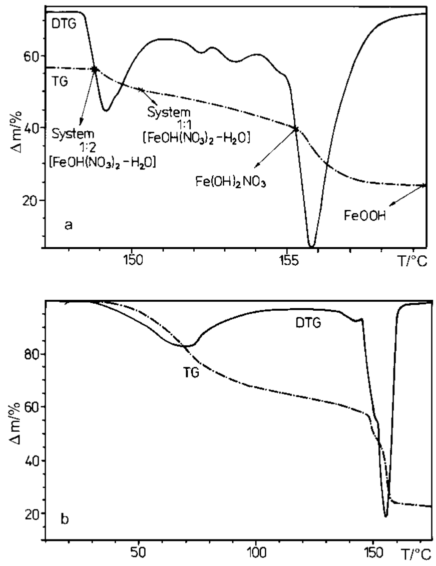

Fig. 2 The parts of the TG/DTG curves of $Fe(NO_3)_3{\cdot}9H_2O$ at different temperature range

The extended first part of TG/DTG curves, shown in Fig. 2b, reveals a decrease in mass with overlapping several steps. The beginning of the thermal decomposition involves melting of the iron(III) nitrate in its own water of crystallization followed by evaporating/boiling and simultaneous precipitation of $Fe(OH)(NO_3)_3$ as a result of the first step of hydrolysis. The existence of $FeOH(NO_3)_3$ – water system (the molar ratio of 1:2) is observed.

The results of the isothermal gravimetric experiments show that α-Fe_2O_3 is the final product of $Fe(NO_3)_3{\cdot}9H_2O$ decomposition reaction carried out at temperature from a broad range (75, 105, 200 and 400°C). Although, there is different time-period required obtaining the crystalline anhydrous iron oxide. For example, the residue of decomposition taking place at 75°C for 22 weeks, comprises about 21.2% of

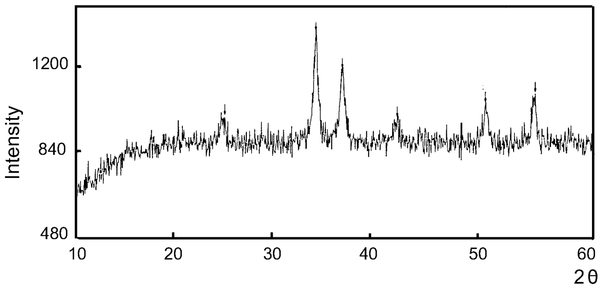

Fig. 3 The X-ray powder diffraction patterns (CuK$_\alpha$) of the final products of $Fe(NO_3)_3{\cdot}9H_2O$ decomposed at 75°C for 22 weeks. The peaks correspond to low crystalline α-Fe_2O_3 (JCPDS 33-0664)

the initial mass of nanohydrate iron nitrate. It corresponds to the mixture of α-Fe_2O_3 (theor.19.8%) with FeOOH (theor. 22.2%). Whereas, on heating at 105°C for only 4 days, the anhydrous α-Fe_2O_3 appears in the decomposition product crystallizing from the amorphous phase of hydrous iron oxide named as ‘colloidal gel’ [3, 4]. The confirmation is given by X-ray diffraction results shown in Fig. 3, where the peaks of α-Fe_2O_3 and the background with significant intensity can be seen.

Conclusions

Based on the thermal and the analytical chemical data, the thermal decomposition of the nanohydrate iron nitrate can be described as follows:

$$Fe(NO_3)_3{\cdot}9H_2O \longrightarrow \text{liquefaction} \longrightarrow \text{evaporation + hydrolysis (1st step)}$$

$$\xrightarrow{-\{HNO_3\ -H_2O(1:6)\}} \text{system } Fe(OH)(NO_3)_2{:}H_2O = 1{:}2 \longrightarrow \text{evaporation} \xrightarrow{-H_2O}$$

$$\text{system } Fe(OH)(NO_3)_2{:}H_2O = 1{:}2 \longrightarrow \text{hydrolysis (2nd step)}$$

$$\xrightarrow{-HNO_3} Fe(OH)_2NO_3 \longrightarrow \text{decomposition} \xrightarrow{-HNO_3} FeOOH \longrightarrow$$

$$\text{dehydroxylation} \xrightarrow{-H_2O} \alpha\text{-}Fe_2O_3$$

From the methodological point of view, the computerized processing of TG and DTG curves appears particularly effective when the decomposition process includes consecutive and/or overlapping reactions in a narrow temperature range.

The presented thermal techniques of measurements are useful in the study on the mechanism of thermal decomposition of salt hydrates. Thermogravimetry under nonisothermal conditions in comparison to isothermal gravimetric determinations is preferable, as enable to follow the changes continuously over a relatively large temperature range, though the disadvantage is that the intermediates are being more difficult to separate and also it is not possible to observe their formation. There are several problems, which are still not clear so far, and these will be the subject of further investigations.

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