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Original Research Paper

Controlled synthesis of dense $MgFe_2O_4$ nanospheres by ultrasonic spray pyrolysis technique: Effect of ethanol addition to precursor solvent

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ABSTRACT

We present the results of controlled synthesis of spherical shape magnesium ferrite ($MgFe_2O_4$) dense nanoparticles by using ultrasonic spray pyrolysis (USP) method without any post-annealing processes. A new strategy was proposed to improve nano-crystallinity and observed morphology by ethanol (EtOH) addition in the initial precursor solution of $MgFe_2O_4$. Influence of EtOH, not only decrease the synthesized secondary particle size but also enhancing crystallization into $MgFe_2O_4$ single phase cubic structure. We observe that average nanosphere size decrease from 220 to 189 nm but increases of crystallite size from 9.6 to 19.2 nm with increasing the amount of EtOH from 0 to 20 vol%. Also, surface morphology revealed that nanospheres with some irregular shape and rough surface appear in case of EtOH additives. The magnetic properties are studied and different parameters viz. saturation magnetization, remanence, and coercivity have been correlated with crystallite size.

1. Introduction

Magnesium ferrite ($MgFe_2O_4$) nanocrystalline particles are promising materials for use in not only technological applications but also various biomedical fields such as magnetic hyperthermia, MRI contrast agent, drug carrier, etc. because of its low toxicity, lower magnetic anisotropy, and high chemical stability [1–8]. For practical applications, proper particle size, morphology, crystallinity, and magnetic properties are vital parameters which strongly depend on the preparation methods. Thus, it is essential to develop or select an appropriate method for preparing $MgFe_2O_4$ nanostructured powders.

Previously, some standard methods such as coprecipitation method [9] sol-gel method [10], mechanochemical processing [11] combustion method [12] microwave hydrothermal method [13] and polymerization method [14] have been used for the synthesis of $MgFe_2O_4$ nanoparticles. Most of these methods resulted in the very low crystallinity of the resulting particles from a precursor, and the post-annealing or calcination process is inevitable for enhancing crystallinity which is an inconvenience and leading to generate irregular with necking of particles and broader size distribution [1,15]. Also, some of these procedures take long time, multiple steps, expensive and difficult to scale-up. Besides, single crystalline nanoparticles synthesized by above methods tend to agglomerate to minimize the surface energy. Such agglomeration of nanoparticles may block the capillary blood flow and is threatening for *in vivo* use of magnetic nanoparticles for biomedical applications [16–18].

In recent years, ultrasonic spray pyrolysis method (USP) has been developed and used to synthesize a wide variety of nanostructured materials in powder. Compare to above synthesis techniques, spray pyrolysis has several advantages such as simple operation, high purity, chemical uniformity, a continuous operation of large-scale production, etc. [19–25]. Here, the resulting nanospheres are usually named as secondary particles which arise through the growth and aggregation of nano-assembles (single crystallites), called primary particles. This method is an inexpensive and facile way to synthesize $MgFe_2O_4$ nanospheres from metal salt precursors using the continuous, scalable process. Notably, the USP process has been applied to the preparation of the $MgFe_2O_4$

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particles [26]. However, crystallite sizes are almost same for different precursor concentration where secondary particle size increase with increasing concentration. The Problems such as the generation of particles with larger size or agglomeration were not resolved. Thus, it is necessary to control the size and morphology of both primary and secondary particles.

In spray pyrolysis, morphologies of the secondary particles are affected by the preparation condition such as droplet size, solution concentration, precursor type, reactor temperature and residence time in the reactor. In the one-particle-per-droplet mechanism of spray pyrolysis, the relationship between the diameter of obtained particle (D_p) and the precursor droplet (d) can be expressed by the following equation

$$D_p = d\left(\frac{C.\rho_s}{\rho_p}\right)^{\frac{1}{3}} \quad (1)$$

where C, ρ_s, and ρ_p are the precursor solution concentration, density of the precursor solution and density of the final particles, respectively [27]. Thus, if droplet size decrease, obtained particle size will be decreased accordingly. Then, the mean droplet diameter atomized by ultrasonic vibrator is expressed by Lang's equation [28]

$$d = 0.34\left(\frac{8\pi\gamma}{\rho f^2}\right)^{\frac{1}{3}} \quad (2)$$

where d, is average droplet diameter (μm), γ is the liquids surface tension (Nm^{-1}), ρ is the density of solution (kg m^{-3}), and f is the ultrasonic frequency (MHz). According to the above relation, the initial droplet size directly depends on the surface tension of the precursor solution, where droplet size decrease with decreasing surface tension. We know, the surface tension of EtOH is 0.026 Nm^{-1} at 20 °C, which is 0.3 times of that of water [29]. Therefore, the total surface tension of ethanol-water solution can be decreased with increasing the volume fraction of ethanol [30]. According to these equations, it is found that the mean droplet diameter, as well as final particle size, will be decreased as a result of decrease in the surface tension of the ethanol-water solution. The evaporation rate of ethanol is comparatively high than water, and the addition of EtOH to the precursor solution is expected to accelerate the crystallinity for the preparation of specific oxide nanoparticles [31]. Thus, the average size and the size distribution of the final synthesized particles can be controlled by the EtOH added precursor solution using implementing the mechanism.

In the present work, the morphological control of particles in large-scale spray pyrolysis was attempted introducing EtOH added precursor solution. In this study, we used the EtOH as alcohol into the precursor solvent for the preparation of $MgFe_2O_4$ nanospheres. The effects of EtOH on the nanospheres size, crystallinity with surface morphology were experimentally investigated and the magnetic properties viz. saturation magnetization, remanence, and coercivity were also analyzed.

2. Experimental details

2.1. Materials and method

For the synthesis of the targeted composition of $MgFe_2O_4$, a precursor solution was prepared by dissolving a stoichiometric ratio of iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) and magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) in a mixture of EtOH and distilled water. All analytical grades reagent (purity >99%) were purchased from Kanto Chemical Co. Tokyo and used without further purification. The vol% of distilled water and EtOH in the precursor was adjusted to prepare 0.06 M precursor concentration. The final solution was continuously stirred for 12 h using a magnetic stirrer at room temperature that was used for spray atomization in the particle synthesis via ultrasonic spray pyrolysis method.

The as-synthesized $MgFe_2O_4$ nanospheres were prepared using the hand-built ultrasonic spray pyrolysis system, and the flowchart of the synthesis process has shown in Fig. 1. As dried powder by USP technique can be continually obtained through the following three steps: (i) atomization of droplets, (ii) transport of droplets into particles synthesis in the heating zone and (iii) capture of the synthesized powder. The precursor solution was atomized in the three-neck round flask on ultrasonic aqueous bath by an ultrasonic vibrator with a constant frequency of 1.6 MHz (Model: MH-1630, Honda Electronics Co. Ltd., Japan). The mist was delivered by the carrier gas (N_2) with a constant flow rate of 3 L/min to a horizontally oriented tubular quartz reactor zone (90 cm long and 30 mm diameter). The reactor temperature (here 700 °C) maintained constant, resulting in a droplet/particle residence time inside the reactor was ~0.6 s. The gas leaving the reactor contains both $MgFe_2O_4$ particles and water vapor. Removing the evaporated solvent is critical for the preparation of non-agglomerated as-dried spherical particles because solvent vapor enhanced particles agglomeration with wet [29]. The removal of evaporated solvents was performed by the water jet air pump. A sample holder with a membrane filter was used for collecting the generated $MgFe_2O_4$ particles, and it has been maintained warm condition (~70 °C) using ribbon heater. When whole precursor solution had atomized, or enough products were stored, then the system was turned off, and the product on the filter paper was collected as a dried powder. The as-prepared particles were directly used for further characterizations.

2.2. Characterization techniques

The crystal structure of as-synthesized materials was investigated using an X-ray powder diffractometer (D8 Advance; Bruker Analytik, Germany). The X-ray generator was operated at an accelerating voltage of 40 kV and tube current 40 mA with Cu $K\alpha_1$ radiation (λ = 0.1542 nm). XRD patterns were recorded in step scan mode with scanning rate employed in 2θ of 0.01 s^{-1}. After background subtraction and performing $k_{\alpha 2}$ stripping, the mean crystallite size, and crystal parameters were determined by TOPAS software utilizing the ICSD PDF database [16]. The surface morphology of the powder samples was inspected by field emission scanning electron microscopy (FE-SEM) (Model: JSM-700F, JEOL Ltd., Japan). The accelerating voltage of the electron gun was 15 kV with a working distance of 10 mm. FE-SEM samples were pre-

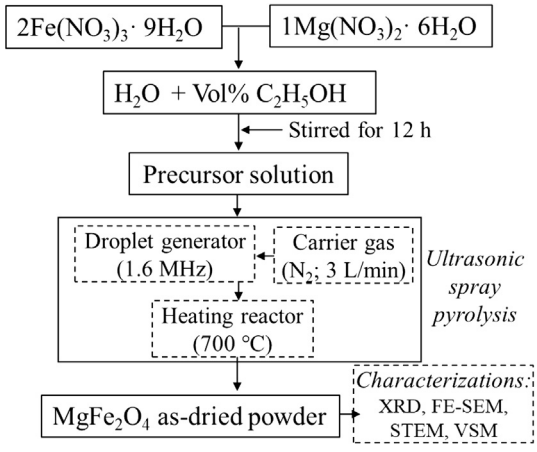

Fig. 1. A general flowchart of the synthesis process of magnesium ferrite nanospheres by ultrasonic spray pyrolysis (USP).

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