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Thermal behavior studies of the homopolynuclear coordination compound iron(III) polyoxalate

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ABSTRACT

The thermal decomposition in dynamic oxidative atmosphere of the new homopolynuclear coordination compound $[Fe(C_2O_4)(OH)(OH_2)]_n \cdot 0.3nH_2O$ was investigated by simultaneously using TG, DTG and DTA techniques. Solid-state decomposition products formed during heating at different temperatures (350 °C, 800 °C and 1000 °C) were analyzed by physical-chemical methods, including electronic spectroscopy (diffuse reflectance technique), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis data show that the final decomposition product, namely hematite (α-Fe_2O_3), is relatively well crystallized, while SEM images reveal that the particles exhibit irregular forms, their size being widely distributed between 6 nm and 4 μm.

1. Introduction

Because of the rapid development of modern technologies, oxidic systems are nowadays required in increasing quantities. These are used in various fields, including ceramic pigments, catalysis and electrocatalysis, electronics, physical supports and carriers in devices intended for the processing of information, and in pharmaceutical industry. A wide range of methods are being used for their preparation. One of the fast evolving synthetic pathways consists in the thermal conversion of homo- and heteropolynuclear metal complexes with anions of carboxylic acids as ligands [1–14].

In some previous papers [15–29] we have investigated the oxidation of several diols, such as ethylene glycol, 1,2-propanediol and 1,3-propanediol, using different metal nitrates. All the coordination compounds obtained by this process contain anions as ligands, i.e., glyoxylate, oxalate, lactate or 3-hydroxypropionate. As they contain relatively simple organic ligands, these coordination compounds have at least one main advantage over other complexes: they undergo thermally induced degradation to simple or mixed metal oxides at relatively low temperatures, with the release of gaseous species such as carbon oxides, hydrocarbons and water. These studies proved that it is possible, via this new pathway, to synthesize some polynuclear coordination compounds with ligands consisting in carboxylate or hydroxycarboxylate anions. It was also demonstrated that, by thermal treatment of these species at considerably low temperatures, they were degraded to powders consisting of metals, alloys and/or oxidic systems, depending on both the coordination compound structure and the thermal treatment that was applied.

Literature [15,20,26] specifies that, depending on the experimental conditions, the reaction between ethylene glycol and metal nitrates occurs with the oxidation of the former to either glyoxylate or oxalate anion. Illustrating this, the synthesis and characterization of the new homopolynuclear coordination compound $[Fe(C_2O_4)(OH)(OH_2)]_n \cdot 0.3nH_2O$, obtained by an original method through the redox reaction between ethylene glycol and

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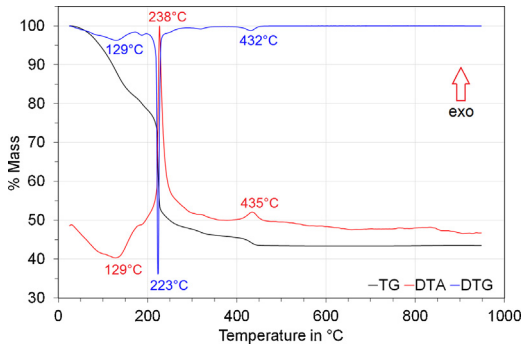

Fig. 1. Thermoanalytical curves (TG, DTG and DTA) for the aerobic decomposition of iron(III) polyoxalate.

$Fe(NO_3)_3{\cdot}9H_2O$ in acidic medium, were reported in our recent work [29].

Several authors investigated the thermal decomposition of Fe(II)- and Fe(III)-oxalate salts and conflicting results have been published [3,30–33]. Also, the properties and the applicability of α-Fe_2O_3 (hematite) in different domains were presented in various studies [34,35], while the formation of γ-Fe_2O_3 (maghemite) by thermal decomposition of a mixture of Fe(II)- and Fe(III)-oxalate salts was investigated using X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and FTIR spectroscopy [3].

The aim of this paper is to investigate the thermal decomposition of the new iron(III) polyoxalate hydrate [29], having the formula $[Fe(C_2O_4)(OH)(OH_2)]_n{\cdot}0.3nH_2O$, and to analyze its decomposition products formed during its controlled heating.

2. Experimental procedures

The synthesis of $[Fe(C_2O_4)(OH)(OH_2)]_n{\cdot}0.3nH_2O$, namely iron(III) polyoxalate hydrate, was described in a previous paper [29].

The TG, DTG and DTA thermoanalytical curves were recorded simultaneously using a Mettler TGA/SDTA 851/LF/1100 thermoanalyzer system in the 25–1000 °C temperature range, with a 10 °C min^{-1} heating rate. The measurements were conducted in aerobic dynamic atmosphere at an air flow rate of 0.05 L min^{-1}, using 150 μL alumina crucibles. The mass sample was around 20 mg.

The diffuse reflectance spectra were recorded with a PerkinElmer Lambda 950 spectrophotometer, using Spectralon® (a sintered polytetrafluoroethylene material) as reflection standard.

The Fourier transform infrared (FTIR) spectra were recorded using KBr pellets on a Jasco FT/IR-410 spectrometer, in the 400–4000 cm^{-1} range.

The powder X-ray diffraction (XRD) patterns of the decomposition products were recorded at room temperature using a Rigaku Ultima IV diffractometer with CuK_α radiation (λ = 1.5406 Å). The average crystallite size (d), lattice parameters (a, b, c), and phases proportions of the samples were calculated using the whole pattern profile fitting (WPPF) method. The instrument influence was subtracted using the diffraction pattern of a Si standard recorded in the same conditions.

The surface morphology was studied by scanning electron microscopy (SEM), using an Inspect S PANalytical model coupled with the energy dispersive X-ray analysis detector (EDAX Genesis XM 2i, FEI Company, Netherlands).

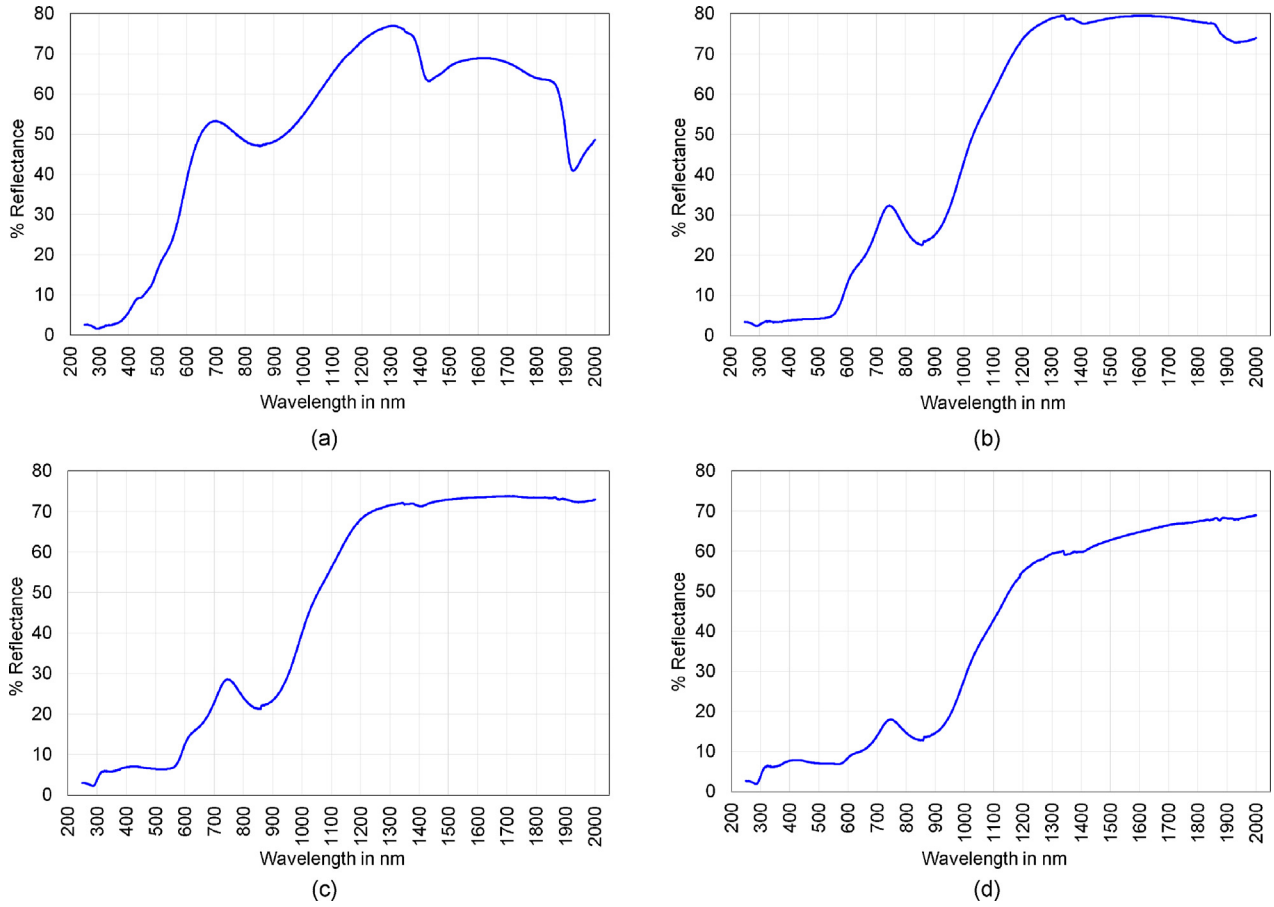

Fig. 2. Diffuse reflectance spectra for iron(III) polyoxalate (a) and its decomposition products at: 350 °C (b), 800 °C (c) and 1000 °C (d).