The influence of reduction process on transformation iron-cobalt oxide nanoparticles in MCM-41 silica

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Abstract. ((Fe⁰.⁹Co⁰.₁)Oₓ/MCM-41 nanocomposite material was prepared by wet impregnation of the silica mesoporous template with iron and cobalt mixture of aqueous salt solutions. The phase analysis of the obtained samples carried out by X-ray diffraction method and studies of magnetic properties using ⁵⁷Fe Mössbauer spectroscopy revealed the presence of nanostructured magnetite- and maghemite-like phases. The transformation to bimetallic Fe⁰.⁹Co⁰.₁ and fayalite phases accompanied the reduction process in hydrogen at 1073 K. The contribution of ferrimagnetic phases in relation to superparamagnetic phases increases when temperature changes from 295 K to 13 K in the sample before reduction what is characteristic for nanoparticles.

1. Introduction
In the last decades the decrease of the grain size of magnetic materials to the nanometer scale has opened new perspectives in materials science. Nano-sized materials possess many unique properties, which are intermediate between the molecular or atomic level and the properties of the corresponding bulk materials. In particular nanoparticles of materials which are ferromagnetic in bulk exhibits superparamagnetic (SPM) properties [1]. Studies of magnetic properties of nanoparticles are important from both fundamental and technological point of views. Such materials have potentially, and even in some cases nowadays, a wide field of applications ranging from storage information technology [2] through catalysts in chemical technology to biomedical applications [3].

The main factor influencing physical, chemical and other properties of these objects is limitation by small sizes in artificial boundaries. There exists possibility to produce relatively easily nanoparticles based on ferromagnetic and/or ferrimagnetic oxide materials in nanometric voids of different porous media [4] by the direct hydrothermal and/or wet impregnation methods. In particular mesoporous channel-type matrices such as MCM-41 can be used as porous media for obtaining Fe-based nanocrystallites [5]. The main advantage of this method is that it allows the synthesis and/or incorporation of the noticeable amount of magnetic nanomaterials. In a case of such composites the problem of chemical and structural stability occurs [6]. The growth of the nanocrystallites during calcination and reduction stages of chemical synthesis can be influenced by the metal-support interactions, and the way of thermal treatment. It is also considerably harder to produce pure ferromagnetic metallic or bimetallic nanoparticles in this way. The use of materials with a more
complicated composition than simple metals gives possibility to control technologically useful and important properties.

In framework of this work an attempt to obtain structurally and chemically stable oxide and bimetallic Fe-Co nanocrystallites in magnetically ordered state in MCM-41 template was made. Structural and magnetic properties of obtained composites were studied and reported.

2. Experimental

The synthesis of MCM-41 silica template was accomplished using the modified procedure detailed described in [7]. In order to prepare bimetallic system on the support MCM-41 5 wt% solutions containing metal ions (Fe$^{3+}$ and Co$^{2+}$) were mixed in 9:1 ratio and then used as solution for the impregnation of the silica material. At the next stage the sample was subjected to low temperature treatment (drying) at 423 K for 1 hour. The next step involved calcination in air atmosphere at 573 K for 1 hour. As a result of such a procedure there should be formed oxide system deposited on silica framework of general formula (Fe$_{0.9}$Co$_{0.1}$)O$_x$/MCM41. In the next stage the samples were reduced and passivated. In this case a sample (0.25 g) was placed in a flow quartz reactor with an internal diameter 10 mm. A 6% H$_2$–Ar mixture was used as carrier gas at a flow rate of 30 cm$^3$/min. The temperature of the sample was increased up to 1073 K with the linear ramp rate 10 K/min. The temperature of reactor was maintained at 1073 K for 3 hours. Then sample was cooled to room temperature, flushed with helium (0.5 hour at a flow of 30 cm$^3$/min) and next passivated in the 5 % O$_2$–He mixture (0.5 hour at flow of 30 cm$^3$/min). Such procedure allowed formation of the thin oxide layer on the surface of the metal crystallites and prevented deep oxidation of the species.

The XRD and Mössbauer measurements were performed for the samples after calcination and after reduction/passivation treatment. The XRD patterns were measured on the Philips X’Pert PW 3040/60 X-ray diffractometer with the CuK$_\alpha$ radiation at room temperature. They were fitted by the use of the FULLPROF program for Rietveld method refinement. The $^{57}$Fe Mössbauer spectra of the investigated sample were measured in transmission geometry at different temperatures using a constant acceleration spectrometer with the $^{57}$Co/Rh source. The isomer shift $\delta$ was calibrated against a metallic iron foil at room temperature.

3. Results and discussion

The XRD measurements were carried out in order to obtain information about changes of structures of crystallites embedded in the silica template at two stages of chemical treatment. The XRD patterns for the sample before (a) and after (b) reduction are shown in Figure 1. The smoothly varying broadened component in the begin of measurement range results from the amorphous silica support.

![Figure 1](image_url)
Refinement by Rietveld method of well-resolved peaks in spectrum (a) revealed the presence of two crystalline phases: magnetite- and maghemite-like with partial replacement some Fe atoms with Co ones. The lattice parameters are 8.37(1) Å and 8.38(1) Å, respectively. In the sample after reduction also two phases were identified: bimetallic Fe$_{0.9}$Co$_{0.1}$ structure and (Fe$_{1-x}$Co$_x$)$_2$SiO$_4$ (fayalite). The lattice parameters of these phases are equal to $a = 8.39(1)$ Å and $8.39(1)$ Å, respectively. In particular large broadening of the XRD diffraction lines in this sample indicates an occurrence of the crystallites with very small sizes. Average sizes $D$ and strains $\eta$ in the crystallites for phases giving well-resolved peaks were determined from the broadening of XRD diffraction peaks by using the Hall-Williamson method. In the sample before reduction for magnetite-like phase $D = 26.5$ nm, $\eta = 8.13 \times 10^{-4}$. In the sample after reduction for Fe$_{0.9}$Co$_{0.1}$ phase $D = 68.5$ nm, $\eta = 4.73 \times 10^{-4}$ and for fayalite $D = 32.1$ nm, $\eta = 8.81 \times 10^{-4}$.

Figure 2a shows the Mössbauer spectra of the (Fe$_{0.9}$Co$_{0.1}$)O$_x$/MCM-41 sample before reduction measured at different temperatures. All three patterns consist of three sextets, superimposed one doublet and a monoline. Two sextets are related to Fe atoms located at two non-equivalent tetrahedral (A) and octahedral (B) sites in the magnetite-like structure. In pure magnetite the relation of occupancies of A and B sites is equals to 1:2. In obtained spectra this relation is clearly distorted. This experimental result points to necessity of taking into account one more sextet component in the fitting procedure. All hyperfine parameters values for the third component are close to values for Fe probes in nanocrystallites with maghemite-like structure.

![Mössbauer spectra](image)

The sextet lines are broadened in comparison to respective bulk phases as a result of small crystallite sizes. The obtained values of isomer shifts $\delta S$ for ferromagnetic components are consistent with that for Fe oxidation states in magnetite (Fe$^{3+}$)$_3$(Fe$^{2+}$)$_2$O$_4$ and maghemite (Fe$^{3+}$)$_3$(Fe$^{3+}$)$_{5/3}$/O$_4$, where $\square$ denotes a vacancy.

From temperature evolution of Mössbauer spectra for the sample before reduction it is evident that relative contribution of ferromagnetic components in relation to a paramagnetic doublet and monoline components increases with the decrease of sample temperature. Thus the paramagnetic component represents the superparamagnetic phase (SPM) of the both iron oxides resulting from the relaxation phenomenon due to the intrinsic finite-size effect. The presence both the doublet and monoline in the spectra for the superparamagnetic state can be explained on the basis of core-shell model [8]. The superparamagnetic doublet with a significant quadrupole splitting value equals to 0.86(3) mm/s origins.
from $^{57}$Fe nuclear probes in non-spherical local surroundings occurring in the surface shells of the nanoparticles. A monoline component present in obtained spectra results also from nanoparticles in the superparamagnetic state. However, in this case $^{57}$Fe probes located in the core of nanoparticles are a source of a signal. They have spherical local surroundings without an electric field gradient. The relatively considerable contribution of this component even in the spectrum measured in 13 K suggests that many nanoparticles have sufficiently small sizes in order to their blocking temperature lies below the lowest temperature of measurements.

The Mössbauer spectra of the $(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_x$/MCM-41 sample after reduction measured are presented in figure 2b. The patterns measured at temperature 295 K consists of one sextet and two doublets. The sextet has hyperfine parameters characteristic of bimetallic $\text{Fe}_{0.9}\text{Co}_{0.1}$ phase in which Fe atoms occur in $\text{Fe}^0$ state. The doublets are assigned to $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions in the octahedral sites of $(\text{Fe}_{1-x}\text{Co}_x)_2\text{SiO}_4$ phase. The fayalite remains paramagnetic up to $T_N = 66$ K. Below critical temperature $T_K = 23$ K antiferromagnetic structure changes into complex structure with canted AF arranged spins in M1 sublattice and antiferromagnetically at M2 sites [9]. At temperature $T = 13$ K Mössbauer spectrum consists of three sextets and a doublet. Two sextets with the largest and the smallest hyperfine splitting are related to $^{57}$Fe probes located in fayalite. The third origins from bimetallic phase. The doublet is connected with fayalite nanoparticles in superparamagnetic state.

In high temperature reduction process highly dispersed in MCM-41 matrix Fe/Co oxides nanoparticles (SPM phase before reduction) interacting with walls of silica nanochannels form $(\text{Fe}_{0.9}\text{Co}_{0.1})_2\text{SiO}_4$ phase. In connection with that the doublet related to SPM phase present before reduction completely disappears in the MS spectra of the sample after reduction. The Fe/Co oxides nanocrystallites of the larger sizes primary giving the sextets are reduced to bimetallic $\text{Fe}_{0.9}\text{Co}_{0.1}$ nanoparticles. In this way pure ferromagnetic Fe nanoparticles stabilized with Co addition were obtained in the nanocomposite.

4. Summary
Magnetite- and maghemite-like nanocrystallites in MCM-41 matrix were obtained by co-impregnation method. The MS investigations showed the coexistence of ferrimagnetic and superparamagnetic nanoparticles in the sample before reduction from 13 K to room temperature what is undesirable. From the point of view of technological applications it is desirable to obtain the template-based nanocomposites which would not include any superparamagnetic phases. In this work it was achieved by the reduction of the $(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_x$/MCM41 sample at 1073 K in hydrogen and then passivation at the flow of $\text{O}_2$/He mixture at room temperature what is prove by Mössbauer spectroscopy.

References
[1] Dormann J L, Fiorani D, Cherkaoui R, Tronc E, Lucari F, D’Orazio F, Spinu L, Noguès M, Kachkachi H and Jolivet J P 1999 J. Magn. Magn. Mater. 203 23
[2] Moser A, Takano K, Margulies D T, Albrecht M, Sonobe Y, Ikeda Y, Sun S and Fullerton E E 2002 J. Phys. D 35 R157
[3] Ambashta R D, Yusuf S M, Mukadam M D, Singh S, Wattal P K and Bahadur D 2005 J. Magn. Magn. Mater. 293 8
[4] Bengoa J F, Cagnoli M V, Gallegos N G, Alvarez A M, Mogni L V, Moreno M S and Marchetti S G 2005 Micropor. Mesopor. Mater. 84 153
[5] Cagnoli M V, Alvarez A M, Bengoa J F, Gallegos N G, Mogni L V, González Oddera M X, Marchetti S G and Mercader R C 2003 Hyperfine Interact. 148-149 185
[6] Grün M, Unger K K, Matsumoto A, Tsutsumi K 1997 Characterization of porous solids IV, eds. McEnaney B, Mays J T, Rouquerol J, Rodriguez-Reynoso F, Sing K S W, Unger K K (The Royal Society of Chemistry) p 81
[7] Gac W, Goworek J, Wójcik G and Kępiński L 2008 Adsorption 14 247
[8] A.M. Van der Kraan, Hyperfine Interact. 40, 211, (1988)
[9] R.P. Santoro, R.E. Newnham, S. Nomura, J. Phys. Chem. Solids 27 (1966) 655–666

International Conference on the Applications of the Mössbauer Effect (ICAME 2009) IOP Publishing
Journal of Physics: Conference Series 217 (2010) 012113 doi:10.1088/1742-6596/217/1/012113