PREPARATION AND CHARACTERIZATION OF MAGNETITE–BASED SILICA NANOCOMPOSITE

Mihaela Popovici, Cecilia Savii, Daniel Nižnanský, Jan Šubrt, Eva Vecernikova, Corina Enache and Claudia Ionescu

Sol-gel method and successive thermal treatments in vacuum and nitrogen atmosphere were employed to synthesize magnetite nanoparticles isolate them with the aid of amorphous silica. Thermogravimetric and differential thermal analyses coupled with mass spectrometry, X-ray diffraction, transmission electron microscopy, Mössbauer spectroscopy and vibrating sample magnetometry measurements were performed on the obtained nanocomposites. The effect of atmosphere on the formation of magnetite phase was remarkable.

KEYWORDS: Sol-gel; nanocomposite; magnetite; Mössbauer spectroscopy

INTRODUCTION

In the last decade, the iron oxide-silica nanocomposite system has been the subject of intense researches due to the potential applications in magnetic-tape media (1), color imaging (2), magnetic memories for computer, magneto-optical devices (3), magnetic refrigerators (4), bioprocessing (5), catalysis (6–8) and ferrofluids (9). A critical obstacle in obtaining and maintaining of a material in the nanometer scale is the tendency of the particles to aggregate. By using silica as non-magnetic amorphous matrix, it is possible to isolate magnetic nanoparticles (10-12). The influence of Si⁴⁺ on the crystallization of Fe oxides or oxide-hydroxides, i.e., its influence on the phases, subjected to heating and/or aging, was reported in several papers (13-15). The presence of Si⁴⁺ in solution plays an important role in this process by affecting the nature, the shape, and the size of the Fe precipitates even at low levels of silica content (16). However, a study of this system in
large a range of iron concentrations has not been done up to now. Usually, the system was studied in the case of iron oxide content less than 50 wt%. In this paper, results concerning the preparation and characterization of iron oxide/silica nanocomposites with iron oxide content higher than 50 wt% were presented. As a reference, a sample consisting only of iron oxide was prepared under the same conditions. The Fe$^{3+}$/organics ratio, which is supposed to be responsible for the reduction of Fe$^{3+}$ to Fe$^{2+}$ (17) and therefore for the formation of spinel iron oxide phases, was kept constant.

The main objective of this work was to prepare magnetite nanoparticles isolated by means of amorphous silica by sol-gel processing and thermal treatment in vacuum and then in nitrogen atmosphere.

**EXPERIMENTAL**

The gel samples were synthesized by sol-gel method from a sol containing iron nitrate (Riedel-de Haen, 96%) and tetraethoxysilane, TEOS (Fluka, 98%) as precursors, in the presence of a mixture of alcohol, (ethanol EtOH and isopropanol, iPrOH) and water. The mole ratio chosen for the preparation of the gels was as follows: H$_2$O/TEOS/EtOH/iPrOH =6:1:6:2 for the range of iron oxide compositions presented in Table 1. The iron nitrate was solved in the alcohol-water mixture and tetraethoxysilane was added dropwise to the desired Fe$^{3+}$/silica ratio.

The corresponding gels obtained after drying at 30°C were opaque due to reduced content of silica except for the S6 sample. After next drying for 48 h at 60°C, the gels were finely crushed in an agat mortar and subjected to thermal treatment in vacuum at 300°C. Subsequently, they were heated up to 400°C in the nitrogen flow for 3 hours. The samples were denoted as SX T, where X represents the weight percent of Fe$_2$O$_3$ and T denotes the temperature of thermal treatment.

**Table 1.** The ratio of Fe$_2$O$_3$ and SiO$_2$ in the gels S6–S10

<table>
<thead>
<tr>
<th></th>
<th>S6</th>
<th>S7</th>
<th>S8</th>
<th>S9</th>
<th>S10</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt % Fe$_2$O$_3$</td>
<td>68</td>
<td>76</td>
<td>85</td>
<td>93</td>
<td>100</td>
</tr>
<tr>
<td>% SiO$_2$</td>
<td>32</td>
<td>24</td>
<td>15</td>
<td>7</td>
<td>0</td>
</tr>
</tbody>
</table>

The thermogravimetric (TG) and differential thermal analyses (DTA, DTG) curves were recorded on a NETZSCH 409/429-403/QMS apparatus in the temperature range 20-550°C and a heating rate of 5°C/min. Mass spectrometry (MS) is used to identify the decomposition products from TG experiments. MS spectra indicate ion current intensities evolution with temperature of $m/z$ species. This technique allows distinguishing the relevant temperature at which specific species (expressed by $m/z$ mass numbers) are released with maximum intensity from the studied sample.

The crystalline phases obtained in the composites were identified by X-ray diffraction (XRD), using a Siemens D 5005 X-ray powder diffractometer, with diffracted beam monochromator, and CuKα radiation. The pattern was recorded from 20° to 80° with a step of 0.1° and a scanning rate of 15 s per step. Transmission electron microscopy (TEM) observations were performed using a Hitachi H-7000 electron microscope operating at 300 keV. For the microscopic analyses the samples were crushed, ultrasonically dispersed in
ethanol and subsequently deposited onto a copper grid. Mössbauer spectra were taken at room temperature. Measurements were done in the transmission mode with $^{57}$Co diffused into a Cr matrix as the source moving with constant acceleration. The spectrometer was calibrated using a standard Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed with the help of the NORMOS program. Magnetic measurements were performed on the vibrating sample magnetometer (VSM) PAR 4500 at room temperature and magnetic field of 2 T.

RESULTS AND DISCUSSION

The thermal evolution of the reference sample S10 (100 wt.% Fe$_2$O$_3$) (Figure 1) was registered by means of TG and DTA coupled with MS. The mass loss occurs almost continuously up to 230-240°C. In the first stage, between room temperature and 150°C, 10.8 % mass losses correspond firstly to elimination of the rest of ethanol introduced in the system as solvent (around 60-70°C on the MS curve), and then to release of physisorbed water (maximum at 114°C on the curve and endothermic effect on the DTA curve around 122°C), which is relatively weakly bonded to the particles.

![Fig. 1. Thermal evolution of S10 sample (TG, DTA, DTG and MS analyses)](image-url)
The mass loss can be partially attributed to nitrate removal as NO and NO₂. The carbonization of organic parts begins above 100°C. In the 170-235°C temperature range, mass loss is about 22.5 % and corresponds to release of the ethanol formed as result of hydrolysis of tetraethoxysilane, the rest of NO and NO₂ and the amount of water more strongly bonded in the structure, probably as surface hydroxy groups and organics (CO₂ signal in MS curve). In a third stage up to 400°C (mass loss about 7.3%), elimination of the rest of organics contribute, by reduction processes, to formation of magnetite, the fact being confirmed by the exothermic effect on DTA curve between 280-310°C. A weight loss of only 0.3% is registered on TG curve above 400°C, indicating that at this temperature practically remain just the oxide phases more or less crystallized, depending on the duration of thermal treatment.

Fig. 2. X-ray patterns of S6, S9, S10 samples treated at 300°C in vacuum

Fig. 3. X-ray patterns of the samples treated in the nitrogen atmosphere

The X-ray diffractograms of the samples S6, S9 and S10, treated in vacuum up to 300°C (see Figure 2), display relatively broad peaks, which suggests particle size in nanometer range. The spinel structure of iron oxide (magnetite and/or maghemite) is formed in all three samples. Due to the fact that at this temperature the composites still contains some organics, an additional thermal treatment of some samples was done in nitrogen atmosphere (at higher temperatures for the samples having lower content of iron), in order to induce stronger crystallization. By thermal treatment under N₂ atmosphere, the colour of the sample turns to black and we obtain mainly magnetite, as can be seen from the recorded XRD patterns (see Figure 4), probably as a result of reduction of a part of Fe³⁺ to Fe²⁺ by residual carbonaceous species remained in the composites. However, the presence of maghemite cannot be excluded.
For the same temperature of thermal treatment the particles size increases proportionally to the iron oxide content in the nanocomposite. The average diameters obtained by applying Scherrer formula (18) increase from 12 nm in the case of S6 400N sample to 14 nm in the case of S9 300 sample. The subsequent thermal treatment is favourable to the growing of particle size (average diameter of 15 nm for S9 300N sample).

The particles are nearly spherical shape, partially agglomerated in clusters that are relatively homogeneously dispersed (Figure 4). Mean diameter of the particles in the case of S6 400N sample determined from TEM micrographs is about 10 nm.

The X-ray diffraction results were confirmed by Mössbauer spectroscopy and magnetic measurements data realized by vibrating sample magnetometry at room temperature. Magnetization is expressed in e.m.u./g of iron oxide.

![Fig. 4. TEM picture of S6 400 sample](image)

The Mössbauer spectra, recorded at room temperature, of the samples S6 300, and S9 300 (thermal treatment in vacuum at 300°C), and S6 400 N and S9 300N (subsequent thermal treatment in nitrogen flow at 400°C for 3 hours), are presented in Figure 5 and Figure 6, respectively.

In the case of S6 sample, obtained at 300°C (S6 300), the Mössbauer spectrum recorded can be deconvoluted only in doublets due to iron present in para- or superpara-magnetic state. At higher concentration of iron oxide in the composites or at higher temperature of thermal treatment, magnetic ordering can be evidenced at room temperature by splitting the spectra in several sextets beside a low amount of para- and/or superpara-magnetic iron. It is known that for magnetite, above Verwey transition, the A (tetrahedral) sites are populated by Fe$^{3+}$ ions only and the B (octahedral) sites by both Fe$^{3+}$ and Fe$^{2+}$ ions, but electron hopping between ions gives an effective charge at each B site of 2.5+, over
the time scales used in the Mössbauer studies. The Mössbauer subspectra of magnetite consist of one sextet due to Fe$^{3+}$ ions presence in A sites, and two or three sextets having mixed Fe$^{3+}$ and Fe$^{2+}$ ions placed in B sites. According to the obtained results (Figure 5 and Figure 6) if can be generally concluded that the subspectra having isomer shift values of 0.20-0.34 mm/s and hyperfine fields values of 46.3-48.3 T are assigned to Fe$^{3+}$ ions in tetrahedral A sites. The non-equivalent B sites corresponding to Fe$^{2.5+}$ (averaged valency), are characterised by higher values of isomer shift (0.40-0.51 mm/s) with corresponding lower hyperfine fields up to 38.0 T. The reduced values of the hyperfine field compared with bulk magnetite indicated that very fine magnetic particle were present in the system. For the whole magnetic components (sextets), the quadrupole shift was smaller than 0.1 mm/s, and this fact reveals a high symmetry (cubic spinel).

Thus, the fitting results of S6 400N sample show that magnetite is the phase present in magnetic ordered state. The sextet having isomer shift of 0.34 mm/s and hyperfine field of 46.3 T was attributed to Fe(III) ions situated in tetrahedral site and the other two sextets with lower hyperfine fields, having isomer shift values around 0.5 mm/s, were assigned to iron (II) and (III) placed in the octahedral sites.

![Mössbauer spectra of S6 300 and S9 300 samples](image1)

![Mössbauer spectra of S6 400N and S9 300N samples](image2)

Magnetic measurements of S6 300 sample indicate a weak superparamagnetic behaviour. The same sample treated at 400°C under nitrogen flow presents a hysteresis loop (Figure 7) and displays a magnetic moment estimated at 37.5 e.m.u./g of iron oxide at room temperature and having a coercivity of ~ 619 Oe.

In the case of S9 sample annealed at 300°C, beside magnetite (49.4%) as magnetic ordered phase, a small amount of maghemite (~5% evaluated from the relative area of the corresponding subspectra) is present in the system. The amount of para- or superpara-magnetic iron decreases by subsequent thermal treatment in nitrogen flow (S9 300N sample)
due to the particle size growing process. The gamma phase dissapears due to partial reduction of Fe$^{3+}$ to Fe$^{2+}$.

The S9 300N sample shows ferrimagnetic behaviour (Figure 8) characterized by a magnetic moment of the particles, obtained by linear extrapolation from the high field region to zero field, of 43.3 emu/g.

CONCLUSION

In the Fe$_2$O$_3$-SiO$_2$ system, nanocomposites at concentrations between 67-100% wt. Fe$_2$O$_3$ were synthesized.

A relatively high amount of organics (higher EtOH/TEOS ratio, and supplementary use of isopropanol as solvent), together with thermal treatment in vacuum and nitrogen flow led to formation of very fine particles of magnetite. The magnetization values decrease in the system with the increasing amounts of silica, simultaneously with the decrease of particle sizes of magnetic iron oxide, probably due to surface effects and spin canting. The obtained particles are in nanometer range, between 10-16 nm (average diameter), having a narrow distribution of particles size. All the samples treated at 400°C present ferrimagnetic behaviour and the magnetization increases proportionally to the amount of iron oxide.

The maximum value of magnetic moment of the particles estimated at 56 emu/g was obtained for the sample containing 100% iron oxide in the form of maghemite mixed with magnetite.
ACKNOWLEDGEMENTS

This work is a part of the project NATO No.6/2001 of the Czech Republic and has been partially supported by Project CNCSIS No. 40223/2003, Ministry of Education and Research of Romania. The authors thank Romanian Academy and Academy of Sciences of the Czech Republic.

REFERENCES

15. Schwertmann, U. and H. Thalmann: The influence of (Fe (II)), (Si) and pH on the formation of lepidocrocite and ferrihydrite during oxidation of aqueous FeCl solutions. Clay Miner. 11 (1976) 189.


ДОБИЈАЊЕ И КАРАКТЕРИЗАЦИЈА НАНОКОМПОЗИТА МАГНЕТИТА У ОСНОВИ СИЛИКЕ

Mihaela Popovici, Cecilia Savii, Daniel Nižnanský, Jan Šubrt, Eva Vecernikova, Corina Enache, Claudia Ionescu

Сол-гел метода и термичка обрада у вакууму и атмосфери азота су коришћени за синтезу магнетитних наночестица изолованих аморфном силиком. Добијени нанокомпозит је испитиван термогравиметријском и диференцијалном термичком аналиозом, масном спектрометријом, рентгенском дифракцијом, трансмисионом електронском микроскопијом, Mössbauer спектроскопијом, а извршена су и мерења магнетних особина. Запажен је значајан утицај атмосфере на образовање магнетитне фазе.

Received 6 February 2004
Accepted 9 July 2004