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Review

Influence of intrinsic parameters on the particle size of magnetic spinel nanoparticles synthesized by wet chemical methods

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ABSTRACT

The synthesis of magnetic spinel ferrites at the nanoscale is a field of intense study, because the mesoscopic properties enable their novel applications. Spinel nanoparticles have a promising role because of their extraordinary properties compared with those of micro and macro scale particles. Several colloidal chemical synthetic procedures have been developed to produce monodisperse nanoparticles of spinel ferrites and other materials using sol–gel, co-precipitation, hydrothermal, and microemulsion techniques. To improve the synthesis method and conditions, quality and productivity of these nanoparticles, understanding the effect of extrinsic (pH, temperature, and molecular concentration) and intrinsic parameters (site preferences, latent heat, lattice parameters, electronic configuration, and bonding energy) on the particle size during synthesis is crucial. In this review, we discuss the effect of the intrinsic parameters on particle size of spinel ferrites to provide an insight to control their particle size more precisely.

Contents

Introduction

Magnetic materials have played a number of crucial roles in the daily life (Kurmude, Barkule, Raut, Shengule, & Jadhav, 2014; Gul, Ahmed, & Maqsood, 2008) and in some cases, there are no alternative materials (Sharifi, Shokrollahi, Doroodmand, & Safi, 2012). Among magnetic materials, magnetic oxides or ferrites have received special attention because of chemical stability as well as high electrical resistivity (Rodriguez & Fernández-García, 2007; Shokrollahi & Janghorban, 2007; Shokrollahi, 2008; Faraji, Yamini, & Rezaee, 2010). The extrinsic properties of these materials are highly dependent on their microstructure and control of domains. The efficient use of ferrimagnetic compound materials (ferrites) is dependent on improving their design and controlling their microstructure. The effect of particle size on microstructure is evident. Therefore, understanding the effect of extrinsic (pH, temperature, and molecular concentration) and intrinsic parameters (site preferences, latent heat, lattice parameters, electronic configuration, and bonding energy) on the particle size during synthesis is important. Spinel type magnetic oxides are exemplified by the spinel structure ferrite (MFe_2O_4) where M is a divalent metal ion and Fe is a trivalent (ferric) iron ion.

The spinel structure can be described by the formula AB_2O_4 where A and B refer to tetrahedral (8(a)), and octahedral (16(d))

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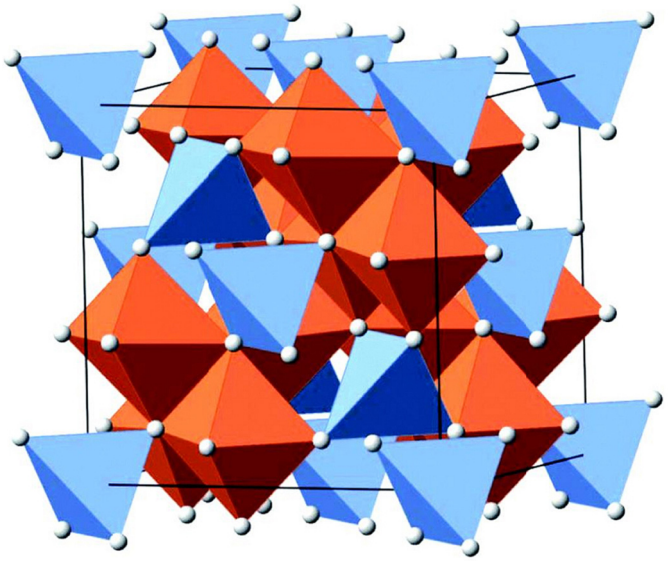

Fig. 1. Cubic spinel structure of $CoFe_2O_4$. The white spheres represent the oxygen atoms, and the tetrahedral and octahedral sites are indicated with blue and orange polyhedrons, respectively (Andersen & Christensen, 2015). Reproduced by permission of The Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

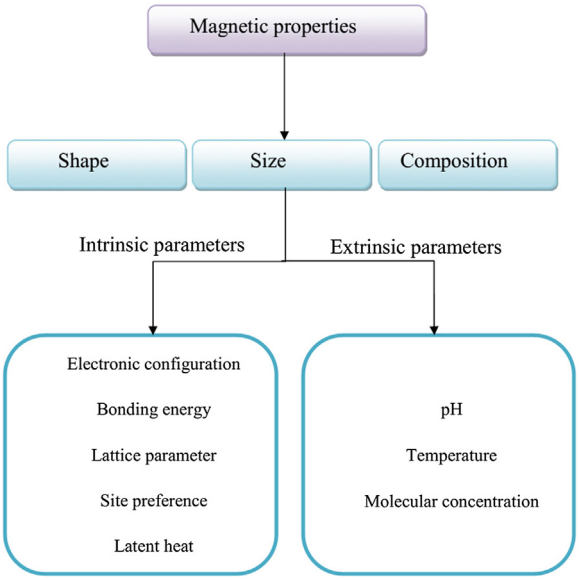

Fig. 2. Parameters influencing particle size.

cation sites, respectively (see Fig. 1 from Andersen & Christensen, 2015). The oxygen anions are arranged in a face-centered cubic lattice. Each unit cell contains eight formula units with O^{2-} anions at the 32(e) sites, and M^{3+} and M^{2+} cations occupying the 16(d) and 8(a) sites. The space group of ferrites is $Fd\bar{3}m$, and the lattice parameters are typically ~8.5 Å. The occupation of the tetrahedral site entirely with a divalent transition metal (such as Zn) produces a normal spinel structure, whereas occupation of the octahedral site with the divalent transition metal ions yields an inverse spinel structure. If divalent transition metal ions are present on both A and B sub-lattices, the structure is mixed or disordered (Willard, Nakamura, Laughlin, & McHenry, 1999; Harrison & Purnis, 1996).

Spinel ferrite nanoparticles with a high surface to volume ratio have received great attention because of their useful, nonlinear optical behavior, increased mechanical strength, enhanced diffusivity and suitable specific heat, high electrical and high magnetic properties (Gubin, Koksharov, Khomutov, & Yurkov, 2005; Chauhan et al., 2013; Kruis, Fissan, & Peled, 1998; Gleiter, 2000). These properties make them good candidates for application in magnetic fluids, magnetic data storage devices, magnetic information storage, xerography, electronics (recording media), catalysis, magnetic diagnosis, as well as therapeutics and environmental remediation (Solyman, 2006; McCarthy & Weissleder, 2008; Jordan, Scholz, Wust, Fähling, & Felix, 1999; Ozatay, Mather, Thiele, Hauet, & Braganca, 2009; Bystrzejewski, Lange, Huczko, Elim, & Ji, 2007; Yu, Oduro, Tam, & Tsang, 2008; Hong et al., 2008; Carta et al., 2010). Furthermore, during the last two decades, due to the rapid development of nanotechnology, wet chemical synthesis methods have been widely used to synthesize nanostructures (Veiseh, Gunn, & Zhang, 2010; Ahmed, Okasha, & El-Dek, 2008; Lakshman, Rao, & Mendiratta, 2002). Numerous publications about magnetic spinel materials have described efficient routes to attain shape-controlled, highly stable, and narrow sized distributed magnetic nanoparticles (Leslie-Pelecky et al., 1998; Iida, Takayanagi, Nakanishi, & Osaka, 2007; Wei et al., 2012). Several chemical methods including co-precipitation (Sugimoto, 2000; Pillai & Shah, 1996; Zhang, Zhong, Yu, Liu, & Zeng, 2009; Qu et al., 2006), microemulsion (Liu, Zou, Rondinone, & Zhang, 2000; Bellusci et al., 2007), sol–gel (Lee & Kim, 2005), and hydrothermal routes (Xu & Teja, 2008; Hao & Teja, 2003) have been proposed by different researchers to synthesize magnetic nanoparticles. As mentioned before, the particle size strongly affects the properties and applications of spinel materials, and the synthesis method directly influences the particle size (Kasapoglu, Birsöz, Baykal, Köseoglu, & Toprak, 2007; Ahmed & El-Khawlani, 2009).

The particle size can be changed by the extrinsic synthesis variables such as pH, temperature, and molecular concentration (Kim, Mikhaylova, Zhang, & Muhammed, 2003; Meng et al., 2012; Long et al., 2008), as well as the intrinsic parameters, including site preference, latent heat, electronic configuration, bonding energy, and lattice parameters (Qu et al., 2006; Sun, 2007; Atif, Hasanain, & Nadeem, 2006) (see Fig. 2). Numerous investigations have focused on the extrinsic variables (Nishimura, Abe, & Inoue, 2002; Tada, Hatanaka, Sanbonsugi, Matsushita, & Abe, 2003). For example, Joseyphus, Narayanasamy, Shinoda, Jeyadevan, and Tohji (2006) have shown that for $Mn_{0.67}Zn_{0.33}$ ferrite, the decrease in particle size for higher concentrations of the oxidant (KNO_3) is because of the faster oxidation of the ferrous ion to the ferric state, and consequently an increase in the nucleation rate of ferrite nanoparticles. However, lower molar concentrations of the oxidant have resulted in a wide distribution of particles with large diameters because of the varying time intervals for nucleation (Joseyphus et al., 2006; LaMer & Dinegar, 1950). Another extrinsic key point is the quantity of the chelating agent. Sajjia, Oubaha, Prescott, and Olabi (2010) indicated that, in the synthesis of cobalt ferrite, the use of larger quantities of the chelating agent tends to produce larger particles (at the same heat treatment temperature).

The pH is another effective extrinsic parameter, as demonstrated by Hosono et al. (2009). The particle size of magnetite decreases from 14 to 12 nm as the reaction pH increases from 9.5 to 11.2. This finding indicates the variation in nucleation rate, which is a function of reaction pH. The nature of the base is the next extrinsic parameter to influence the particle size. Three bases have been used as co-precipitating agents: NaOH, CH_3NH_2, and NH_3 (Shokrollahi, 2008). Auzans, Zins, Blums, and Massart (1999) have shown that for Mn–Zn ferrite in the case of NaOH, with a ~0.4 M base concentration, there is a pH = 12.5–13.0 after co-precipitation. For the two other bases, CH_3NH_2 and NH_3, the base concentration of 0.8–1.0 M results in the pH after co-precipitation of 10.5–11.0 and 9.5, respectively. To explain the effect of pH, we should mention that most of the physicochemical properties

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