Journal of Magnetism and Magnetic Materials 405 (2016) 66–71

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Phase composition, magnetic properties and thermal behavior of a novel Fe_2O_3–SiO_2 composite material

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ARTICLE INFO

Article history:
Received 10 August 2015
Received in revised form
19 November 2015
Accepted 27 November 2015
Available online 18 December 2015

Keywords:
Composite materials
Nanoparticles
Magnetic properties
Iron oxides
Transition temperature

ABSTRACT

An Fe_2O_3–SiO_2 composite was prepared by controllable Fe^{3+} and SiO_3^{2-}hydrolysis. Scanning (SEM) and transmitting (TEM) electron microscopy images showed particles with an average size of 10–30 nm composed of an iron-containing core covered with a silica shell. The FT-IR, vibrating sample magnitometer (VSM), thermogravimetric analysis and Mössbauer spectroscopy study confirmed that the core consisted of ferrihydrite. Heating at 300 °C did not result in any noticeable phase transitions, whereas 800 °C heating caused the formation of the maghemite γ-Fe_2O_3 phase. Such improvement of the thermal stability of maghemite is promising for development of heat-resistant magnetic materials.

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1. Introduction

Silica-based porous structured materials are of great interest for practical application as catalyst supports, sensing materials, adsorbents, and carriers for targeted drug delivery. The advantages are their ordered structure, highly specific surface, adjustable porosity and narrow pore size distribution.

Silica is widely used as a support material as its morphology and particle size can be easily controlled in comparison with other materials, and it has high thermal stability and mechanical strength. However, the separation of silica from a dispersion medium is inconvenient, which significantly narrows its application.

The combination of porous silica and magnetic nanoparticles is one way to produce new magnetic composite materials. Particles of this kind can be displaced by applying an external magnetic field, e.g. for the magnetic separation of a sorbent from a solution or for the targeted delivery of adsorbed drugs. Depending on the area of application of such materials, there are different requirements for their composition, morphology, adsorption and magnetic properties [1–5].

For optimal steerability of a composite material by an external magnetic field, its magnetization saturation (M_s) and magnetic susceptibility (χ) in weak fields have to be maximal. In contrast, remanence (M_r) and coercitivity (H_c) should be minimal to simplify dispergation and avoid the aggregation of particles. Low remanence assists in the aggregative stability of particles; from this perspective, magnetite Fe_3O_4 and maghemite γ-Fe_2O_3 have optimal magnetic properties among iron oxides. Besides, it is necessary to take into consideration that heat treatment of a magnetic material, for example, for regeneration of a sorbent, may change its magnetic properties, including irreversible phase transition.

Successful application of magnetic nanoparticles is highly dependent on the stability of the particles under a different external media. A nanoparticles are often chemically highly active due to high surface area, resulting generally in loss of magnetism. To chemically stabilize the magnetic nanoparticles they can be covered by protective silica layer. This kind of core–shell materials is attracting increasing attention [2,6,7].

Current methods for producing magnetic silica materials generally consist of the two-stage synthesis of a composition material from silicon dioxide and iron oxides. Such techniques imply the usage of organosilicon precursors, which is acceptable for laboratory synthesis, but significantly narrows their large-scale application in industry [8]. In this paper, we propose a new approach to a

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http://dx.doi.org/10.1016/j.jmmm.2015.11.087
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simple, cost efficient and environmentally safe synthesis of magnetic silica composite materials. The influence of synthesis conditions on structure, phase composition, and magnetic properties of the material have been investigated.

2. Experimental

2.1. Materials

Deionized water was used throughout this work. Iron chloride $FeCl_3 \cdot 6H_2O$ was chemical grade; all other chemicals, such as silica $SiO_2 \cdot nH_2O$, hydrochloric acid, sodium chloride, sodium hydroxide, ammonia (25% water solution) and acetone were of analytical grade and used as received.

2.2. Synthesis of magnetic composite materials

The composite materials Fe_2O_3–SiO_2 were prepared by two procedures. The first (I) consisted of the simultaneous hydrolysis of Fe^{3+} and SIO_3^{2-} ions followed by the formation of a co-precipitated non-structured composite material. For this purpose, $SiO_2 \cdot nH_2O$ was dissolved in 5 M NaOH, then the solution, under vigorous stirring, was slowly added to $FeCl_3 \cdot 6H_2O$ dissolved in 5% HCl at room temperature. Adding a relevant volume of HCl maintained the acidity at a predetermined constant level. The precipitate was centrifuged, washed with water and acetone and then air dried for 1 h at 105 °C (sp. I-1 – I-11 in Table 1).

The second procedure of composite synthesis (II) consisted of the deposition of silica layer on the colloid-size particles of iron hydroxide, forming a core–shell structure. Due to the addition of an excess of 25% ammonia solution to $FeCl_3 \cdot 6H_2O$ aqueous solution, a residue formed; this was filtered and washed with water. Hydrochloric acid was dropwise added into the water suspension of the fresh residue at 90 °C up to its full peptization. Then, the solution of SiO_2 in 5 M HCl was very slowly added at a temperature of 90 °C. The required amount of HCl was been added to maintain a constant pH = 9. After adding a predetermined amount of silica-containing solution, the acidity was adjusted to pH = 5 by HCl, and NaCl was added to an Na^+ concentration of 0.35 M. The reaction mixture was maintained at 90 °C for 1 h. The residue was filtered, rinsed with water and dried in air at 105 °C (sample II-105). Then, the material samples were annealed in a muffle furnace for 3 h at 300 and 800 °C (samples II-300 and II-800 correspondingly).

Table 1
Compositions of Fe_2O_3–SiO_2 composite materials depending on the synthesis conditions.

Synthesis procedures	Sample	Initial molar ratio Si: Fe	pH	Content, %	
				Fe_2O_3	H_2O
procedure I (drying at 105 °C)	I-1	1:0.1	1.3	13.9	22.8
	I-2	1:0.1	1.5	14.3	22.0
	I-3	1:0.1	1.6	18.6	21.8
	I-4	1:0.1	1.7	23.9	24.0
	I-5	1:0.1	1.8	29.8	20.2
	I-6	1:0.1	1.9	34.4	25.4
	I-7	1:0.1	2.2	34.2	24.6
	I-8	1:0.1	2.6	34.1	22.0
	I-9	1:0.25	2.6	36.3	18.0
	I-10	1:0.5	2.6	45.4	26.4
	I-11	1:1	2.6	63.9	11.8
procedure II	II-105	1:0.3	9.0	25.7	11.6
	II-300	1:0.3	9.0	26.8	9.0
	II-800	1:0.3	9.0	29.3	2.7

2.3. Characterization

The content of iron in the samples was determined by titration with Trilon B. Water content was determined gravimetrically after calcination at 1000 °C for 3 h. IR spectra were recorded on a Shimadzu FTIR Prestige-21 spectrophotometer at frequency range 4000–400 cm^{-1} and samples were measured in Vaseline mull. XRD measurements were performed on a Bruker D8 ADVANCE diffractometer, using Cu K_α radiation. The thermal analysis was done using a MOM Q-1000 derivatograph, heating rate of 5 K/min, the samples masses were 250 mg and 110 mg (samples I-3 and II-105 correspondingly), alumina calcinated up to 1000 °C was used as a reference. The particle size and morphology of the materials were observed by LEO EVO-50 XPV scanning electron microscope and Zeiss Libra 120 transmission electron microscope, respectively. The magnetic measurement was examined by Quantum Design PPMS 9 T ECII vibrating sample magnitometer (VSM) at temperatures of $2-300$ K and fields up to ± 5 T. Magnetic susceptibility χ was calculated in a weak field. The Mössbauer study was carried out by MOS-TEC MS1101E instrument, at room temperature. The γ-ray source is the isotope Co^{57}. The Mössbauer spectra are calibrated by means of a spectrum for a standard α-Fe sample.

3. Results and discussion

The co-precipitated (procedure I) composite materials are fine reddish-brown powders. Chemical analysis shows (Table 1) that iron content, calculated as Fe_2O_3, increased from 13.9% to 34.4% with an increase in pH from 1.3 to 1.9 (at initial molar ratio Si: Fe = 1:0.1). Further pH increase did not lead to growth of the iron content. Composite materials with an iron content up to 63.9% were obtained by varying the ratio of the initial reagents.

Procedure II was based on fact that SIO_4^{2-} anion hydrolysis in acidic media leads to gel formation, and also in basic media, to form polysilicic acid, directly from SiO_2 sole, so-called “active silica”. The deposition of silica in basic media is some slower, but allows a desired morphology to be obtained, e.g. silica coatings on particles of another substance [9]. The iron content in the as-synthesized composite material was 25.7% (sample II-105).

In co-precipitated composite material (sample I-4) according to SEM data particles size is about 100–150 nm. Isometric particles without any faceting forms aggregates that are 3 to 5 μm in size. Fig. 1 shows the SEM and TEM images of the composite material, obtained as per procedure II (sample II-105), which are composed of isometric particles with a size of ca. 10–30 nm, without faceting. From the TEM image (Fig. 1b), it can be seen that particles consist of a dark core (iron oxide), covered with a lighter shell (silica).

All of the synthesized composite materials are amorphous; the diffractograms (Fig. 2) exhibit two broad peaks at about $2\theta = 35°$ and 63°, typical of poorly crystalline iron oxides (ferrihydrite, maghemite and hematite) with crystals smaller than 3 nm [10,11]. In the case of iron content lower than 36.3% (samples I-1 – I-9) an additional peak appears at $2\theta \approx 24°$, which is typical for amorphous SiO_2 [5]. For the nanosized particles, XRD-based identification of a particular iron oxide is difficult because of significant peak broadening due to the size effect.

It is well known that the hydrolysis of acidic solutions of iron salts can result in various iron oxides and oxohydroxides, depending on the initial compounds and reaction conditions. The fast hydrolysis of Fe^{3+} solutions typically produces an amorphous non-stoichiometric hydrated oxohydroxide $Fe_2O_3 \cdot nH_2O$, which is also known as ferrihydrite. Its crystallinity, i.e. crystal size and ordering, is mostly lower than in any other iron oxide compounds. For poorly crystalline ferrihydrite, the presence of two broad peaks

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