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Synthesis and characterization of FeO(OH)/Fe_3O_4 nanoparticles encapsulated in zeolite matrix

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Nanoparticles and nanoclusters of FeO(OH)/Fe_3O_4 have been incorporated by co-precipitation in the clinoptilolite channels. In the present study, we demonstrate the coexistence of paramagnetic and superparamagnetic Fe(III) in clinoptilolite. The bound of trivalent iron in clinoptilolite results in the formation iron oxide nanoclusters in microvoids, and stabilize AlO_4 tetrahedral in the aluminosilicate matrix. The resulting non-framework and bound Fe(III) exhibit superparamagnetic and paramagnetic properties, respectively. The dual behavior of Fe(III) in CLI is deduced using various analytical and spectroscopic techniques, e.g. X-ray diffraction (XRD), diffuse reflectance ultraviolet-visible (DRUV-VIS) and magnetization measurements at room temperature with vibrating magnetometer.

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1. Introduction

Nanosized materials have received significant attention due to their outstanding physic-chemical properties. Several diverse applications of these materials, e.g. high density magnetic recording, magnetic fluids, colors imaging, magnetic refrigeration as well as in photocatalysis, nonlinear optics, solar cells, photosensors and light emitting diodes, have triggered considerable research activities in the area of nanotechnology [1]. Also, nanoscale magnetic particles exhibit a remarkable physical phenomenon, videlicet. superparamagnetism [2] and we known as clusters is related of the concept so-called quantum size effect, which arises as a result of the (blue) shift in the optical absorption edge of nanoparticles [3]. Nevertheless, from a viewpoint of nanoclusters in confined environment, e.g. micropore of certain molecular sieves (zeolites), only little effort has been directed. The well-defined and regular pore structure of zeolites offer a unique microenvironment for the confinement of nanosized material [4], thereby, the smaller pore sizes of these materials amplify their selectivity as molecular hosts. On the other hand, recently zeolites, natural and synthetic, and their ion exchanged forms have been reported as precursors for various nanomaterials [5]. The tetrahedral members of the natural family, CLI, have been considered ideal hosts for a number of potential guest molecules [6].

In view of the possibility of Fe(III) occupying the various available sites in the silicate matrix, non-framework and extra framework positions, we have carried out a careful investigation on the incorporation of iron oxide nanoparticles in clinoptilolite in order to unravel mechanisms involved in these systems, videlicet to determine the features of iron in the zeolitic structure and the particle size distribution of the iron conglomerates produced in the confinement process. All the samples were systematically characterized using various physic-chemical methods such as X-ray diffraction (XRD), UV–Visible spectroscopy, and room temperature magnetic measurements via magnetic method.

2. Synthesis nanoparticles of FeO(OH)/Fe_3O_4 in clinoptilolite

2.1. Theoretic Model

Chemical coprecipitation can provide uniform nucleation, growth and aging of the nanoparticles in the zeolite channels on base a two models: The electrostatic model, fig.1, is for determine optimum operation conditions for ionic exchange and the thermodynamic model, fig.2, is for simulate different chemical reactions taking place in the system of concern to synthesize the magnetic nanoparticles of customized size and shape. Under surrounding conditions, thermodynamic modeling of the different phase formation can be calculated from the changes of the free energy, ΔG, of the reaction under given conditions. Iron exists in three oxidation states, therefore, redox reactions must be taken into consideration. The formation of the different iron species are correlated through different redox reactions: $Fe(s) \rightarrow Fe^{2+} \rightarrow Fe^{3+}$ (1). Magnetite can be obtained by controlled oxidation of Fe^{2+} in solution according to the following equation

$$3Fe^{2+} + O_2 + 2OH^- \rightarrow Fe_3O_4 + 2H^+ \qquad (2)$$

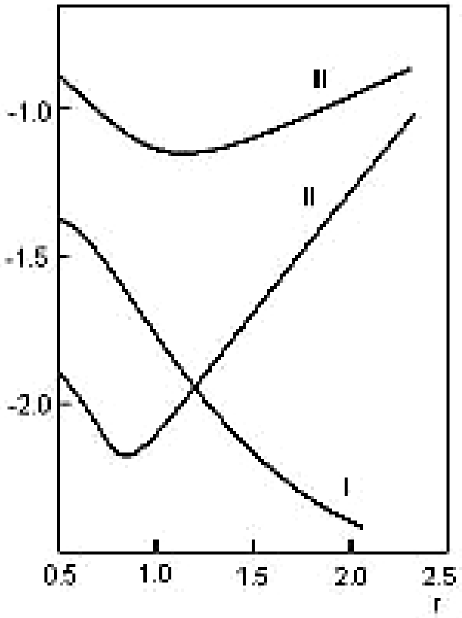

Fig.1.The variation of reduced ionic potential vs. ionic ray of Fe^{2+} and Fe^{3+} cation in CLI

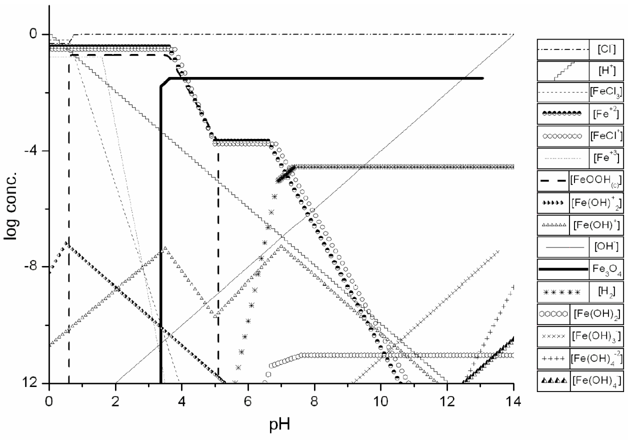

Fig. 2.Thermodynamic calculations of the concentrations of Fe^{2+} and Fe^{3+} species formed at different solution pHs.

The kinetics for the oxidation of Fe^{+2} is slow and is difficult to control, therefore, it is more practical to control the formation of magnetite through the use of the mixture of Fe^{2+} and Fe^{3+} salts. In this case, the oxidation of Fe^{2+} should be avoided. The control of the size, shape and composition of nanoparticles depends on the type of salts used (chlorides, sulphates, nitrates, perchlorates, etc.), Fe^{2+} and Fe^{3+} ratio, pH and ionic strength of the media [7].

According to the thermodynamics model, alongside of magnetite it is formation lepidocrosite in small amount by redox reaction and the active centers of zeolite are deactivation with some ultrastable species of the trivalent ion bound tetrahedral.

3. Experimental Part

3.1. Starting materials

The following materials were used for the loading *$FeO(OH)/Fe_3O_4$*. Natural zeolite clinoptilolite of grain size 0.3-0.5 nm from the locality Mârşid-Romania, Sodium hydroxide (NaOH; Loba, 98%), Iron(III) chloride nonahydrate ($Fe(Cl)_3$; Alfa, 98%), iron(II) nitrate anhydrous ($Fe(NO_3)_2.6H_2O$, 98%), and distilled water. All the chemicals were used in the as-received forms without any further purification. In order to remove the impurities, the powdered clinoptilolite was submitted to an acid treatment, using 1N HCl solutions and thermally treated in their sodium cation form at 673K during 4h.

3.2. Encapsulate of $FeO(OH)/Fe_3O_4$

Natural zeolite clinoptilolite was added into the solution of iron ions (0.009M) after purify, decationisation at 333K temperature action period of six hours in solution 0.018N of NH_4OH ammonium hydroxide and thermally treated, prepared from $Fe(NO_3)_2.6H_2O$ and $FeCl_3$ anhydrous salts (Fe2+/ Fe3+ = 0.5) by continuous stirring for 1h in nitrogen atmosphere at selected temperatures 60, 70, 80, 90°C. The amount of zeolite was adjusted to obtain the zeolite/iron oxide ratio of 5:1. A solution of NH_4OH (0.005M) was added drop by drop to the suspension of zeolite and iron ions to precipitate particles of iron oxides. The final product was filtrated, washed and dried at temperature 70 °C.

3.3. Characterization

The crystalline structure of the parent zeolite and modified zeolite were studied by X-ray diffraction analyses. Powder XRD patterns were recorded in the large angle ($2\theta=30\text{-}80^{\circ}$) region with DRON 2 diffractometer using a $CoK_{\alpha 1}$ radiation (U: 25KV, I: 20mA, U_d: 40V) with wavelength of 1, 7889 Å and a step size of 0.01° in laboratory of structural analysis of faculty of physics by Iaşi. 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).

4. Results and discussions

Fig. 3 shows the diffraction patterns of $Fe(OH)/Fe_3O_4$CLI sample and pure clinoptilolite. It is clear from the figure that the loaded samples retain monoclinic CLI structure even after the loading and the subsequent treatments. It is expected that the loaded nanoparticles preferentially reside in the microporous of clinoptilolite and therefore no considerable change is anticipated in XRD data.

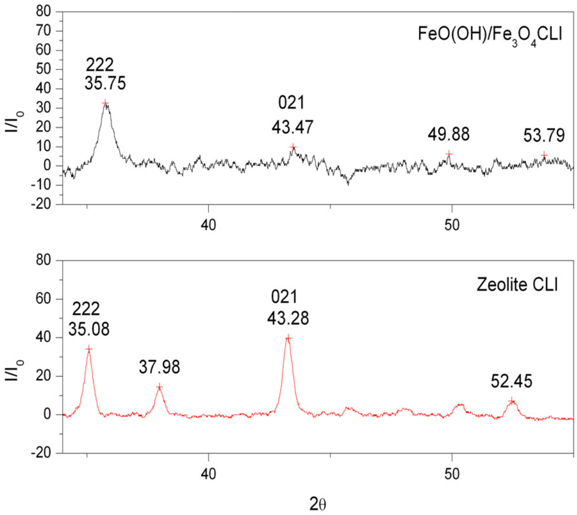

Fig.3. XRD patterns of zeolite CLI and FeO(OH)/Fe_3O_4CLI.

It is important to note that the d_{222} spacing values of the loaded samples d_{222}=2.860Å for Fe(OH)/Fe_3O_4CLI were increased significantly as compared to the unloaded sample d_{222}=2.555Å for CLI. Such an expansion in the unit cell dimension may possibly due to the isomorphous substitution of trivalent iron for the tetravalent aluminum in the framework.

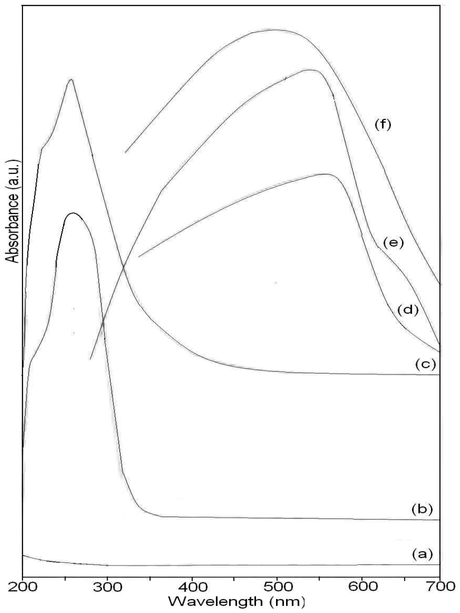

Fig.4. DR UV-VIS spectra of: (a) calcined CLI; (b) FeO(OH)/Fe_3O_4CLI; (c) FeCLI; (d) Fe_3O_4; (e) FeO(OH); (f) calcined FeO(OH).

The DRUV-VIS spectra, fig.4, of loaded samples show absorption band at approximately 250nm, whereas the bulk FeO (OH), Fe_3O_4 and calcined FeO(OH), show strong maxima at 535, 560 and 515nm, respectively [8]. It is interesting to note that FeCLI also absorbs nearly in the same region about 250 nm as that of loaded samples [9].

Thus, the occurrence of these absorption bands in this range can be interpreted for both framework trivalent iron and magnetite nanoparticles (non-framework) inside the micropores. Hence, must be taken in deducing the information regarding the nature of the species on the basis of DRUV-VIS spectra alone.

In this DRUV-VIS study, we have not observed the formation of iron oxide particles on the outer surface of clinoptilolite, unless iron salt concentration (0.03M) is increased, which gives the absorption in the range of 350-550 nm.

The Figs. 5, 6, 7, 8, 9 and 10 show the magnetization measurements which are carried out at room temperature and represent the samples obtained at 333, 353, 363, 373, 393 and 413K respectively. From this figures is seen that the samples obtained at different temperature have a paramagnetic, supeparamagnetic comportment which co-exist, thus at a critical value of magnetic field about 3KOe to take place the fluctuation of molecular field. This phenomenon appear because magnetic structure of magnetite is under the form of star and is specific for low dimensional magnetic particles about <2nm. The size and direction of the magnetization vector of a magnetic sample are influenced of the distribution of Fe^{2+} and Fe^{3+} ions in agreement with electrostatic model, the electronic configuration and the electrostatic energy. This structure is stable only at low temperature.

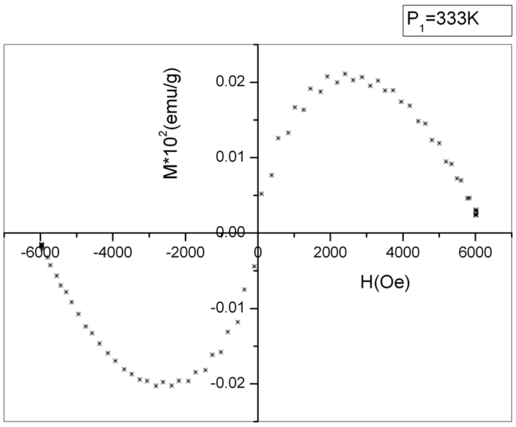

Fig. 5. Magnetization measurement of the 333K obtained sample at 293K (vibrating magnetometer).

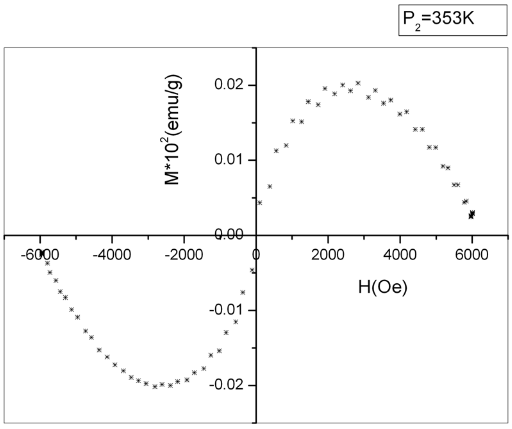

Fig.6. Magnetization measurement of the 353K obtained sample at 293K (vibrating magnetometer).

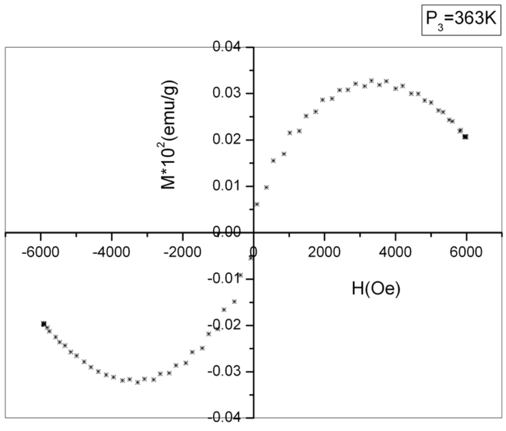

Fig.7. Magnetization measurement of the 363K obtained sample at 293K (vibrating magnetometer).

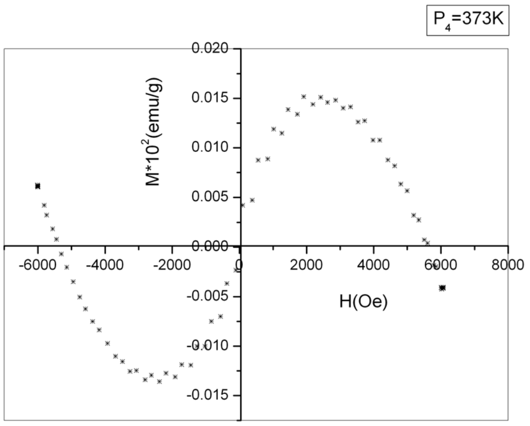

Fig. 8. Magnetization measurement of the 373K obtained sample at 293K (vibrating magnetometer).

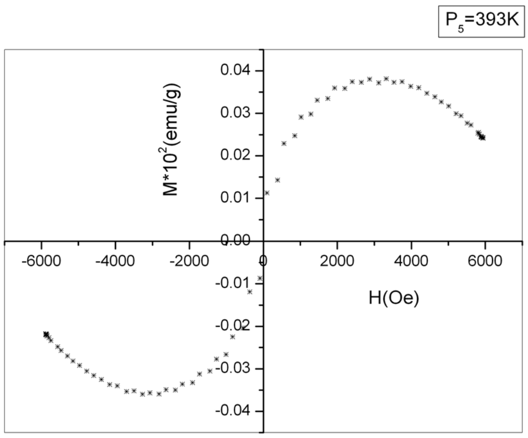

Fig. 9. Magnetization measurement of the 393K obtained sample at 293K (vibrating magnetometer).

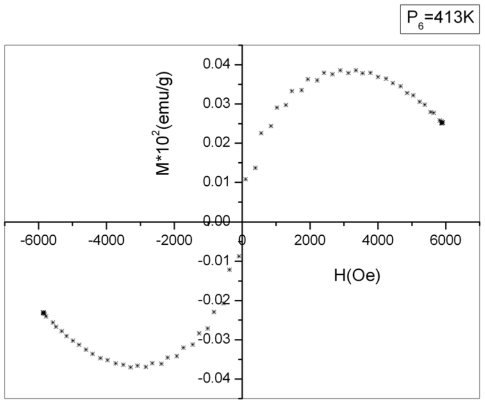

Fig.10. Magnetization measurement of the 413K obtained sample at 293K (vibrating magnetometer).

5. Conclusions

The wet chemical routes to magnetic nanoparticles encapsulated in the zeolite matrix are simpler, more tractable and more efficient with appreciable control over size, composition and the shape of nanoparticles obtained into the clinoptilolite channels. Iron oxides (Fe_3O_4 and FeO(OH)) can be synthesized through the co-precipitation of Fe^{2+} and Fe^{3+} aqueous salt solutions in the zeolite channels by adding of a base conform both the electrostatic and thermodynamic models.

Singlecrystalline nanoparticles of Fe_3O_4 and FeO(OH) of size ranging between 4-7Å were prepared in the aluminosilicate matrix and characterized by the magnetic measurements. These results show that co-precipitation process is well adapted for isolating controlled size magnetic nanoparticles.

FeO(OH)/Fe_3O_4CLI systems showed evidence for the co-existence of paramagnetic and superparamagnetic Fe(III) in microporous matrix.

The absorption band of the isomorphously substituted Fe(III) in microporous framework, i.e. FeCLI, also appears in the same region with FeO(OH)/Fe_3O_4CLI.

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