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Stability and magnetic interactions between magnetite nanoparticles dispersed in zeolite as studied using Mössbauer spectroscopy

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ABSTRACT

Stability of superparamagnetic magnetite nanoparticles as formed in Zeolite has been addressed in a detailed manner based on isochronal annealing studies using Mössbauer spectroscopy. A strong binding of these nanoparticles in Zeolite has been deduced as the coarsening of the nanoparticles is observed following annealing treatments beyond 825 K. In addition, the magnetic interactions between these superparamagnetic magnetite nanoparticles in the as dispersed condition in Zeolite have been elucidated by means of low temperature Mössbauer studies. A strong dependence of the dipole–dipole interactions between superparamagnetic particles of cubic iron oxides is deduced based on this study.

1. Introduction

Nanoparticles of magnetite and maghemite find a number of applications involving high density magnetic recording, drug delivery and hyperthermia [1–3]. For a reliable application of these cubic iron oxide nanoparticles it is important that these nanoparticles remain quite stable both physically and chemically. Stability of the nanoparticles is in general achieved by means of growing the nanoparticles in desirous templates or by using suitable capping agents. With respect to high temperature applications it is important to understand the aspects of thermal stability of the nanoparticles. Especially a strong binding of the nanoparticles in the chosen template structure is preferred for any high temperature applications. In order to prepare these nanoparticles by different methods [4,5] either with desirous capping structures or with templated structures of these nanoparticles [4–7] based upon the applications, it is very important that the magnetic interactions between the nanoparticles is understood [8–11].

Zeolite 13X, a bio compatible matrix, consisting of basic tetrahedral structural units of SiO_4 and AlO_4 with Si or Al in the center of the tetrahedron is chosen as a template for the present study. Tetrahedral structural units of SiO_4 and AlO_4 are joined to form a larger sodalite unit (SU) with [Si]/[Al] ratio close to 1.23 and the cavity inside SU is known as beta cage. Zeolite has been extensively used for binding heavy cations in pores and cages. In addition the binding of nanoparticles of different metal and oxide particles by Zeolites has been reported in the literature [12–17]. Mössbauer spectroscopy has been established as one of the powerful techniques [7–11] for understanding the various structural and magnetic properties of magnetic nanoparticles.

Considering single domain magnetic particles, the relaxation time for magnetization reversal τ, is given by the Neel-Brown expression as $\tau=\tau_o \exp [K_{eff}V/k_BT]$. Where K_{eff} is the magnetic anisotropy constant, V is the particle volume and k_B is the Boltzmann's constant. The value of τ_o is of the order of 10^{-12}–10^{-9} s and is almost temperature independent [7,8,10,11]. If the particle magnetic moment reverses at times shorter than the experimental time scales, the system comprising of such particles is in a superparamagnetic state. If the spin reversal time of these magnetic nanoparticles is longer than the measurement time then the system is understood to be in a blocked state.

In the case of ^{57}Fe based Mössbauer spectroscopy the experimental measurement time is represented by the isomeric state lifetime corresponding to the level $I=3/2$ of the ^{57}Fe resonant absorbers (≈ 10 ns). Thus the ^{57}Fe based Mössbauer spectroscopy has been used to study the spin relaxation behavior of magnetic nanoparticles.

Power of the Mössbauer spectroscopy to distinguish between isolated superparamagnetic particles of iron oxides as bound in the Zeolite and the coarsened particles formed subsequent to detrapping and migration of nanoparticles has been exploited in the present study. Further this work is motivated at studying the magnetite interactions between magnetite nanoparticles in the as formed condition in Zeolite matrix. A detailed comparison of these results (obtained in both of the above studies with that of bare nanoparticles of magnetite prepared using similar method) is

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made to elucidate the binding of magnetite nanoparticles as dispersed in Zeolite and the magnetic interactions between them.

2. Experimental details

Bare magnetite nanoparticles were prepared using coprecipitation method with $FeCl_3$ and $FeSO_4$ $7H_2O$ as the precursor solutions of Fe^{3+}, Fe^{2+} respectively taken in appropriate compositions as described elsewhere [4,7,8,17]. In order to prepare magnetite dispersed Zeolite system, dried Zeolite is first immersed in the Fe precursor solution with the ratio of concentrations of $Fe^{2+}$and Fe^{3+}as $[Fe^{2+}]$:$[Fe^{3+}] \approx 1{:}2$ and then ultrasonicated for 1 h. NaOH solution was added rapidly to raise the pH up to 10. The precipitate is separated after mixing and washed with water to get rid of radicals and then dried at 373 K. These samples are characterized by XRD using Cu-K_α radiation. TEM analysis was carried out using a Philips CM 12 microscope with super twin objective lens at 120 kV.

SQUID based magnetometer is used for studying the variation of magnetization with temperature in the zero field cooled and field cooled conditions of the magnetite formed in the zeolite. ^{57}Fe Mössbauer studies have been carried out using Wissel based spectrometer operated in transmission geometry and in constant acceleration mode. ^{57}Co dispersed in Rh matrix to a specific activity of 50 mC has been used as a source for Mössbauer measurements. Each Mössbauer spectrum has been acquired in 1024 channels. Mössbauer Spectra were fitted to Lorentzian line shapes of line width Γ_i using a non linear least squares program to obtain hyperfine parameters such as isomer shift δ_i, quadrupole splitting Δ_i and magnetic hyperfine fields B_{hf}^i experienced by relative fractions f_i of distinct ^{57}Fe absorber atoms. The velocity calibration were carried out using 10 μm thick iron foil at 300 K. The values of isomer shifts presented in this study are given with respect to that of α-Fe absorber.

Binding of nanoparticles by Zeolite is addressed by means of carrying out isochronal annealing studies. Bare and zeolite dispersed nanoparticles were subjected to isochronal annealing at different temperatures and at a partial pressure of 2×10^{-6} mbar for a step time of 1 h. Subsequent to each annealing step the Mössbauer measurements have been carried out at 300 K. In order to address the magnetic interactions between the nanoparticles, the Mössbauer studies have been carried out at different temperatures from 300 K down to 85 K in both bare and zeolite dispersed magnetite nanoparticles.

3. Results and discussion

XRD patterns corresponding to bare, Zeolite dispersed nanoparticles in the as prepared condition and subsequent to annealing at 973 K are shown in Fig. 1. These show that all the samples crystallize with cubic spinel structure, having a space group Fd-3m. Mean size of the as prepared particles are deduced to be around 5 nm while annealing treatment at 973 K is seen to result in the coarsening of the particles to an average size of 8 nm. Based on the XRD patterns corresponding to bare and zeolite dispersed nanoparticles, it is interpreted that these nanoparticles are due to magnetite.

TEM micrograph of these Zeolite dispersed nanoparticles is shown in Fig. 2. It is observed that the nanoparticles are in the size range of 3–8 nm, with a mean value close to 5 nm matching with the particle size deduced by XRD. The high resolution image provided in the inset of Fig. 2, shows the presence of (400) lattice planes of magnetite.

Mössbauer spectra obtained in the case of bare and Zeolite

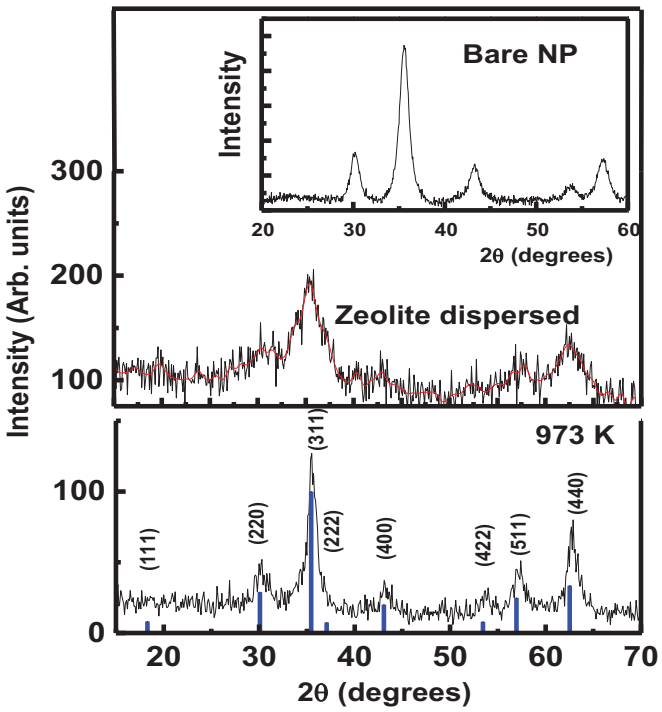

Fig. 1. XRD patterns corresponding to magnetite nanoparticles as dispersed in Zeolite matrix and subsequent to annealing treatment at 973 K. (hkl) indices are indexed for magnetite peaks.

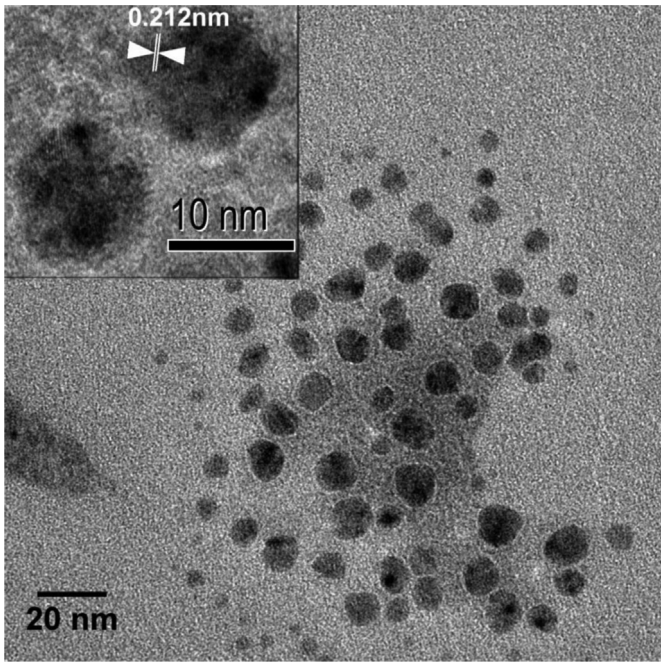

Fig. 2. TEM micrograph of Zeolite dispersed with magnetite nanoparticles with inset showing the HREM image of the (400) planes in a magnetite particle.

templated magnetite nanoparticles result in a doublet as shown in Fig. 3. This is understood to be due to the superparamagnetic nature of these cubic iron oxide nanoparticles as formed in Zeolite. This implies that the spin of Fe atoms associated with magnetite nanoparticles fluctuate at a rate close to or higher than $1/\tau$, thus resulting in a superparamagnetic relaxation of spins [10,11]. The hyperfine parameters as deduced based on the analysis of the spectra result in an almost similar values of isomer shifts and quadrupole splitting in both of these cases as shown in Table 1