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Thermal studies of magnetic spinel iron oxide in solution

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Small particles of iron – based magnetic spinel oxide are technologically interesting because of their magnetic properties. The synthesis from solution, generally achieved by coprecipitation, offers some advantages: simple and rapid preparation, control of particle size and composition, various possibilities to modify the particle surface state allowing to make homogeneous and stable dispersion in liquid or solid media. This work reports the thermal studies of magnetic iron spinel oxide nanoparticles. For this study, the Fe^{2+}-Fe^{3+} mixture (Fe^{2+}/Fe^{3+}=0.5) was introduced in an alkaline solutions of which the pH was kept constant. The influence of the particles sizes on the γ→ α□□Fe_2O_3 transformation is analyzed.

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1. Introduction

Iron oxide nanoparticles are currently the subject of intense research work due to their properties which could have promising applications in technology [1-2]. Magnetic nanoparticles with the size of 2-10 nm are particularly important because they are potentially useful in terabit magnetic storage [3] magneto-optical devices [4], catalysis [5], ferrofluids [6], as carries for biochemical complexes, as MRI contrast enhancing agents and therapeutic agents in cancer treatment [7-14].Applications in biology and medical diagnosis and therapy require the magnetic particles to be stable in water at neutral pH and physiological salinity. The colloidal stability of this fluid will depend first on the charge and surface chemistry witch give rise to both, steric and coulombic repulsions and first on the dimensions of the particles, which should be sufficiently small so that precipitation due to gravitation forces can be avoided [15].

Thus, developing new synthesis routes for magnetic nanoparticles and the investigation of their properties are of great importance [16-18]. Nanostructured materials are now being studied intensively, as their physical properties are quit different from those of the bulk [19-21].

Nanoparticles of spinell iron oxide are characterized by the superparamagnetic relaxation phenomenon, with is strongly dependent on the particle size and shape on the magnetic interactions between particles and on various surface effects [22-25]. The problem is that the traditional methods of synthesis from material science are not able to produce uniform and reproductible particles in the nanometer size range.

This work describes the synthesis and physical characterization using X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermal analysis (TG/DTA) of the spherical magnetic spinel iron oxide nanoparticles.

2. Experimetal

Preparation of samples

Cationic γ-Fe_2O_3 aqueous sols were prepared according to the Massart's method [26-28]. The Fe_3O_4 precipitate was prepared by slowly adding an aqueous mixture of $FeCl_3$ (Fe^{2+}/Fe^{3+}=1/2) to a base with vigorous stirring. By varying the conditions in the precipitation (NH_3 for samples D1 and NaOH for sample D2) the mean particle size was varied. The precipitate of magnetite of magnetite was converted into γ- Fe_2O_3 particles by repeated treatment with HNO_3 (2M) and $FeNO_3$ (0.3 M) solutions in according to [29]. The acidic precipitate was isolated by decantation on a magnet, separated by centrifugation (6000 rpm), washed in acetone and dispersed in pure water at pH≈2.5.

Characterization of samples

Crystalographic analysis of the powder samples was performed using X-ray diffraction (XRD). Diffraction patterns of intensity vs. 2θ were recorded with a Philkips PW 1050 diffractometer. A continuous scan mode was used to collect 2θ data from 10 to 70^0.

The transmission electron microscopy (TEM) experiments was carried out using a JEOL 200 CX equipment. The sample was prepared from the particles suspension in deionized water. A drop of well-dispersed supernatant was placed on a carbon – coated 200 mesh copper grid, followed by drying the sample at ambient conditions before it is attached to the sample holder on the microscope.

Thermogravimetric analysis (TG, DTG) and differential thermal analysis (DTA) of these samples were carried out on a Perkin Elmer Diamond thermal analyzer in the presence of static air in the range from 25 °C to 800 °C.

3. Results and discussions

The diffraction patern (Fig. 1) shows the peaks that coresponds to an fcc cubic maghemite structure. The average sizes <D> of the nanoparticles were computed using Scherrer's formula [30]:

$$D = \frac{K\lambda}{B\cos\theta}$$

The equation uses the reference peak width at angleθ, were λ is the X-ray wavelength (1.5416 Å), B is the width of the XRD peak at half height and K is a shape factor, which is about 0.9 for spheric nanoparticles.

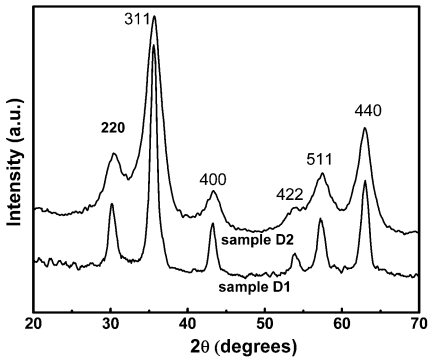

Fig. 2. X-Ray diffraction pattern of samples D1(<D>=9.2 nm) and D2 (<D>=7.2 nm).

Fig. 2 shows a TEM image that was used to determine particle size distribution and morphology for samples D1 and D2. Spherical particles with a diameter around 10±1 nm (sample D1) and 8±1nm (sample D2) were found. Particle size distribution were determined by measuring the mean diameter, D, of ca. 500 particles on the micrographs.

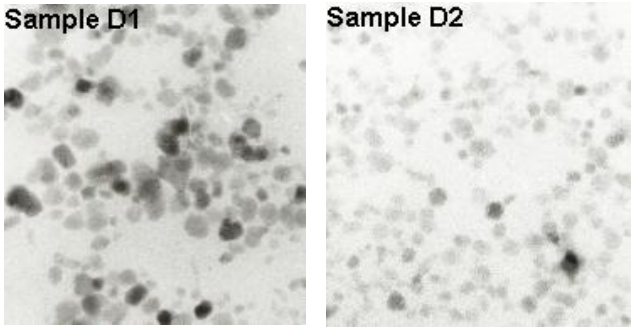

Fig. 2. TEM images of the samples D1 and D2.

Thermal analyses of samples D1 and D2 carried out using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) are shown in Fig. 3.

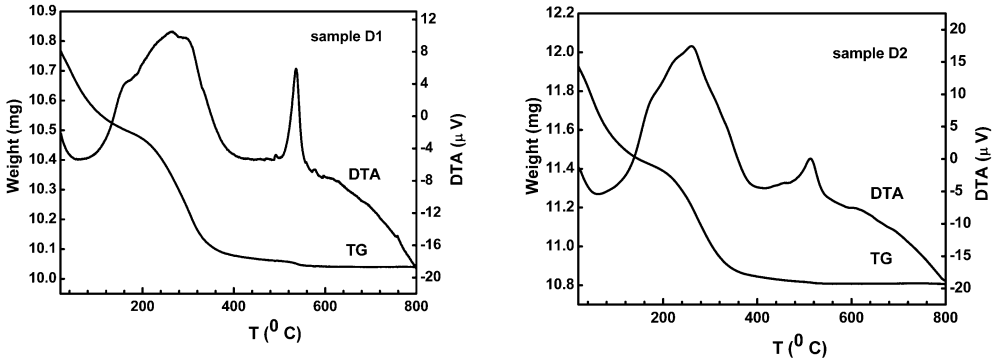

Fig. 3. TG and DTA evolution curves of the D1 and D2 samples.

A loss mass up to the transformation into α –Fe_2O_3 represents 6.22% for sample D1 and 9.36% for sample D2. The total mass loss represents only the water layer around each particle. The first mass loss (2.97% for sample D1 and 4.54% for sample D2) corresponds to the elimination of water physisorbed to the particles. The second mass loss (3.25% for sample D1 and 4.82% for sample D2) corresponds to water chemisorbed to the particles. DTA curve analysis showed that water was removed below 300^0C. The conversion of γ-Fe_2O_3 particles flocculated a pH≈8 into α –Fe_2O_3 take place around 540 ^{o}C (DTA exothermic peak) for sample D1 and around 515^0C (DTA exothermic peak) for sample D2.

4. Conclusions

Uniform spheric maghemite particles were prepared by the coprecipitation of Fe^{2+}-Fe^{3+} mixture (Fe^{2+}/Fe^{3+}=0.5). The present studies provide evidences for the influence of the pH and ionic strength in the phase stability and the size of γ-Fe_2O_3 particles. The temperature transformation of γ-Fe_2O_3 into α –Fe_2O_3 is dependent on the preparation conditions.

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