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The colloidal route of the sol-gel process - an alternative to produce Fe_3O_4-SiO_2 nanocomposites

M. RĂILEANU*, M. CRIŞAN, A. BALLO[b], C. COSMA[b], J. PETRE[b],
C. STAN, D. PREDOI[a], C. M. VALSANGIACOM[a], F. TOLEA[a], C. SECU[a]
Roumanian Academy, Institute of Physical Chemistry "Ilie Murgulescu",
202 Splaiul Independenţei, 060021, Bucharest, Roumania
[a]*National Institute for Physics of Materials, P.O. Box MG 07, Bucharest, Măgurele, Roumania*
[b]*INCD-ECOIND, 90-92 Panduri Street, 050663, Bucharest, Roumania*

The iron oxide-based nanomaterials have a great importance because of their impact on a wide number of industries. They have many properties and applications in domains as: environmental protection, biomedical, catalysis, information displays and electronics. In order to avoid the tendency of nanoparticles to aggregate, they are often included in sol-gel derived silica matrices, thus being also ensured a homogeneous dispersion of the ultra-fine metal oxide particles in the host matrix. The reasons of the attempt are both an economic and a non-pollutant one, tacking into account the fact that it is well known that aqueous silica sol is cheaper and less toxic than TEOS. The Fe3O4 was introduced in the reaction mixture as aqueous suspension. A final iron content related to SiO2 of 3% wt. was chosen for the prepared nanocomposite. Thermal analysis, IR spectroscopy, XRD and TEM methods have been used for the structural characterisation,.Some experiments of water depollution (from As) have been proceeded using the prepared Fe_3O_4-SiO_2 nanocomposite.

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1. Introduction

The term of "nanocomposite" was introduced by Roy, Komarneni, and co-workers [1], during the period 1982-1983, in order to evidence a change in the conceptual direction of the sol-gel process. They underline its use for create rather heterogeneous than homogeneous materials. "Nanocomposites" refer to composites of more than one Gibbsian solid phase where at least one dimension is in the nanometre range and typically all solids phases are in the 1-20 nm domain. This new category of materials arouses a special interest, due to their exquisite properties which proceed from the small dimension of particles (nanometre particles).

The iron oxide-based nanocomposites represent one of the most important category of this type of materials. They have a great importance because of their impact on a wide number of industries. They have many properties and applications in domains as: environmental protection, biomedical, catalysis, information displays and electronics.

Nanocystalline iron oxide particles have attracted an increasing interest in the field of nanoscience and nanotechnology based on their unique and novel physical and chemical properties, compared to the properties corresponding to their crystalline counterparts [2, 3, 4].

Various methods have been reported for the synthesis of iron oxide nanoparticles, such as sonochemical synthesis, the wet chemistry, and the sol-gel process [5]. In order to avoid the tendency of nanoparticles to aggregate, they are often included in sol-gel derived silica matrices, thus being also ensured a homogeneous dispersion of the ultra-fine metal oxide particles in the host matrix. Moreover, the sol-gel method is a procedure which allows obtaining special nanomaterials by possibility of controlling the microstructure and homogeneity.

In this moment, the obtaining of the nanocomposites by the sol-gel method is well accepted for catalytic, optic and electro-ceramic materials as well as for sensors. As concerns the synthesis of iron oxide particles by the sol-gel method over the past years, a lot of work has been done [3, 6, 7].

The literature highlights many studies which have as purpose to obtain Fe_xO_y-SiO_2 nanocomposites using the alkoxide route of the sol-gel method, starting especially from tetraethoxisilan (TEOS) as SiO_2 source. The present work proposes the use of the other alternative of the sol-gel process, respectively the aqueous (colloidal) route, which is less toxic and less expensive than the alkoxide one, in order to obtain a Fe_3O_4-SiO_2 nanocomposite. In order to demonstrate the validity of the obtained sol-gel nanomaterial, some attempts have been done in order to establish its capacity to hold. The obtained results have been very promising, even for the small iron content of 3wt. % of the prepared nanocomposite.

2. Experimental

A Fe_3O_4-SiO_2 nanocomposite with a Fe content of 3 wt. % related to the SiO_2 was prepared, using the aqueous (colloidal) route of the sol-gel method. The silica source was a colloidal silica sol Ludox SM 30 type, from Aldrich having a SiO_2 content of 30 wt. %. The Fe_3O_4 was

laboratory prepared and introduced in the reaction mixture as aqueous suspension obtained by sonication for 15 min., followed by NH_4OH 25 % addition until achievement of a neutral pH, as described in a previous paper [8].

The gelation was accomplished by destabilizing the silica sol with a HNO_3 p.a. solution of 25 wt. % (from Merck), followed by the Fe_3O_4 aqueous suspension addition. The reaction mixture was heated at 60°C and maintained at this temperature, under continuous stirring, until the gelation occured at pH = 9 (gelation time = 0.5 hour).

Crystalographic analysis of the samples was performed by powder X-ray diffraction (XRD). Diffraction patterns of intensity vs. 2θ were recorded with a Philips PW 1050 diffractometer. A continuous scan mode was used to collect 2θ data from 10 to 70^0. The iron oxide nanoparticles were observed in electron micrographs obtained with a TEM (JEOL 200 CX).

TG/DTA of the samples was carried out to determine the phase changes as well as the weight loss of the samples using a Perkin Elmer Diamond thermal analyzer. The temperateure was increased at a rate of $10\ ^0$C/min.

IR spectroscopic studies were performed in the range 1800-400 cm^{-1} using a FTIR Spectrum BX spectrometer. Samples dehydrated at room temperature were pelleted with dried KBr.

3. Results and discussion

In the Fig. 1 the XRD spectra of samples M heated at different temperatures are presented. In all the samples, an amorphous character of the silica matrix with a slight tendency to crystallize the Fe_3O_4 phase can be noticed.

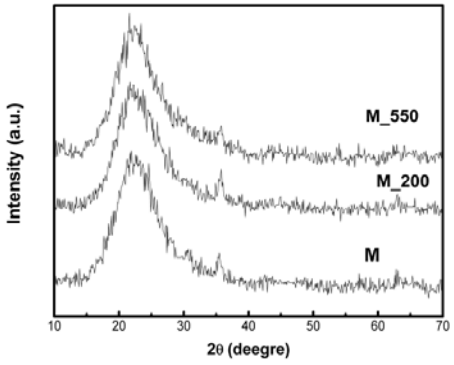

Fig. 1. XRD patterns of the studied samples M, M_200 and M_500.

Fig. 2 shows a TEM image that was used to determine particle size distribution and morphology for Fe_3O_4 nanoparticles. There is a wide size distribution of the Fe_3O_4 particles dispersed in the silica matrix. The particles appear spherical in shape with average sizes smaller than 20 nm.

The IR spectra of the prepared samples were collected between 2000 and 400 cm^{-1}. In all cases the characteristic vibration bands of a SiO_2 gel, mainly: ν_{as}(Si-O-Si) at 1200 $cm^{-1}$and 1075 cm^{-1}; ν_{as}(Si-OH) at 970 cm^{-1}; ν_s(Si-O-Si) at 795 cm^{-1}; ν(Si-O-Si) from cyclic tetramers at 540 cm^{-1} and δ(Si-O-Si) at 460 cm^{-1}were identified in accord with literature data [9-11]. The ν(Fe-O) vibration band (530 cm^{-1}) appears distinctly in all samples [10].

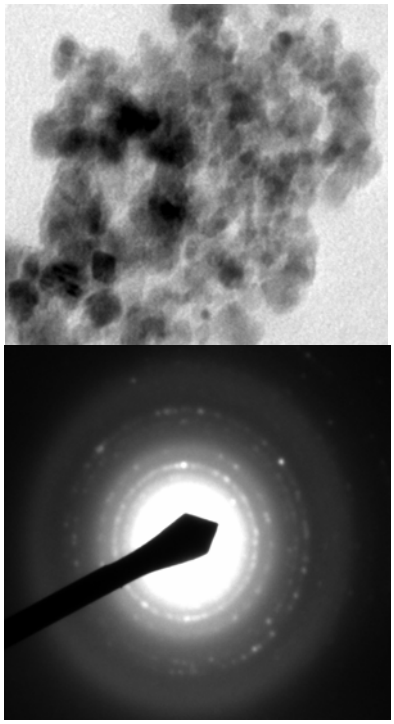

Fig. 2. Transmision electron microscopy (MET) and electron diffraction photography of the sample M.

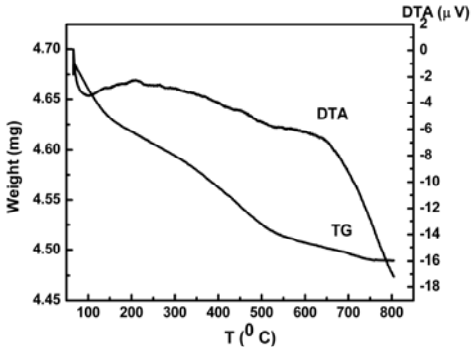

Fig. 3. TG and DTA curves of sample M (heating rate =10^0C/min).

The TGA curve of the sample M (Figure 3) presents three main steps of thermal decomposition: (1) 7.09 % wt.

loss between 45 °-250 °C, assigned to the desorption of the water and ethanol form the matrix, (2) 1.89% wt. between 250°-500°C, assigned to the decomposition of the organic part of the gels [12], (3) 0.72 % wt. loss between 500°-800°C, assigned to the re-organization of the inorganic matrix after the removal of the organic component. The sample shows a low-temperature endothermic peak (DTA curve), 80-100°C [13], which can be assigned to the loss of volatile components such as alcohol and water molecules. A large exothermic peak can be observed at 530-690°C, associated with the transformation the Fe_3O_4 in to γ-Fe_2O_3. X-ray diffraction analysis and the Mössbauer spectroscopy of the samples after heating at 550°C give only Fe_3O_4.

Possible application of the prepared Fe_3O_4 nanomaterial

The prevention and the control of the effects of different pollutants on the environmental medium represent one of the most acute problems that humanity must confront our days. Between the most important aspects concerning the pollution, one can refer to that concerning the water. There is a natural pollution (depending on the chemical composition of the rocks from the supply basin and from the water course), which is inevitably, and a chemical (artificial) one (which can be done to some industrial and/or domestic residues), which can and must be controlled. In fact, there are certain permitted limits of pollutant concentrations which are settled by law.

Between the most frequent and dangerous natural and drinking water pollutants, some metals can be mentioned, as: As, Cu, Cr, Pb, Cd, Hg. These can be efficiently separated by using some adequate sorbents, as the iron oxide- and hydroxide-based materials [14-17]. They represent the active component for the toxic metals separation, being generally dispersed in synthetic resins. In this context, the Fe_xO_y dispersion in sol-gel silica matrices becomes a modern tendency in order to prepare some efficient sorbents for water decontamination.

Based on literature data [18-21], when iron oxides are used as sorbents, the efficiency of the adsorption, which is strongly dependent of pH, is maximum in the acid domain. So, an acid pH (2.60-2.62) was chosen in our experiments. The prepared Fe_3O_4-SiO_2 nanocomposite tested as sorbent for As (V) was finely grinded and passed through sieves in order to obtain 2 granulometric fractions: < 0.2 mm, respectively 0.2-0.4 mm. The experimental technique used in the adsorption tests consisted in the following steps:

- the preparation of an aqueous solution containing 1,049 mg As(V) / l;
- the pH correction of the prepared solution (pH = 2.60-2.62);
- the sorbent addition and the checking of the pH, considered as initial pH (pH_i) ;
- the stirring of the samples (in closed Erlenmayer vessels) on GFL 3006 type magnetic stirrers, with 150 rot./min.;
- the final pH measurement (pH_f);
- the filtration of the samples.

The analytical control was realized through the remanent As content and concentration of dissolved Fe determinations. The As concentration was determined by the spectrophotometric method, using diethylditiocarbamate silver, according to SR ISO 6595:1997 standard regarding the water qualities. The Fe content was also spectrophotometricaly determined, using orto-phenantroline, according to SR ISO 6332:1996. Both granulometric fractions of sorbent were tested at two contact times (15, respectively 40 hours), determining for each case the quantity of remanent As (as a measure of the water clean efficiency), and of dissolvedFe. The ratio between the adsorbed As and Fe in sorbent has also been determined. Table x presents the obtained results.

Table 1. Comparative study regarding the As(V) holding using the prepared Fe_3O_4-SiO_2 nanocomposite.

Contact time [h]	Grain size [mm]	pH_i / pH_f	Dissolved Fe [mg/l]	Remanent As [mg/l]	η of As removal [%]	mmoles adsorbed As/mmoles Fe
15	< 0.2	2.80 / 2.89	0.65	825	21.35	0.93
	0.2 - 0.4	2.72 / 2.91	0.65	948	9.63	0.42
40	< 0.2	2.80 / 2.95	0.75	820.5	21.78	0.95
	0.2 - 0.4	2.72 / 2.95	0.62	828	21.67	0.92

From Table 1 it can be seen that the addition of the sorbent leads to a slight increase of the pH, from 2.60-2.62 to 2.72, respectively 2.80, depending on the sample granulation. This pH value, considered as "initial" (pH_i) modifies further, during the contact time between sorbent and polluted water, until the "final" pH (pH_f) is reached. Concerning the dissolved Fe and remanent As concentrations, it can be seen that there are approximately in the same limits, no mater the granulation and the contact time. A prolonged contact time doesn't significantly influence these concentrations, instead it improves the efficiency of the As removal. The decrease of the granulation also leads to a better efficiency of the As removal, probably by the increase of the specific surface area.

The obtained experimental results, although susceptible to be completed and improved, are very promising, allowing considering the prepared Fe_3O_4-SiO_2 nanocomposite as a possible sorbent for As removal from the polluted waters.

4. Conclusions

The aqueous (colloidal) route of the sol-gel method has been proposed as an alternative, in order to prepare a Fe_3O_4-SiO_2 nanocomposite. The reasons of this route selection consist in the advantages of being less toxic and cheaper than the alkoxide one, because it uses the aqueous colloidal silica sol, instead of tetraethylortosilicate (TEOS), as SiO_2 source. The obtained material was structurally characterized with the usual techniques (RXD, TEM, IR spectroscopy). Although the prepared nanocomposite had a low content of Fe related to SiO_2 (3 wt. %), it was proved to be suitable for water decontamination, being tested in As removal.

References

[1] S. Komarneni, J. Mater. Chem. **2**(12), 1219 (1992).
[2] L. Zhang, G. Papaefthymiou, R. F. Ziolo, J. Y. Ying, Nanostruct. Materials **9**, 185 (1997).
[3] J. L. Dormann, D. Fiorani, Magnetic Properties of Fine Particles, North-Holland, Amsterdam, 1992.
[4] A.B. Bourlinos, A. Bakandritsos, V. Georgakilas, D. Petridis, Chem. Mater. **14**, 3226 (2002).
[5] S. J. Lee, et al, J. of Magnetism and Magn. Mat. **282**, 147 (2004).
[6] D. D. Awschalom, D. P. DiVicenzo, Phys. Today **4**, 43 (1995).
[7] D.L. Leslie-Pelecky, R. D. Rieke, Chem. Mater. **8**, 1770 (1996).
[8] A. Jitianu, M. Răileanu, M. Crişan, M.Zaharescu, M. Jitianu, L. Stanciu, D. Predoi, J. Sol-Gel Sci. Tech., 2006, in press.
[9] S. Bruni, F. Cariati, M. Casu, A. Lai, A. Musinu, G. Piccaluga, S. Solinas, NanoStructured Materials, **11**(5), 573 (1999).
[10] C. Chaneac, E. Tronc, J. P. Jolivet, J. Mater. Chem. **6**(12), 1905 (1996).
[11] C. A. Capozzi, L. D. Pye, R. A. Condrate, Mat. Lett. **15**, 130 (1992).
[12] M. Guglielmi, G. Principi, J. of Non-Crystalline Solids **48**, 161 (1982).
[13] F. del Monte, M.P. Morales, D. Levy, A. Fernandez, M. Ocana, A. Roig, E. Molins, K. O'Grady, C. J. Serna, Langmuir, vol. 13, 1327 (1997)
[14] S. Khaodhiar, M.F. Azizian, K. Osathaphan, P. O. Nelson, Water, Air, and Soil Pollution **119**, 105 (2000).
[15] C. H. Lai, S. L. Lo, H. L. Chiang, Chemosphere **41**, 1249 (2000).
[16] V. M. Georgeaud, J. P. Ambrosi, J. Y. Boterro, P. Rochette, Goldsmith Conference Toulouse, pp. 513, 1998.
[17] M. Nagtegaal, P. Stroeve, J. Ensling, P. Gütlich, M. Schurrer, H. Voit, J. Flath, W. Tremel, Chem. Eur. J. **5**(4), 1331 (1999).
[18] P. J. Swedlund, J. G. Webster, Water Research, **33**(16), 3413 (1999).
[19] E. N. Smith, S. Chatterjee, Water Sci. & Technol., **42**(1-2), 347 (2000).
[20] S. Khaodiar, M. F. Azizian, K. Osathaphan, P. O. Nelson, Water, Air, and Soil Pollution, **119**, 105 (2000).
[21] I. Peleanu, M. Zaharescu, I. Rău, M. Crişan, A. Jitianu, A. Meghea, J. Radioanalytical Nuclear Chem., vol. 246, 2005.

*Corresponding author: mraileanu@icf.ro