

# Mössbauer study of stability and growth confinement of magnetic $\text{Fe}_3\text{O}_4$ drug carrier

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**Abstract** Bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ /zeolite composites have been investigated by Mössbauer spectroscopy. A confined growth of the nanoparticles has been observed after introduction of zeolite in the process of precipitation. Increase in the concentration of zeolite further decrease the particle size. A comparative study on the synthesis with zeolites 13x and ZSM5 has been done. Annealing on these nanoparticles shows that apart from the confinement of nanoparticles, zeolite enhances stability on the nanoparticles.

**Keywords** Mössbauer spectroscopy · Zeolite · Superparamagnetic iron oxide

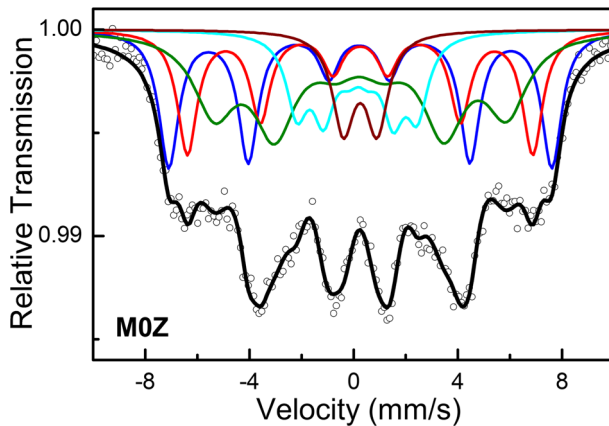
## 1 Introduction

Magnetic nanoparticles have wide applications e.g. miniaturization of devices, drug delivery, hyperthermia, heavy ion separations and batteries etc. Magnetic iron oxides i.e. magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles are important magnetic nanoparticles having various applications as mentioned [1–4].  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized through various methods such as co-precipitation, sol gel, solvothermal, plasma, reverse micelle etc [5–9]. However synthesized nanoparticles have a wide distribution in particle size. A remedy to narrow down the particle size distribution is to synthesize into a template [10]. In the present study, zeolites 13x and ZSM5 were used as template for synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles as they have specific charge affinity sites which may act as nucleating center of the nanoparticles [11] and they contain nontoxicity materials which are often used for loading the drug such as doxorubicin [12]. Tetrahedral groups of  $\text{SiO}_4$  and  $\text{AlO}_4$  are the basic units of zeolite, with Si and Al at the center of the tetrahedron. Each  $\text{AlO}_4$  tetrahedral group has an uncompensated charge  $e^-$  and therefore a positive ion such as  $\text{Na}^+$ ,

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**Fig. 1** Mössbauer spectrum of the bare  $\text{Fe}_3\text{O}_4$

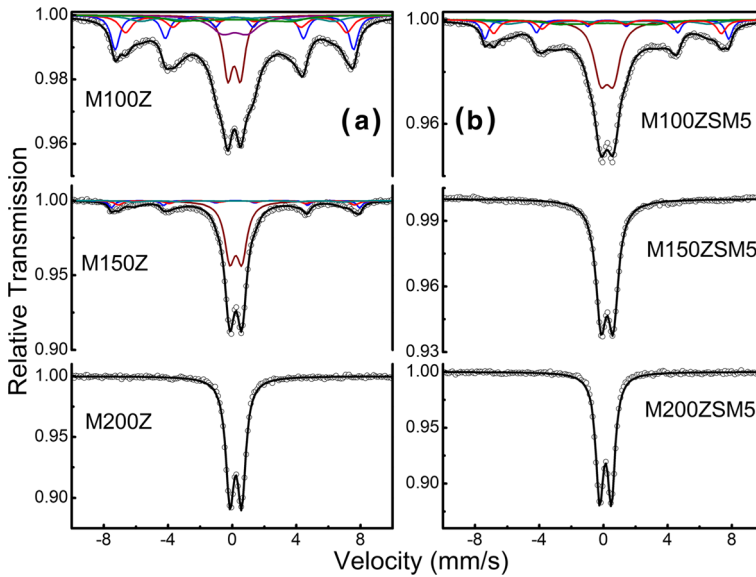
$\text{Ca}^{2+}$  etc. occupy sites near to  $\text{AlO}_4$  in the course of formation. The stoichiometric formula for zeolite 13X is  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$  [13] and ZSM5 is represented by  $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O}$ , where  $n < 27$  [14]. Zeolite has been reported to have high affinity to cations such as Ru, Cu etc [15, 16]. The high adsorbing characteristics of the zeolite has been utilized to confine the growth of iron oxide particle.

## 2 Experimental details

$\text{Fe}_3\text{O}_4$  nanoparticles were synthesized through co-precipitation route. Precursor solutions of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were taken into 1:2 molar ratios. NaOH was added rapidly when the solution achieved 333 K and the pH was maintained at 10 to precipitate  $\text{Fe}_3\text{O}_4$  nanoparticles. To prepare composites of zeolite and iron oxide nanoparticles, zeolite 13x and ZSM5 were crushed using agate mortar and heated at 523K for 2 h in order to remove water molecules adsorbed on the surface and bound in the structure. The dried zeolite of different weight was mixed with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3$  solution and the same procedure is followed as in the case of bare  $\text{Fe}_3\text{O}_4$ . The samples are represented as  $\text{MxZ}$ , where x gives the weight of zeolite taken for synthesis and Z for zeolite 13x. The composites synthesized by ZSM5, by using a similar procedure as for 13x, are represented by  $\text{MxZSM5}$ . The precipitates were washed with distilled water till the pH reaches 7. Room temperature Mössbauer spectra were recorded using  $^{57}\text{Co}$  source dispersed in Rh matrix with an initial activity of 25 mCi. All spectra were least square fitted using Mösswin.

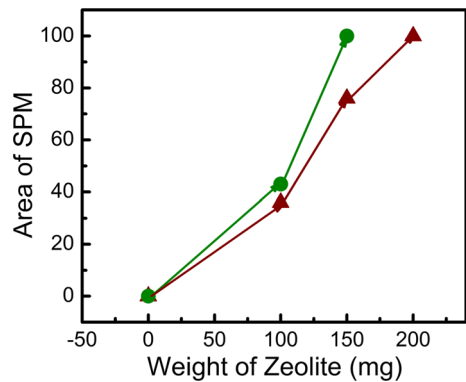
## 3 Results and discussions

Figure 1 shows the Mössbauer spectrum of the bare  $\text{Fe}_3\text{O}_4(\text{M0Z})$  fitted with four sextets and a doublet. The doublet representing the superparamagnetic particles comprise of 7 %. The subspectra experiencing hyperfine parameters of 14 and 35 T, isomer shifts of 0.27 and 0.34 mm/s, quadrupole splittings of -0.04 and 0.05 mm/s with area of 61 % is assigned to the surface disordered spin component. The fourth and fifth component with magnetic



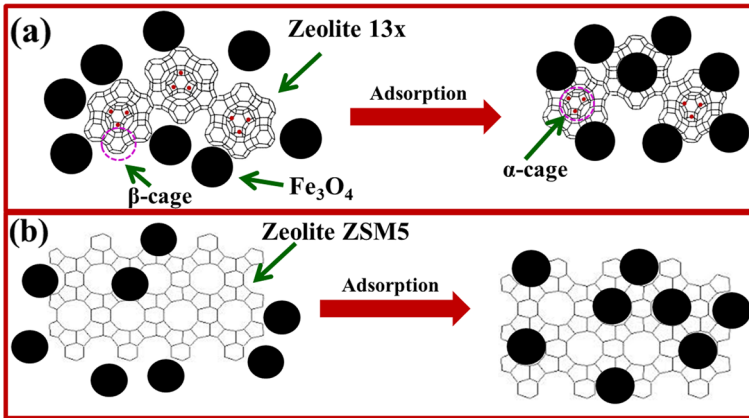
**Fig. 2** Mössbauer spectra of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized in the presence of 100 mg (M100Z), 150 mg (M150Z), 200 mg (M200Z) of Zeolite 13x (A), 100 mg (M100ZSM5), 150 mg (M150ZSM5), 200 mg (M200ZSM5) of zeolite ZSM5 (B)

**Fig. 3** Area of superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized with various concentration of zeolite 13x (▲) and ZSM5 (●)

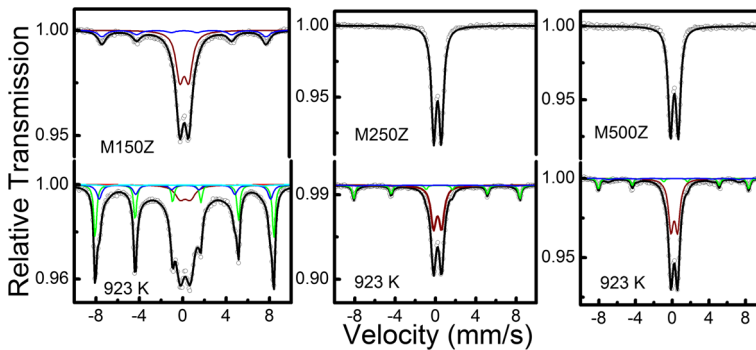


hyperfine fields of 45.6 and 41.1 T, represents the Fe atoms of tetrahedral and octahedral core sites of Fe<sub>3</sub>O<sub>4</sub>.

Zeolite is known for its high adsorption characteristics of heavy ions and molecules [17]. The adsorption effect on the growth of Fe<sub>3</sub>O<sub>4</sub> nanoparticles are investigated using zeolites 13x and ZSM5. Bare Fe<sub>3</sub>O<sub>4</sub> nucleates to a larger particle size and distribution, whereas narrowing down of the particle size is observed as zeolite is introduced during coprecipitation. Depending upon the type of zeolite the adsorption activities differs with one another. The structure is the main factor for the selective adsorption [18, 19]. The adsorption properties of Zeolites affecting the growth of Fe<sub>3</sub>O<sub>4</sub> nanoparticles are represented by the Mössbauer spectra shown in Fig. 2.



**Fig. 4** Adsorption of  $\text{Fe}_3\text{O}_4$  nanoparticles by zeolite 13x (a) and zeolite ZSM5 (b)



**Fig. 5** Mössbauer spectra of  $\text{Fe}_3\text{O}_4$  synthesized in the presence of 150 mg (M150Z), 250 mg (M250Z), 500 mg (M500Z) Zeolite 13x. And the corresponding annealed spectra at 923 K below the respective spectrum

Figure 2a shows the Mössbauer spectra of  $\text{Fe}_3\text{O}_4$  grown in Zeolite 13x, and the Fig. 2b depicts the  $\text{Fe}_3\text{O}_4$  grown in the presence of ZSM5. The superparamagnetic particles increase to 45 % from 7 % as the zeolite 13x increases to 150 mg from 100 mg. A complete superparamagnetic doublet is observed as the zeolite goes to 200 mg. But in the case of ZSM5 the particles become pure superparamagnetic by 150 mg. Therefore the adsorption of  $\text{Fe}_3\text{O}_4$  nanoparticles by ZSM5 is more significant than the zeolite 13x. The area of the superparamagnetic doublet of  $\text{Fe}_3\text{O}_4$  grown in the zeolite 13x and ZSM5 template is shown in Fig. 3. The adsorption of the nanoparticles can be further understood from the structure point of view. Figure 4 shows the structure of the zeolite and the adsorption of the nanoparticles.

Zeolite 13x has two types of cages,  $\beta$ -cage or known as sodalite unit and  $\alpha$ -cage. The diameter of  $\alpha$ -cage is 1.3 nm with the window of 0.8 nm and the  $\beta$ -cage diameter is approximately 0.6 nm and the window is of 0.22 nm. ZSM5 has 0.5 nm pore size. The growth of the  $\text{Fe}_3\text{O}_4$  nanoparticles initiates with the nucleation at the charge affinity sites of the zeolite. Higher number of nucleation center will provide finer particles, the accessibility of the pores for nucleation of  $\text{Fe}_3\text{O}_4$  is higher in ZSM5 and is

**Table 1** Least square fitted Mössbauer parameters of IS (Isomer shift), QS (Quadrupole splitting), and B<sub>hf</sub> (Internal magnetic field)

Temp (K)	IS / Fe (mm/s)	QS (mm/s)	B <sub>hf</sub> (T)	Area
M0Z	0.36(3)	1.30(0)	-	07(1)
	0.27(3)	-0.04(4)	14.3(3)	12(2)
	0.34(2)	0.05(3)	34.8(5)	49(4)
	0.36(1)	-0.01(2)	41.1(3)	15(4)
	0.34(1)	0.04(2)	45.6(2)	17(2)
M150Z	0.33(0)	0.75(0)	-	76(0)
	0.49(4)	0.06(0)	40.6(3)	10(1)
	0.41(2)	-0.06(3)	45.6(2)	08(1)
M200Z	0.32(1)	0.00(2)	47.9(1)	06(1)
	0.33(0)	0.72(0)	-	100(0)
	0.33(0)	0.80(0)	-	43(0)
M100ZSM5	0.35(2)	-0.06(4)	18.9(2)	20(0)
	0.43(2)	-0.04(0)	38.8(4)	19(2)
	0.38(2)	-0.03(2)	44.0(1)	10(2)
	0.33(1)	-0.02(1)	47.1(1)	08(1)
M150ZSM5	0.34(0)	0.75(0)	-	100(0)
M200ZSM5	0.34(0)	0.73(0)	-	100(0)

reflected in Fig. 3 where the lower particles size were achieved in the coprecipitation with ZSM5. Nanoparticles dimension is influenced by the pore size of the template. Iron oxide nucleated at higher pore size template results in higher particle size [10]. Therefore in addition to the availability of the pores for nucleation the formation of smaller particles in ZSM5 is understood as due to the lower pore size. At the initial concentration of zeolite the nucleation center at the pores is not sufficient to accommodate all the iron ions in the solution and hence the remaining iron ions precipitate on the surface of the zeolite. For the application purpose of these nanoparticles, the stability is a critical point to be established. Therefore a series of heat treatment were performed on the Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized with 150 mg (M150Z), 250 mg (M250Z) and 500 mg (M500Z) of zeolite 13x.

Figure 5 shows the the Mössbauer spectra of the as prepared and the corresponding annealed sample at 923 K for 2 h in air. Heat treatment at 923 K of M150Z results in the increased in the sextet to 63 % from 24 %, however in the case of M250Z and M500Z increased to 20 and 19 % respectively. The increased in the sextet is understood as due to the prevention of the nanoparticles from agglomeration. Therefore the trapping center at the zeolite provides stability in the nanoparticles Table 1.

#### 4 Conclusions

Synthesis of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the presence of zeolites narrows down their particle sizes as evaluated by Mössbauer studies where the superparamagnetic area increases as Zeolite concentration increases. The growth of the nanoparticles is confined when the

nanoparticles nucleate from the pores of the zeolites. A comparative studies on the growth of nanoparticles in zeolite 13x and ZSM5, proves that ZSM5 has more efficiency on confining the nanoparticles. Other than confinement of the particles growth, it provides stability to the nanoparticles. Therefore the Fe<sub>3</sub>O<sub>4</sub> nanoparticles grown in the presence of nanoparticles can be utilized in biological, environmental and high temperature applications.

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## References

- Candiani, A., Konstantaki, M., Margulis, W., Pissadakis, S.: A spectrally tunable microstructured optical fibre Bragg grating utilizing an infiltrated ferrofluid. *Optics Express* **18**, 24654 (2010)
- Zhang, J., Zhao, S., Zhu, M., Zhu, Y., Zhang, Y., Liud, Z., Zhang, C.: 3D-printed magnetic Fe<sub>3</sub>O<sub>4</sub>/MBG/PCL composite scaffolds with multifunctionality of bone regeneration, local anticancer drug delivery and hyperthermia. *J. Mater. Chem. B* **2**, 7583 (2014)
- Dib, S., Boufatit, M., Chelouaou, S., Sadi-Hassaine, F., Croissant, J., Long, J., Raehm, L., Charnay, C., Durand, J.O.: Versatile heavy metals removal via magnetic mesoporous nanocontainers. *RSC Adv.* **4**, 24838 (2014)
- Lee, S.H., Yu, S.-H., Lee, J.E., Jin, A., Lee, D.J., Lee, N., Jo, H., Shin, K., Ahn, T.-Y., Kim, Y.-W., Choe, H., Sung, Y.-E., Hyeon, T.: Self-Assembled Fe<sub>3</sub>O<sub>4</sub> nanoparticle clusters as high-performance anodes for lithium ion batteries via geometric confinement. *Nano Lett.* **13**, 4249 (2013)
- Bello, S.M., Luckie, R.A.M., Santos, L.F., Hinestroza, J.P., Mendieta, V.S.: Size-controlled synthesis of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles onto zeolite by means of a modified activated-coprecipitation method: effect of the HCl concentration during the activation. *J. Nanopart. Res.* **14**, 1242 (2012)
- Zhang, J.-M., Zhai, S.-R., Zhai, B., An, Q.-D., Ge, T.: Crucial factors affecting the physicochemical properties of sol–gel produced Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–NH<sub>2</sub> core–shell nanomaterials. *J. Sol-Gel Sci. Technol.* **64**, 347 (2012)
- Zheng, J., Liu, Z.Q., Zhao, X.S., Liu, M., Liu, X., Chu, W.: One-step solvothermal synthesis of Fe<sub>3</sub>O<sub>4</sub>@C core–shell nanoparticles with tunable sizes. *Nanotechnology* **23**, 165601 (2012)
- Lei, P., Boies, A.M., Calder, S., Girshick, S.L.: Thermal plasma synthesis of superparamagnetic iron oxide nanoparticles. *Plasma Chem. Plasma Process* **32**, 519 (2012)
- Yao, Y., Jiang, H., Wu, J., Gu, D., Shen, L.: Synthesis of Fe<sub>3</sub>O<sub>4</sub> /polyaniline nanocomposite in reversed micelle systems and its performance characteristics. *Procedia Eng.* **27**, 664 (2012)
- Alam, S., Anand, C., Ariga, K., Mori, T., Vinu, A.: Unusual magnetic properties of size-controlled iron oxide nanoparticles grown in a nanoporous matrix with tunable pores. *Angew. Chem.* **121**, 7494 (2009)
- Gal, I.J., Radovano, P.: Ion-exchange Equilibria of Synthetic 13X Zeolite with Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> Ions. *J. Chem. Soc., Faraday Trans. I* **71**, 1671 (1975)
- Arruebo, M., Pacheco, R.F., Irusta, S., Arbiol, J., Ibarra, M.R., Santamaria, J.: Sustained release of doxorubicin from zeolite–magnetite nanocomposites prepared by mechanical activation. *Nanotechnology* **17**, 4057 (2006)
- Habrowska, A.M., Popiel, E.S.: Positron annihilation in zeolite 13X. *J. Appl. Phys.* **62**, 15 (1987)
- Kokotailo, G.T., Lawton, S.L., Olson, D.H., Meier, W.M.: Structure of synthetic zeolite ZSM-5. *Nature* **272**, 437 (1978)
- Zahmakiran, M., Ozkar, S.: Zeolite-confined ruthenium(0) nanoclusters catalyst: record catalytic activity, reusability, and lifetime in hydrogen generation from the hydrolysis of sodium borohydride. *Langmuir* **25**, 2667 (2009)
- Zahmakiran, M., Durap, F., Ozkar, S.: Zeolite confined copper(0) nanoclusters as cost-effective and reusable catalyst in hydrogen generation from the hydrolysis of ammonia-borane. *Int. J. Hydrog. Energy* **35**, 187 (2010)
- Erdem, E., Karapinar, N., Donat, R.: The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.* **280**, 309 (2004)

18. Babarao, R., Jiang, J.: Unprecedentedly High selective adsorption of gas mixtures in rho zeolite-like metal-organic framework: A molecular simulation study. *J. Am. Chem. Soc.* **131**, 11417 (2009)
19. Kuznicki, S.M., Bell, V.A., Nair, S., Hillhouse, H.W., Jacobinas, R.M., Braunbarth, C.M., Toby, B.H., Tsapatsis, M.: A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules. *Nature* **412**, 720 (2001)