Journal of Magnetism and Magnetic Materials 324 (2012) 595–601

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetic properties of nanosized γ-Fe_2O_3 and α-$(Fe_{2/3}Cr_{1/3})_2O_3$, prepared by thermal decomposition of heterometallic single-molecular precursor

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ARTICLE INFO

Article history:
Received 24 June 2011
Received in revised form
18 August 2011
Available online 10 September 2011

Keywords:
Superparamagnetism
Nanoparticle
Iron oxide
Iron-chromium oxide
Thermal decomposition
Magnetic property

ABSTRACT

Thermal decomposition of the trinuclear complex $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$ at 300, 400 and 500 °C gave γ-Fe_2O_3 nanoparticles along with amorphous chromium oxide, while decomposition of the same starting compound at 600 and 700 °C led to the formation of α-$(Fe_{2/3}Cr_{1/3})_2O_3$ nanoparticles. Size of γ-Fe_2O_3 nanoparticles, determined by X-ray diffraction, was in the range from 9 to 11 nm and increased with formation temperature growth. Average size of α-$(Fe_{2/3}Cr_{1/3})_2O_3$ nanoparticles was about 40 nm and almost did not depend on the temperature of its formation. γ-Fe_2O_3 nanoparticles possessed superparamagnetic behavior with blocking temperature 180–250 K, saturation magnetization 29–35 emu/g at 5 K, 44–49 emu/g at 300 K and coercivity 400–600 Oe at 5 K. α-$(Fe_{2/3}Cr_{1/3})_2O_3$ nanoparticles were characterized by low magnetization values (2.7 emu/g at 70 kOe). Such magnetic properties can be caused by non-compensated spins and defects present on the surface of these nanoparticles. The increase of α-$(Fe_{2/3}Cr_{1/3})_2O_3$ formation temperature led to decrease of magnetization (being compared for the same fields), which may be caused by decrease of the quantity of defects or non-compensated spins (due to decrease of particles' surface).

1. Introduction

The interest in magnetic nanosized transition metal oxides and materials based thereon is due to their wide use, and further potential for data storage [1], as well as for making functional magnetic materials, such as magnetic sorbents [2] or contrasting reagents for biomedicine [3,4]. In addition, transition metal oxides are considered as promising catalysts of various reactions, particularly oxidation of organic substrates [5]. Varying the fabrication conditions of such oxides is the main method used to control their phase composition, size or surface, and thus their properties, which strongly depend on the above mentioned structural features. Various approaches were proposed for oxide nanoparticles preparation, including precipitation from solution of salts [6], thermal decomposition of inorganic or organic precursors in solid state [7–11] or in solution [12,13], ultrasonic and microwave decomposition of inorganic or organic precursors [14,15], decomposition of precursors in inert matrixes [16], etc. Each of these methods has its own advantages and disadvantages. For example, reactions in solution usually allow preparing oxide samples with narrow particle size distributions [13], but such methods seem to be quite expensive for large-scale industrial production. Thermal decomposition of solid precursors usually leads to samples with rather wide distribution of particles sizes [7,9,10], but in many cases allows to prepare large quantities of materials with low consumption of energy and resources. For this reason, investigation of thermal decomposition of metal-containing compounds and studying the influence of various factors (including composition of precursor, reaction temperature, etc.) on the properties of resulting oxide is the actual task of modern nanochemistry and material science.

Thermal decomposition of single molecular precursor was used for the preparation of homometallic nanoparticles, such as EuS nanocrystals, pyrrhotite (Fe_7S_8) and greigite (Fe_3S_4) nanosheets starting from [Eu(Phen)(Ddtc)$_3$], Fe(Ddtc)$_2$(Phen) and Fe(Ddtc)$_3$ (Phen = 1,10-phenanthroline, Ddtc = diethyldithiocarbamate) [17,18]. However, the main advantage of the approach "from molecule to nanocrystal" is that it may allow achieving almost ideal distribution of different metals in the volume of heterometallic oxides [9,19]. For example, pure stoichiometric ferrites MFe_2O_4 (M = Mg, Co and Ni) with spinel structure and average crystallite size of about 40 nm were obtained by thermal decomposition of the single molecular precursor $[M_{1-X-Y}Fe^{2+}_Y Fe^{3+}_X(OH)_2]^{X+}(SO_4^{2-})_{X/2}\cdot mH_2O$ with $M^{2+}/(Fe^{2+}+Fe^{3+})$ molar ratio equal to 2 and samples were characterized by

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doi:10.1016/j.jmmm.2011.08.049

uniformly distributed cations on an atomic level [19]. Decomposition of trinuclear acetates $[Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$ (M=Mn, Co, Ni) at 320–700 °C was found to lead to nanosized spinel particles MFe_2O_4, which have superparamagnetic behavior [9,11]. It was shown that the average size of the nanoparticles formed in such a way increased with the decomposition temperature. This method is indeed cost-efficient and provides quick way to preparation of heterometallic oxide materials.

Generally, it is supposed that decomposition of polynuclear heterometallic complexes should result in formation of one (monophase) mixed-metal oxide, if the metal ratio in the starting compound corresponds to the metal ratio present in the resulting phase; in other cases formation of several phases is expected [20].

In order to extend the range of oxides (and, hence, the range of available magnetic materials with different properties), which may be prepared by thermal decomposition of coordination compounds, we studied decomposition products of trinuclear iron(III)-chromium(III) acetate $[Fe_2^{III}Cr^{III}O(CH_3COO)_6(H_2O)_3]NO_3$. Unexpectedly, instead of formation of the same oxides in the whole range of studied decomposition temperatures (300–700 °C), and instead of monotonous increase of average particles size and monotonous change in their magnetic properties with the growth of decomposition temperature, abrupt change of phase composition of oxides was found when decomposition temperature increased from 500 to 600 °C. This change was associated with abrupt increase of average particles size, and magnetic behavior of the oxide nanoparticles prepared at low temperatures (300–500 °C) and above 600 °C was radically different.

2. Material and methods

Commercially available reagents were received from Merck and were used without further purification. Trinuclear complex $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$ was synthesized according to a known procedure [21]. Purity and identity of the starting compound was confirmed by analytical data (calculated for $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$, %; C 22.15, H 3.69, N 2.15; found: C 22.23, H 3.77, N 1.97. CHN analysis was performed using a Carlo Erba 1106 analyzer). Powder X-ray diffraction (XRD) patterns were identical to those expected for $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$ [21]. Thermal decomposition of the complex was performed in ceramic crucibles on air at 300, 400, 500, 600 and 700 °C during 5 h at the desired temperature (which was achieved within 20–30 minutes from the beginning of the synthesis), which gave samples **1–5**, respectively. Thermogravimetric analysis was carried out on a Derivatograph Q-1500 D (manufactured by MOM) by heating 90 mg of sample from 20 to 720 °C at 5 °C/min heating rate and aerobic conditions. XRD was measured using DRON-3 X-ray diffractometer with Cu-Kα radiation with 2θ step 0.04°. Samples were characterized by transmission electron microscopy (TEM) using SELMI TEM-125K microscope with a tungsten filament and accelerating voltage 100 kV. For TEM measurements samples were suspended in ethanol and deposited on Cu grid covered with carbon. Statistical treatment of the results of particle size determination was performed as described [22]. Magnetic measurements were performed on solid samples restrained in eicosane (to avoid orientation in magnetic fields) using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 70 kOe magnet. Zero-field cooled and field-cooled magnetization data were collected over the temperature range 5–300 K, with a magnetic field of 100 Oe. Isothermal magnetization studies were performed at 5 and 298 K, under magnetic fields varying from 0 to 70 kOe. Experimental data were corrected for the diamagnetic contributions of the sample holder and eicosane by measurement.

3. Results and discussion

3.1. Synthesis of nanoparticles and their XRD characterization

Thermal decomposition of $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$ in air can undergo the following schemes:

$$[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3 \rightarrow \gamma\text{-}Fe_2O_3 + H_2O + CO_2 + \text{other products} \quad (1)$$

$$[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3 \rightarrow \alpha\text{-}(Fe_{2/3}Cr_{1/3})_2O_3 + H_2O + CO_2 + \text{other products} \quad (2)$$

where 'other products' may include acetic anhydride, ketene and other organic compounds, which are potentially formed by pyrolysis of acetates. In scheme (1) 'other products' can also include amorphous chromium oxide, which was not observed in XRD patterns. Nitrogen from the nitrate anion of the complex is released as N_2 gas or nitrogen oxides. According to the reaction balance, air oxygen is not required for the formation of Fe(III) and Cr(III) oxides by decomposition of the starting compound.

Thermal decomposition of $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$ was studied by TG analysis in the temperature range 20–720 °C (complete decomposition) (Fig. 1). Upon warming, the compound gradually looses weight at 160 °C (5.6%), which may correspond to the loss of two H_2O molecules (theoretical weight loss is 5.5%). Further heating leads to abrupt weight loss, which may be associated with the loss of the third H_2O molecule and with the decomposition of the compound. Though several inflection points may be distinguished along the TG curve (at 180, 250 and 310 °C), it is difficult to assign them to certain decomposition steps. Finally, weight loss reaches 63.3% at 400 °C, and no further changes were observed above this temperature. These results support the formation of a mixture of Fe(III) and Cr(III) oxides (such as Fe_2O_3 and Cr_2O_3, theoretical weight loss is 63.6%). Decomposition between 120 and 190 °C was accompanied by a small endothermal effect which may be assigned to release of coordinated water molecules and potential destruction of the polynuclear core with the loss of acetate. No thermal effect was observed at the decomposition of the compound between 190 and 270 °C. The last decomposition stage (between 270 and 400 °C) was accompanied by high exothermal effect, which may

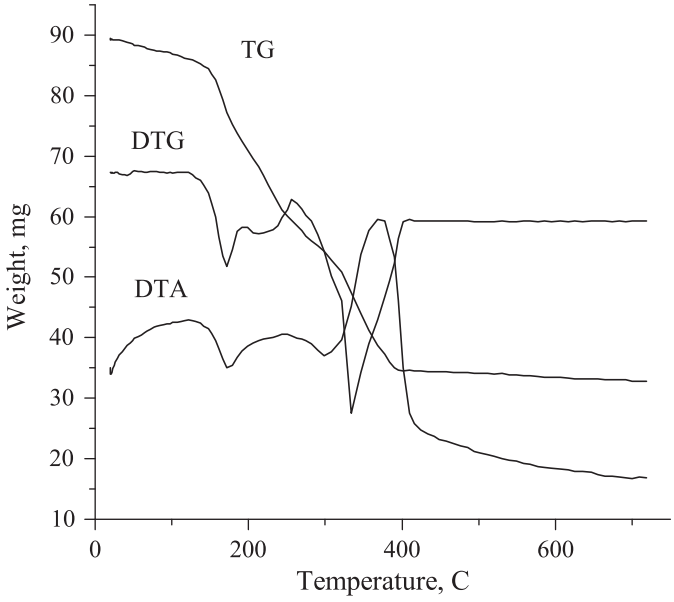

Fig. 1. TG–DTA curves of complex $[Fe_2CrO(CH_3COO)_6(H_2O)_3]NO_3$.