

The magnetic properties optimization in diluted magnetic oxide semiconductor nanoparticles obtained by a modified co-precipitation approach in intrazeolitic networks

R. BOSÎNCEANU*, F. IACOMI

Department of Physics, "Al. I. Cuza" University, Bd. Carol I
Iasi, Romania

Abstract

Ferromagnetism in diluted magnetic semiconductors (DMS) has been a subject of great scientific and technological interest for the past few years due to its implications for spintronics, advanced magneto-optics and sensors applications. Our research involves a modified co-precipitation approach that allows controlled growth of $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ nanocrystals within the superparamagnetic and single domains limits by creating the precipitating conditions with the help of hydrolase reaction of the urea. XRD confirms the formation of the ferrite and the partial loss of host crystallinity observed in X-ray diffraction patterns thereby suggests that the process of cluster formation involves aggregation within the large cages of the zeolite and local destruction of the pores network. Room-temperature M-H measurements verifies the influence of synthesis conditions and crystal size on the magnetic properties of ferrite nanocrystals. Distinct absorption maxima in diffuse reflectance UV-visible spectra and sharp exciton peaks in low-temperature excitation spectra verified the presence of quantum-confined $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$.

Keywords: magnetic properties optimization, diluted magnetic oxide semiconductor, Superparamagnetism.

1. Introduction

Magnetic properties of nanoparticles are subject to intense research activity driven by a fundamental interest in the novel physical properties of the nanoscale system and also potential industrial application of nanostructured materials. This letter reports on the magnetic properties of well-dispersed diluted magnetic oxide quantum systems within an aluminous-silicious matrix. The use of the A zeolite as a self-assembled nanotemplate enables us to synthesize composite materials containing magnetic oxide nanoparticles at different temperature for optimization of magnetic properties. Comparable inorganic methods for the synthesis of nanoscale mixed-metal oxides require heating at high temperatures in order to produce the desired oxide composition and microstructure [1] and [2]. The development of such mixed-metal oxide and zeolite-based nanocomposites is targeting the functionalization into device technologies for sensors and spintronics applications.

The materials challenge is to magnetize functional non-magnetic materials by synthesis dilute concentrations of magnetic species, thereby harnessing the benefits of a magnetic response without significantly affecting the desirable physical properties of the non-magnetic host

3. Experimental Part

3.1. Starting materials

All the chemicals were of reagent grade and used without further purification. The following materials were used for the loading $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ thereby : A zeolite with pore size 0.4 nm and 2.5 nm obtained in Chemical

Science and Technology Laboratory of Faculty of Chemistry from the "Al.I.Cuza" University of Iasi, ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >99%), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, >99%), hydrochloric acid (HCl, 1N) were obtained from KEBO, distilled water and urea (46.66%).

3.2. The construction of the ion exchange isotherms for $\text{Fe}^{+3}/\text{Na-A}$ with a cation exchange capacity of 5.5 meq/g. The procedure carried out was described by Barros et al. (1995) [3]. Fig.1 presents the ion-exchange isotherms experimentally obtained.

One observes from Fig.1 is that the isothermal behaviour is very similar with the type "d" [4] for that from 298K and the type "a" [4] for the rest.

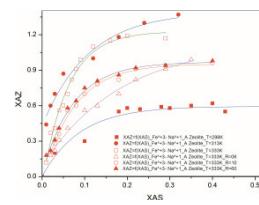


Fig.1. Schematic representation of ion-exchange isotherms for A zeolite to (T=298K, 313K, 333K) and in treated A zeolite with urea (R=6, 10, 60).

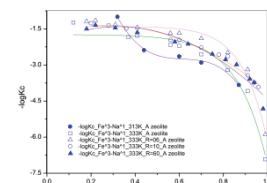


Fig.2. Kielland plots for A zeolite to (T=313K, 333K) and treated A zeolite with urea (R=6, 10, 60) for $\text{Fe}^{+3}\text{-Na}^{+1}$.

However, it is strongly hydrated at 298K, steric problems inhibit in some extent the retention of ferric ions. Possibly, at this temperature, Fe^{+3} cations are only located in the large cages due to the low X_{AZ} values obtained for them. It is also observed at 313K and 333K some overexchanged values ($X_{AZ} > 1$), which is probably due to

some multilayer adsorption. A densely occupied monolayer will act in some degree as an extension of the zeolite, and will be able to attract further cations from the solution phase. The adsorption phenomenon in zeolite ion-exchange isotherms was already seen (Barros et al., 2003) [5] indicating that X_{AZ} values greater than 1 are possible to occur and the hypothesis of experimental errors should be completed discarded.

The functions $X_{AZ}=f(X_{AS})$ are fitted by the Table Curve program.

Construction of Kielland Plots. The Kielland quotients were obtained according to the equation: $\log K_c' = C_0 + 2C_1 X_{AZ}'$, where $C_0 = \log K_B^A$, $2C_1$ is Kielland coefficient and K_c' is the corrected selectivity coefficient. X_{BZ} was considered to be $X_{BZ} = 1 - X_{AZ}$. ZB is the charge of the ferric ion, +3, and, supposing that only sodium ions are exchanged, ZA was considered to be +1. The experimental points of the isotherms were fitted to equations and the functions $X_{AZ}=f(X_{AS})$ calculated with the help of the software package Table Curve and activity coefficients with PHRQPITZ program. In this way, the curve points were normalized and they were used to calculate K_c . Afterwards, the Kielland plots were constructed for isotherms.

With the ion exchange data it was possible to calculate the selectivity coefficients and the respective Kielland plot of each isotherm. The mathematical algorithm performed to obtain the Kielland plot improves the visualization of the straight lines. It indicates that the exchange sites have the same energy. Nevertheless, the mineral analysed display several exchange sites of different energies. As the Kielland plots are linear, we believe that only one kind of site acts in the exchange process with Fe^{+3} . The straight lines present positive values of C_1 , indicating that "W" is exothermic and that the Fe^{+3} ions tend to cluster. The degree of exchange increases as the temperature increases, because it apparently inhibits this tendency to cluster. It is observed that the higher temperature, the more regular the distribution of the Fe^{+3} ions through the sites. Thus, the zeolite is able to shelter a greater quantity of these ions, elevating the inflexion point.

All Kielland plots show non-linear shape for the Fe^{+3} cations investigated. This feature was already expected since NaA framework has sites with distinct energies (Barros, 2003) [5].

3.3. The determination of the optimum urea/ferric ratio.

The change of the pH of each solution with $R=06, 10$ and 60 with reaction time are shown in fig.3.

The pH rate rise rapidly with R and the final pH of the solution became high. The rate of the pH rise slowed down at pH 4-5 in the solution with $R= 6$ and 10 . These phenomena were not observed in the solution with $R=60$.

The products formation to distinct pH values from the solutions with $R=6$ and 60 is shown in fig.4 (a) and (b).

From the pH measurements results of products, β - $FeO(OH)$ was produced at pH 1-2 and magnetite at pH 4-

6. α - $FeO(OH)$ was recognized from the solutions with $R=6$.

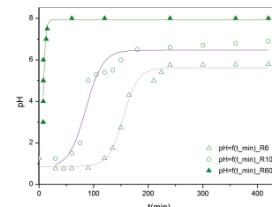


Fig.3. The relation between change of pH and the reaction time for $R=urea/Fe^{+3}$ mole ratio.

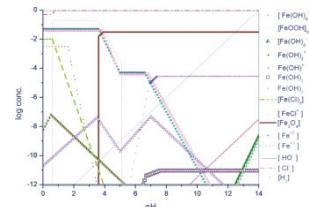


Fig.5. Thermodynamic calculations of the concentrations of Fe^{+2} and Fe^{+3} species formed at different solution pHs [1].

Magnetite and α - $FeO(OH)$ were produced at the same time, after that, α - $FeO(OH)$ gradually decreased and was finally transformed into magnetite. α - $FeO(OH)$ was not observed from the solution with $R=60$. Magnetite was precipitated rapidly since the rate of the rise of pH was quick with an increase in R .

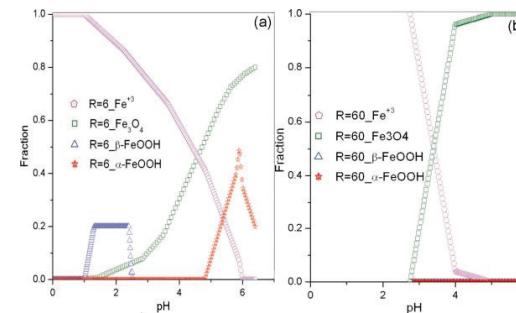


Fig.4. The formation of Fe^{+3} , Fe_3O_4 , β - $FeOOH$ and α - $FeOOH$ to distinct pH values from solutions with (a) $R=6$ and (b) $R=60$.

When R value was small, $R=6$, the rate of the rise of pH was slow and the hydrolysis of urea was a rate-determining step in the formation of magnetite, and the pH of the solution was kept at a constant value of pH about 4.6 during precipitation of magnetite.

When R value was large, the rate of rise of pH was rapid and the pH value quickly reached 7-8, being optimum ratio for the proposal goal.

3.4. Chemical conditions: chemical composition of the zeolitic reaction media, pH, the redox potential, the concentration of the different salts used, the boundary conditions. In this way it is possible to establish, on a rational basis, the chemical conditions as well as the boundary conditions in which magnetite could be formed reproducibly as a pure phase [1].

3.5. The modified co-precipitation of Fe_3O_4/γ – Fe_2O_3 into zeolites

The chemical activation process of zeolites realized on chemical and thermal way, thereby: a) one gram of 200 mesh Na-A dried probe is calcinate at a 550-600 °C temperature in air or nitrogen current for the removal of

the network-forming organic molecules. The activated zeolite probes were washed with distilled water and dried at 105 °C temperature in reaction column, fig.6.

When the ion-exchange isotherm indicates the preset concentration of ferric ions it is stopped the urea-ferric chloride mixture injection and concomitant begin the automated ferrous chloride injection at 98 °C thereby it is realized the ferrous ions absorption and according fig 3. the urea hydrolysis rising to the optimal pH value.

The co-precipitation direction it is realized according diagrams from fig.4 (a) and (b). For the urea excess hydrolysis and the anions removal it is needed the treatment of 30 minutes with steams at 120 °C temperature.

The modified zeolite is dried 20 minutes with air at 105 °C, extracted from column with air jet and transported into vessel for maturing through cyclone and subsequent 20 minutes calcination at 900 °C.

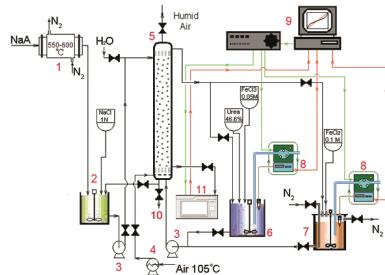


Fig.6. Schematic representation of the batch reactor for the modification of zeolites with magnetic oxides: 1- furnace at 550-600°C., 2-chemical treatment vessel NaCl 1N, 3- electric water pump, 4- electric air blower, 5-reaction column, 6-mixing vessel of solution with $R = (\text{urea}/\text{Fe}^{3+}) = 6, 10, 20, 60$, 7-mixing vessel for FeCl_2 0.1M, 8- masterflex 7521 pump with pH-meter, 9-black star interface, 10-Sewage, 11-Microwave Oven.

3.6. Characterization

The crystalline structure of the parent zeolites and modified zeolites were studied by X-ray diffraction analyses. Powder XRD patterns were recorded in the large angle ($2\theta=30-80^\circ$) region with DRON 2 diffractometer using a $\text{CuK}_{\alpha 1}$ radiation ($U: 25\text{KV}$, $I: 20\text{mA}$, $U_d: 40\text{V}$) with wavelength of 1,5405 Å and a step size of 0.01° in laboratory of structural analysis of faculty of physics by univ. "Al.I.Cuza" Iași.

DRUV-VIS spectra of the samples were recorded (200-700nm) on an SPEKOL ® 1300 UV VIS spectral photometer.

Magnetic measurements are carried out by vibrating magnetometer at the room temperature (293K) were recorded in Center of Applied Research in Physics and Advanced Technologies (CARPATH), Romania.

EPR measurements were performed at room temperature with a RADIOPAN spectrometer in X band.

4. Results and discussions

X-ray powder diffraction patterns for $/ \gamma\text{-FeO(OH)}/\text{A}$ and $II \gamma\text{-FeO(OH)}/\gamma\text{-Fe}_2\text{O}_3/\text{A}$ samples showed

that the zeolite crystallinity was maintained during synthesis, Fig.7.(a) and (b).

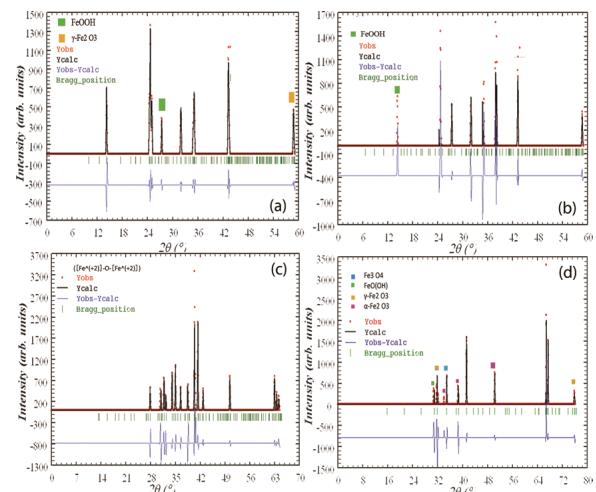


Fig.7. The XRD Spectra of
(a)- $\gamma\text{-FeO(OH)}/\gamma\text{-Fe}_2\text{O}_3/\text{A}$ 0.9 mEqFe $^{3+}$ /1gA
(b)- $\gamma\text{-FeO(OH)}/\text{A}$ 0.15 mEqFe $^{3+}$ /1gA
(c)-(Fe₂O)⁴⁺/A 1.5 mEqFe $^{3+}$ /1gA
(d)-Fe₃O₄/γ-FeO(OH)/γ-Fe₂O₃/α-Fe₂O₃/A 2.2 mEqFe $^{3+}$ /1gA

In the case of $III\text{-(Fe}_2\text{O)}^4\text{/A}$ sample, Fig.7.(c), X-ray absorption spectroscopic measurements could prove the existence of small, slightly disordered iron (III) oxide nanoparticles and $IV\text{-Fe}_3\text{O}_4/\gamma\text{-FeO(OH)}/\gamma\text{-Fe}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3/\text{A}$ sample, Fig.7.(d), XRD confirms the formation of the ferrite and the partial loss of host crystallinity observed in X-ray diffraction patterns thereby suggests that the process of cluster formation involves aggregation within the large cages of the zeolite A and local destruction of the pores network.

The optical absorption spectra give the quantization effect of band gap. The DRUV-VIS , fig.8, of loaded samples show excitonic peak at ~250 nm, whereas the bulk FeO(OH) , Fe_2O_3 and calcined FeO(OH) , show strong maxima at 535, 560, and 515 nm, respectively [6, 7]. However, it is interesting to note that FeA composite also absorbs nearly in the same region (~250 nm) as that of the loaded samples [8, 9]. Thus, the occurrence of these exciton peaks in this range can be interpreted for both framework trivalent iron and iron oxide nanoparticles (non-framework) inside the mesopores. Hence, must be taken in deducing the information regarding the nature of the species on the basis of DRUV-VIS spectra alone. In present DRUV-VIS study, we have not observed the formation of iron oxides particles on the outer surface of A zeolite, unless iron salt concentration (0.01 M) is increased, which gives the absorption in the range of 350-550 nm taking into account, the observation of Abe et al. [8, 9].

We report the first observations of ferromagnetism above room temperature for dilute (<4 at.%) Fe-embedded A zeolite, Fig.9.(d). The Fe is found to carry an average magnetic moment of $0.16 \mu_{\text{B}}$ per ion. Our ab initio calculations find a valance state of Fe^{2+} and

that the magnetic moments are ordered ferromagnetically, consistent with the experimental findings. We have obtained room-temperature ferromagnetic ordering in the powder form of the nanocomposite material. The unique

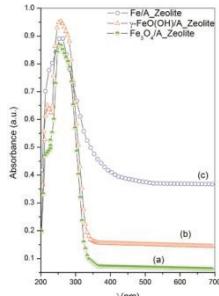


Fig.8. The DRUV-VIS Spectra of

(a)- γ -Fe₂O₃/A,
(b)- γ -FeO(OH)/A,
(c)-(Fe₂O)⁴⁺/A Zeolite.

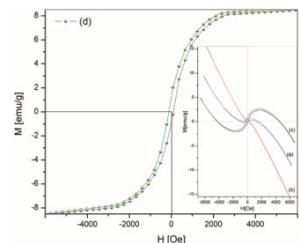


Fig.9. The Magnetization measurements of

(a)- γ -FeO(OH)/ γ -Fe₂O₃/A
mEgFe⁺³/1gA 0.9
(b)- γ -FeO(OH)/A_0.15 mEgFe⁺³/1gA
(c)-(Fe₂O)⁴⁺/A 1.5 mEgFe⁺³/1gA
(d)-Fe₃O₄/ γ -FeO(OH)/ γ -Fe₂O₃/A_2.2 mEgFe⁺³/1gA

feature of our sample preparation was the low-temperature processing. When standard high-temperature ($T > 700$ °C) methods were used, samples were found to exhibit clustering and were not ferromagnetic at room temperature, Fig.9.(a), (b) and (c). This capability to fabricate ferromagnetic Fe-embedded A zeolite semiconductors promises new spintronic devices as well as magneto-optic components.

The electrical conductivity of zeolites in their cation forms and with semiconductor clusters was studied as a function of temperature Fig.10.

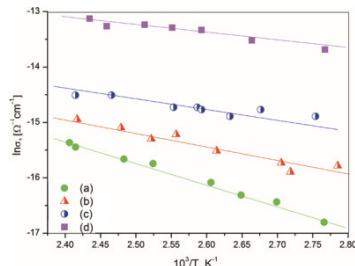


Fig.10. The electrical conductivity as a function of temperature and the iron charge

The formation of semiconductor clusters into the zeolite channels determines the increase in electrical conductivity and the sharp decrease in the activation energy of electrical conductivity, Table 1.

Table 1. The values of activation energy of electrical conductivity.

Sample	(a)	(b)	(c)	(d)
E_a , eV	3.02	1.86	1.51	1.05

The differences in ΔE_a values, calculated from the dependence $\sigma=f(10^3/T)$, can be related to the substitutional or interstitial Na impurities. The changes in electrical properties are due to transformations in the density of electronic levels as a function of the size, known as quantum size effects.

5. Conclusions

In the present study, the superparamagnetic iron oxide nanocomposite with particle size in the order of 200-400 mesh was targeted to satisfy its use in the spintronics domain. In most reports, however, the experimental conditions have been reached through a “trial and error” approach, with little consideration for theoretical basis of the solution chemistry of the reaction system. A rational approach has been adopted to synthesize the magnetic phases of Fe_3O_4/γ - Fe_2O_3 in the zeolithic cavities and channels based on the quantitative analysis of different reaction equilibria. The results of the thermodynamic modeling [1], together with the available kinetic information of relevant reactions, have been used for the selection of the optimum experimental conditions.

Where traditional electronics are based on control of charge carriers [n-type or p-type], practical magnetic semiconductors would also allow control of quantum spin state (up or down). This would theoretically provide near-total spin polarization (as opposed to iron and other metals, which provide only ~50% polarization), which is an important property for spintronics applications, eg spin transistors.

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* Corresponding author: r1bosinceanu@yahoo.com