International Journal of PharmTech Research
CODEN (USA): IJPRIF, ISSN: 0974-4304
Vol.8, No.3, pp 394-397, 2015

High Temperature Structural Transformation Studies in Magnetite Nanoparticles

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Abstract: In this paper magnetite nanoparticles were prepared by co-precipitation method. Ferrite nanoparticles are characterized by thermogravimetric and differential thermal analysis (TG–DTA). The crystalline structure of magnetite nanoparticles were studied by means of X-ray diffraction (XRD). The samples show cubic inverse spinel structure with size ranging from 9 to 26 nm. The effect of the high-temperature heat treatment on carrier transfer in spinel structure of magnetite and nonmagnetic modification has been investigated.
Key words: nanoparticles, magnetite, co-precipitation method.

1. Introduction

One of the most promising of nanomaterial is the ferrite nanoparticles of different compositions. Ferrite nanoparticles offer exciting opportunities in fundamental study and technological applications, such as biomedical applications, bio processing and catalysts, among many others [1-5]. Magnetite (Fe_3O_4) nanoparticles have attracted much interest in the areas of medical care such as drug delivery systems, magnetic resonance imaging, hyperthermia treatment of cancer, biomedical optical imaging, biosensors [5, 6]. Different synthetic methods such as mechanosynthesis, hydrothermal synthesis, co-precipitation, combustion synthesis, sol-gel methods, microwave processing, and thermal decomposition, have been used to produce ferrite nanoparticles [7-10]. Among these methods, co-precipitation in the water solution is the route for preparing ferrite nanocrystals with uniform size, a high degree of crystallinity, and a clearly defined phase structure [10].

Due to the presents of iron (II) cation in the structure of magnetite, it can be oxidized to iron (III) oxide. It is therefore important to study the energy balance of the processes that take place in magnetite particles at different temperatures and determine the final properties of the substance. Thermographic and X-ray analyses confirmed the structure of the synthesized samples of magnetite and their temperature conversion.

2. Experimental

2.1. Synthesis of magnetite nanoparticles

Ultrafine particles of $FeFe_2O_4$ were prepared by co-precipitating aqueous solutions of iron (II) salt ($FeSO_4 \cdot 7H_2O$) and iron (III) salt ($FeCl_3 \cdot 6H_2O$) in an alkaline medium (25% $NH_3 \cdot H_2O$) according to the net ionic equation:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- = Fe_3O_4 + 4H_2O$$

All precursors were purchased from Beijing Chemical Company (Beijing, China). All chemicals with 99.9% of purity which is used as received without further purification.

The reaction mixtures were maintained at 85 - 90°C for 4 hrs. This time was sufficient for the transformation of hydroxides into spinel ferrite. Magnetic particles were collected using magnetic separation. These particles were washed several times with distilled water and dried at room temperature, producing thus samples MNPs20. Samples MNPs20 were heated at 700°C for 2 h, resulting sample MNPs700.

2.2. Characterization

Simultaneous thermogravimetric and differential thermal analysis (TG–DTA) traces were obtained from Q-1500D instruments (MOM, Hungary) at a heating rate of 10°C/min. The X-ray diffraction (XRD) patterns of the samples were recorded on a Siemens D500 X-ray powder diffractometer using copper radiation. Slow scans of the selected diffraction peaks were carried out in the step mode (step size 0.03°, measurement time 75 s. The crystallite size of the nanocrystalline samples was measured from the X-ray line broadening using the Debye-Scherrer formula after accounting for instrumental broadening.

3. Results and discussion

3.2 TG–DTA analysis

The thermal behavior of magnetite nanoparticles was studied by thermal analysis. Figure 1 shows TG, DTG, and DTA curves recorded for MNPs20 sample at a constant heating rate of 10°C min^{-1} in the temperature range of 20°C to 800°C.

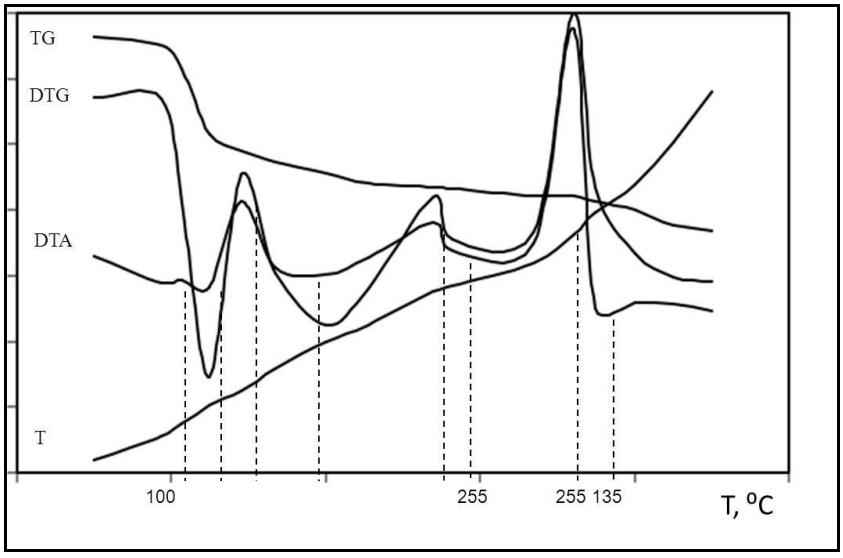

Fig.1 TG, DTG, and DTA curves of MNPs20 sample

It can be seen that at the temperatures 100°C and 135°C endothermic effects (according to temperature curves T and DTA) can be observed, which is accompanied by significant weight loss (curves TG and DTG), about 5 mass. % (86 mg). This is due to loss of moisture that was physically sorbed in the sample (100°C), and then (135°C) the loss of structural - bound (crystallization and chemically - bound) water. The next two endothermic effects (curves T and DTA) were observed at the temperatures 255°C and 458°C. They almost don't lose weight, ~ 0.6 mass.% (8.9 mg). These effects may be associate with changes in physical properties of substance used in the experimental sample (electro conductivity, thermal conductivity) or with insignificant changes of the crystal lattice of the substance, that are caused by the diffusion of oxygen atoms or ions Fe^{2+}, O^{2-}. Exothermic effect (curves T and DTA on fig. 1), which was observed at 625°C also does not accompanied by loss of weight (curves TG and DTG), weight decreases on 6.5 mg (~ 0.4 mass.%). This fact may be associated with phase double transformation of Fe(II) and Fe(III) oxide (Fe_3O_4) on metastable Fe(III) oxide Fe_2O_3 with cubic structure, which detects ferromagnetic properties. With further heating this γ-modification of Fe_2O_3, probably, transforms into diamagnetic rhombohedral modification (hematite) [11]. Temperature of transformation is 695°C (last peak on the curve DTA). Insignificant weight loss (~ 6 mass. %) during all

temperature ranges can be associated with the diffusion of ions Fe^{2+} with Fe_3O_4 and oxygen atoms in crystal lattice Fe_2O_3.

3.2 XRD analysis

The crystallinity of the magnetite sample was investigated by XRD as shown in Fig. 2.

The pattern of the sample of magnetite before heat treatment was indexed to a single phase of magnetite spinel structure with lattice parameters of 0.83716(4) nm. The lattice parameter and interplanar spacing for the prepared sample is lower than the values reported for bulk magnetite JCPDS Card No. (79-0417) (a = 8.394 and d_{311}= 2.531), but these values are closed to the values in some references as in [12-14].

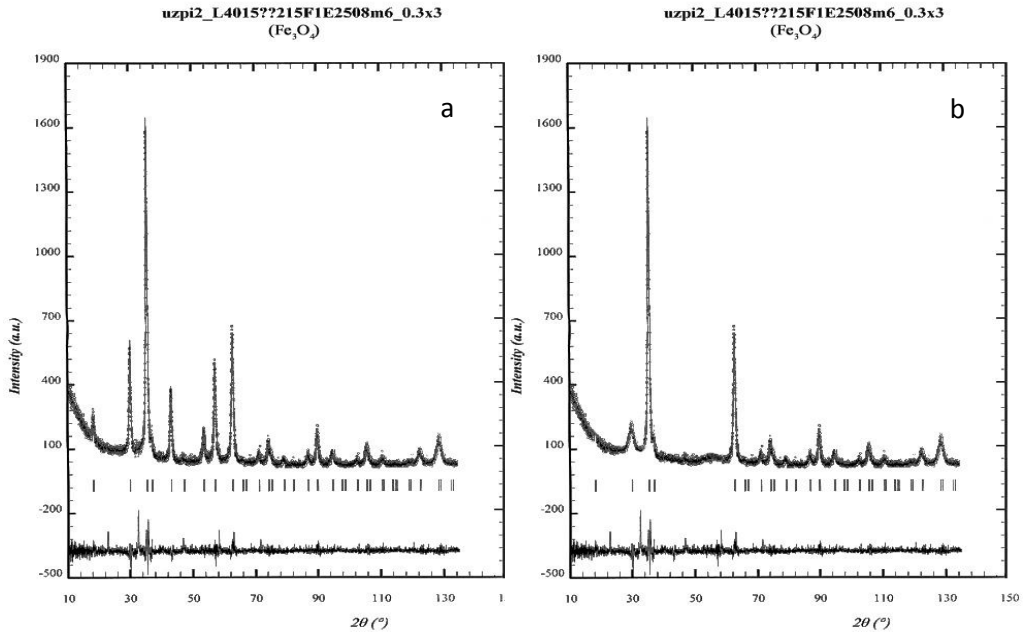

Fig. 2 The XRD diffraction patterns of magnetite samples before heat treatment (a) and after high-temperature (700ºC) heat treatment under normal atmospheric conditions during 2 h (b).

Average grain sizes were estimated from the broadening of the strongest diffraction (at $2\theta \approx 36°$) using the Scherrer method, after subtracting instrumental broadening from the experimental line width. The sample show very broad peaks, indicating the ultra-fine nature and small crystallite size of the particles. MNPs20 sample can be certified as highly dispersed spinel system with an average size of particles ~ 16 nm.

On XRD diffraction pattern the broadening of lines can indicate a slight strain of the crystal structure of particles was observed. It may affect increased ability of the sample to form colloidal solutions. Effect may be associated with a small deficit of cations in tetrahedral and octahedral positions, which can be approximately estimated as 5%, but in general, based on the problem of synthesis of magnetic colloids, are very important and valuable.

The pattern of the MNPs700 sample lines of only one phase (hematite) was observed. This substance is the α – modification of iron (III) oxide, which doesn't have magnetic properties. Determined mass fraction of phase Fe_2O_3 is 96 ± 2%.

4. Conclusion

Magnetite nanoparticles have been synthesized using co-precipitation method. The formation of spinel structure of nanoparticles was confirmed by X-ray diffraction (XRD). At the temperature of 695°C a transition structure of the as-synthesized particles of magnetite into its nonmagnetic modification was determined. The

fixed effect should be used to determine the temperature working range of the synthesized nanoparticles of magnetite in its further usage in medications. It is important to determine the upper limit of this range highly enough. As a result of studies with using thermography methods and X-ray phase analysis structure of the synthesized magnetite nanoparticles and their transformation temperature were investigated. It is proved that the chosen method of synthesis allow to obtain particles of magnetite colloidal size without impurities, with the correct parameters of the crystal lattice.

5. References

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