Magnetic interactions in cubic iron oxide magnetic nanoparticle bound to zeolite

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ABSTRACT

Magnetic interaction of the magnetite (Fe_3O_4) nanoparticles grown on zeolite has been studied. XRD patterns show that in the presence of 25–75 mg of zeolite the average particle size of Fe_3O_4 decreases to ≈ 6 nm, but with the increase of zeolite content (75 mg $< x <$ 200 mg) the Fe_3O_4 particles have 10.6 nm in size saturating to 3 nm above 180 mg. Average hyperfine field of Fe at octahedral and tetrahedral sites vary with particle size. With the increase of zeolite 13x from 0 to 100 mg, the saturation magnetization decreases from 63 to 53 emu/g. Mössbauer studies show the presence of different Fe_3O_4 micro-environments, possibly in pores and on the surface of zeolite. Transformation of the superparamagnetic doublet to sextet at 80 K can indicate a variation in the magnetic interaction. At low temperature the interaction between Fe_3O_4 at the pore and at the surface enhances the magnetic ordering. The nanoparticles in the pores of zeolite are connected with the surface particles in low zeolite content and get isolated as the amount of zeolite increases.

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1. Introduction

Magnetic properties of cubic nano-iron oxides (Fe_3O_4/γ–Fe_2O_3) are of considerable scientific interest because of their applications in memory devices, hyperthermia and enhanced magnetic resonance imaging [1–3]. The semiconducting property and high Curie temperature (T_c) favor the extension of application to spintronics [4]. These magnetic iron oxides have high saturation magnetization and low toxicity which favors their use in bioapplications [5]. Capping the nanoparticles with organic materials or ceramics [6–7] improved the biocompatibility and stability of the nanoparticles. In these processes the nanoparticles were prevented from direct contact with the targets which might reduce the catalytic activities. In the previous studies the growth of Fe_3O_4 nanoparticles was restricted to 3–11 nm depending upon the ratio of the zeolite to Fe_3O_4 precursor salts [8–10]. The onset temperature for the transformation of γ-Fe_2O_3 to α-Fe_2O_3 in the composite with 25 mg of zeolite and Fe_3O_4 was enhanced by more than 100 K as compared to the pure Fe_3O_4. This transformation temperature increases with increase in the zeolite concentration [8–9]. The agglomeration of the nanoparticles synthesized with 1:1 weight ratio of zeolite and Fe_3O_4 precursor salt was observed to have

higher activation energy [11]. The initial temperature of agglomeration was 370 K higher than the pure Fe_3O_4 [11]. The magnetic property of the nanoparticles is in correlation with the morphology and particle size. The Verwey transition was observed in the octahedral shaped Fe_3O_4 whereas it was absent in the similar size spherical particles [12]. The Neel relaxation time, $\tau = \tau_o \exp(KV/kT)$, where, τ_o is a constant with a value of the order of 10^{-10}–10^{-12} s, K is the anisotropy energy per unit volume, V is the volume of the particle, and kT stands for the thermal energy can be used to determine the particle size, since particles with varying volume have different relaxation time. Literature reports show that (local) structural information derived from Mössbauer spectra is in agreement with the size distribution from TEM analysis [13]. Capping of nanoparticles with organic and ceramic materials reduces the interaction among the particles and satisfies the Neel relaxation equation. Among the bare particles, the magnetic interaction is high and can result in a higher blocking point which can be related to deviation from the Neel relaxation equation as: $\tau = \tau_o \exp\{(U_o + \Omega)/kT\}$, where U_o is the single-particle energy barrier and $\Omega = kT \ln(\tau_i/\tau_j)$, where τ_i and τ_j are the relaxation times of the ith and jth samples respectively [14]. Studies on the relaxation phenomenon in the samples with mixed magnetism i.e. existence of superparamagnetism along with magnetically ordered nanoparticles can give the morphological information which may not be possible to be derived from microscopy.

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The magnetization and relaxation effect of the Fe_3O_4 nanoparticles grown systematically with varying zeolite concentration at 300 K and 80 K have been investigated in the present study.

2. Experimental details

2.1. Synthesis

The magnetite nanoparticles were synthesized through co-precipitation [9]. The chemicals $FeCl_3.6H_2O$, $FeSO_4.7H_2O$ and NaOH were purchased from Sigma Aldrich (São Paulo, Brazil) and Zeolite 13x was obtained from Union Carbide. The chemicals were used without further purification. The Fe^{3+} and Fe^{2+} solutions were prepared for 0.4 and 0.2 M in 20 ml using distilled water. The crushed and dehydrated zeolite 13x at 523 K (4 h) was mixed with the Fe precursor solution for 15 min and then NaOH was added rapidly to increase the pH to 10. The solution was maintained at 363 K during the synthesis. The dark brownish black precipitate was washed several times with distilled water and acetone and dried at 333 K for 24 h. Different weights of zeolite were taken for the synthesis which is indicated as FeX (where X: 0, 25, 50, 75, 100, 180, 200 and 250 mg of zeolite 13x).

2.2. Characterization techniques

RIGAKU Ultima IV X-ray diffractometer, with a Cu-Kα as radiation source, and Ni-filtered with CBO monochromator operating at 45 kV and 15 mA has been used for structural identification. The measurements were performed in step width of 0.05 and scan rate of 2°/min. High resolution transmission electron microscopy (HRTEM) images were obtained by using a JEOL 2100 microscope to determine the particle morphology. The Mössbauer spectra were recorded with a constant acceleration velocity transducer coupled to ^{57}Co in Rh matrix source with an initial activity of 25 mCi in the standard transmission geometry at 300 K and at 80 K in a JANIS cryostat. The velocity calibration per channel was done with a (1.9 mg $^{57}Fe/cm^2$) iron foil.

3. Results and discussion

Fig. 1 depicts the X-ray diffraction (XRD) patterns showing single phase of cubic iron oxide (Fe_3O_4). The width of the XRD lines increases at the initial concentration of zeolite (25–75 mg) with the zeolite content, then abruptly decreases when the concentration of zeolite reached 100 mg while it shows a slight increase between 100 and 180 mg. Furthermore, there is substantial increase in the width of the corresponding diffraction lines observed at 180 mg, which remains almost constant above this concentration of zeolite. By using the Sherrer formula the particle size of magnetite was derived from the linewidths of XRDs. The particle size as a function of zeolite content is shown in Fig. 2, together with the dependences of the magnetization and the hyperfine magnetic field. The dependence of the particle size of magnetite on zeolite content first decreases at low zeolite concentration between the 25 mg and 75 mg interval, then there is an abrupt increase at 100 mg followed by a slight decrease till 180 mg. After an abrupt decrease at 180 mg a very slight decrease is characteristic of the tendency of variation of size between 180 mg and 250 mg interval. Very similar tendencies were observed in the magnetization and in the average hyperfine fields (Fig. 2) with the variation of zeolite content too.

Adding zeolite during the preparation of the magnetic particles can allow for the control of magnetic particle growth [10]. To understand this we need to take into consideration that Zeolite
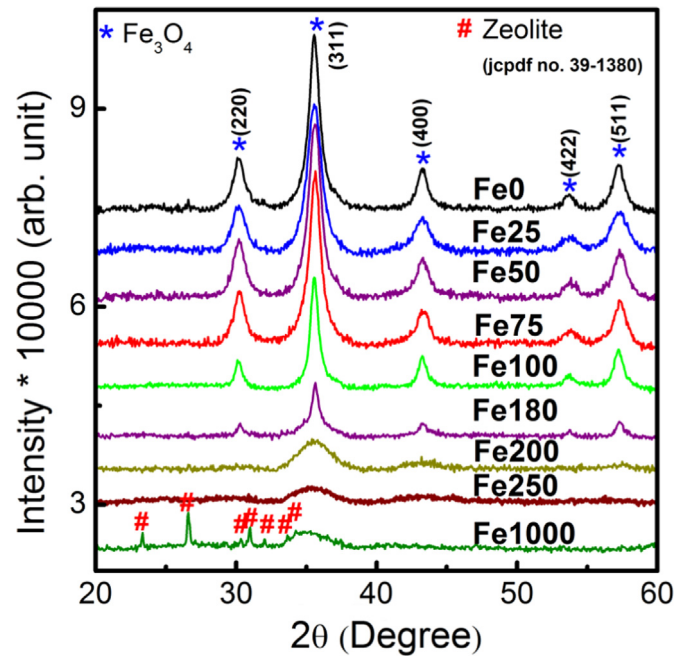

Fig. 1. XRD spectra of Fe_3O_4 with 0 mg (Fe0), 25 mg (Fe25), 50 mg (Fe50), 75 mg (Fe75), 100 mg (Fe100), 180 mg (Fe180) and 200 mg (Fe200), 250 mg (Fe250) and 1000 mg (Fe1000) of zeolite 13x.
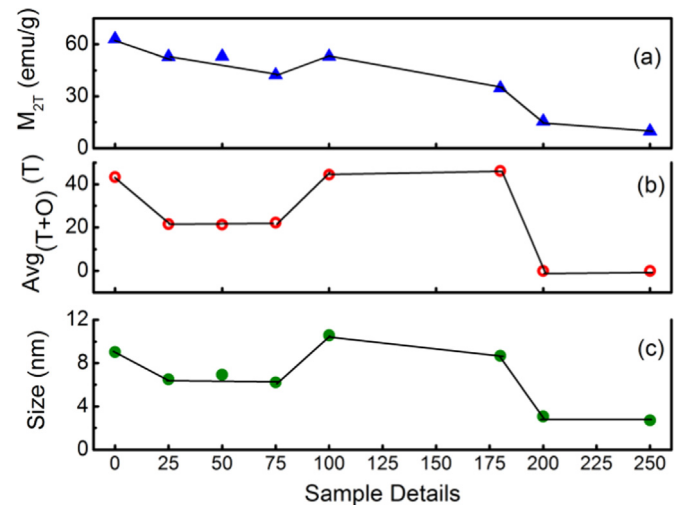

Fig. 2. Magnetization at the external field of 2 T (a), average of the hyperfine field of Fe atoms at tetrahedral and octahedral Fe_3O_4 (b), particle size (c) of the Fe_3O_4 in the presence of 0 (FeO), 25 (Fe25), 50 (Fe50), 75 (Fe75), 100 (Fe100), 180 (Fe180), 200 (Fe200) and 250 mg (Fe250) of zeolite 13x.

13x is a biocompatible inorganic network of SiO_4 and AlO_4 tetrahedrally connected to form two main cages (α and β) [15]. The presence of uncompensated electronic charge (e^-) at the sites of Al causes it to have a high affinity to cations [16]. This results in the nucleation of the nanoparticles in the pores. There is a report that the zeolite can accommodate particles at the pores up to 2 wt% [17]. Higher weight will leads to the nucleation at the pores as well as on the surface.

This decrease in the average magnetic hyperfine field (Fig. 2b) measured via magnetic interaction between the electrons and Fe nuclei in Fe_3O_4 as function of zeolite content is due to the effect of decrease in the particle size [18] and decrease in the magnetization.

The saturation magnetization of the samples (Fig. 2. a) recorded at 2 T external magnetic field shows similar dependence on the