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Characterization of Iron(III) Oxide Nanoparticles Prepared by Using Ammonium Acetate as Precipitating Agent

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Abstract–The effect of precipitating agent on the preparation of iron(III) oxide particles was investigated. Iron(III) oxide particles were prepared by precipitation of aqueous ferric nitrate solution by using ammonium acetate and ammonium hydroxide as precipitating agents. Particle size, shape, chemical composition, crystalline formation rate, crystallinity and magnetic property were measured for Fe_2O_3 particles obtained by precipitating with ammonium acetate, and compared with those of particles formed by using ammonium hydroxide. TGA, DTA, IR, XRD, TEM and VSM were used to characterize the particles. The nanoparticles synthesized with ammonium acetate showed a narrow size distribution, spherical shape, fast crystalline formation rate, high crystallinity and complete hysteresis loop. The better properties of particles formed by using ammonium acetate were originated from the chelating effect of carboxylate ions and higher crystallinity than those synthesized with ammonium hydroxide.

Key words: Iron(III) Oxide Particles, Precipitating Agents, Ammonium Acetate, Chelating Effect, Crystallinity

INTRODUCTION

Nanometer-sized iron oxide particles have great potential applications in information storage [Gunther, 1990], color imaging [Ziolo et al., 1992], bioprocessing [Nixon et al., 1992], catalysts [Yan et al., 1999], magnetic refrigeration [McMichael et al., 1992] and magnetic resonance imaging [Frank et al., 1993]. Their interesting magnetic properties are due to finite-size effects and high surface/volume ratio. However, very different magnetic properties have been observed with materials having similar grain size but produced by different methods, which makes the study of their microstructure very important. Much attention has been focused on magnetic recording media materials, due to the increased need for high density, in particular the conventional magnetic materials for information storage systems such as the oxides of iron, nickel, and cobalt. Conventional magnetic recording media have been prepared by using mixtures of polymeric surfactants and micrometer-size iron oxide particles.

Several methods have been used to synthesize the magnetic particles, such as hydrolysis in solution, sol-gel processes [Brinker and Scherer, 1990], hydrothermal processes, spray pyrolysis [Carreno et al., 1991], co-precipitation method [Hu et al., 1996] and resin-mediated synthesis. In aqueous solution, magnetic spinel iron oxide has been synthesized through co-precipitation of various salts of Fe(III) and Fe(II) in alkaline media [Tronc et al., 1992; Asai et al., 1997]. The syntheses are performed at very high salt and base concentrations but have an advantage in that there is no need of surfactants removal from the nanoparticles before incorporation into an ultrathin film. Organized assemblies have been used to control the particle size. Syntheses of Fe_3O_4 and Fe_2O_3 nanoparticles have been performed in vesicles, cast film, bilayer lipid membrane, polymer matrix, and porous silica microspheres. As in syntheses carried out in homogeneous solution, this induces marked changes at the surface of the particles and makes difficult derive any relationship between magnetic properties and size.

In this work, iron oxide nanoparticles were prepared in aqueous solutions without any surfactants. In particular, the effects of precipitating agent on the formation of Fe_2O_3 particles and properties of iron(III) oxide nanoparticles prepared by co-precipitation were investigated. Two kinds of precipitating agent were used in this study. NH_4OH has been used as the most popular precipitating agent, but the use of ammonium acetate as precipitating agent has never been reported. The particles prepared by ammonium acetate are sample A and those prepared by the ammonium hydroxide are sample B. The process has the advantages of inexpensive precursors, a simple preparation method, and a resulting nano-sized, homogeneous, highly reactive powder. The size and crystallinity of the particles depends markedly on the precipitating agent. In contrast to sample B, sample A is isotropic, optically transparent and thermodynamically stable dispersion of particles in aqueous solution. Such dispersions are formed spontaneously by mixing the ferric nitrate and ammonium acetate solution. Several organic anions such as carboxylate and hydroxyl carboxylate ions on the formation of ferric oxides or hydroxides interfere with the formation and growth of these oxides [Bee et al., 1995; Kandori et al., 1991; Kandori et al., 1992]. The magnetic properties depend on the particle size and, for a given size, on the crystallinity.

Also the particles formed by two different precipitating agents were characterized by TEM (transmission electron microscopy), TGA (thermo gravimetric analysis)/DTA (differential thermal analysis), XRD (X-ray diffraction), FT-IR and VSM (vibrating sample magnetometer).

EXPERIMENTAL

Iron(III) nitrate nine-hydrate ($Fe(NO_3)_3\ 9H_2O$, 99.9%, Cica Re-

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agent Japan) as inorganic salt and ammonium hydroxide (Mallinckrodt Chemicals USA, NH_3 29.7%) and ammonium acetate (CH_3COONH_4, Aldrich, 99.99%) as precipitating agents were used to prepare iron oxide particles. The water used in this work was deionized water (electrical resistivity 18.2 MΩ). 0.1 M iron(III) nitrate was dissolved in deionized water with stirring. Two types of aqueous solution were prepared separately. In the sample A, 0.5 M ammonium acetate solution was added dropwise into 0.1 M iron(III) nitrate solution under vigorous stirring. The volume ratio of two solutions was 1:1. The resulting solution was an optically transparent sol and the color of the solution was changed from light orange to red brown. After reaction, an excess amount of acetone was added to cause the sedimentation of the iron hydroxide particles under vigorous stirring, generating the orange brown precipitate. In the sample B, 0.5 M ammonium hydroxide solution was applied as a precipitating agent into 0.1 M iron(III) nitrate solution under vigorous stirring. In this step, the red brown precipitate was generated instantly. The supernatant was removed from the precipitate by decantation. Deionized water was added to the precipitate and the solution was decanted after centrifugation at 3,000 rpm. The last procedure was repeated three times to remove the impurities. Dry powders were obtained by filtering and drying under vacuum. Each sample was heated at 250 °C for 2 hours in air to get Fe_2O_3 particles from $Fe_2(OH)_6$.

TGA and DTA of the samples were carried out to determine the phase changes as well as the weight loss of the samples using a Shimazu TGA-50 thermal analyzer and Shimazu DTA-50 differential thermal analyzer. The temperature was increased at a rate of 10 °C min^{-1} under a flowing air atmosphere. XRD was used to examine the crystallinity and phase constituents of samples prepared by two processes. XRD measurement was performed with powders packed completely on a hole of holder by a Rigaku D/MAX RINT 2500 X-ray diffractometer operated at 40 kV and 100 mA. The incident wavelength was Cu $K_\alpha 1$ =1.5406 Å and detector moved step by step ($\Delta 2\theta$=0.05°) between 10° and 80°. The scan speed was 7°/min. The FT-IR spectra were recorded on MAGNA-IR 760 SPECTROMETER (Nicolet) by the KBr pellet method. Transmission electron micrographs (TEM) were recorded in a JEM-2010 microscope operating at 200 kV. The powder was dispersed in ethanol and dropped on a conventional carbon-coated copper grid. Magnetic properties of the samples were recorded in a vibrating sample magnetometer (VSM). Saturation magnetisation and coercivity were obtained from the hysteresis loops by applying a magnetic field of 1.5 kOe at room temperature.

RESULTS AND DISCUSSION

1. Chemical Reaction for the Formation of Iron Oxide Nanoparticles

When NH_4OH is used as precipitating agent, the chemical reactions for the formation of iron oxide particles are as follows:

$$2Fe(NO_3)_3 + 6\,NH_4OH \rightarrow Fe_2(OH)_6 \downarrow + 6\,NH_4NO_3$$

As soon as $Fe_2(OH)_6$ particles were formed, they were flocculated and precipitated in the aqueous solution. The $Fe_2(OH)_6$ precipitates were converted into iron oxide by calcination for 2 hours at 250 °C by the following mechanism [Mahan et al., 1987].

$$Fe_2(OH)_6 \rightarrow Fe_2O_3 + 3H_2O \uparrow$$

In case of ammonium acetate, we propose that the chemical reaction mechanism would be very similar.

$$2Fe(NO_3)_3 + 6\,NH_4CH_3COO \rightarrow Fe_2(CH_3COO)_6 + 6\,NH_4NO_3$$

However, the $Fe_2(CH_3COO)_6$ particles during this reaction were not precipitated and formed very stable red-brownish sol. The formation of $Fe_2(CH_3COO)_6$ was proven by FT-IR measurement. The homogeneous transparency of sample A after the reaction indicates that its composition was homogeneous. Organic ions are known to affect the formation of metal oxides or hydroxides through the two following process [Ishikawa et al., 1993]:

(1) chelation of these ions with metal ions prevents nucleation;
(2) adsorption of these ions on the nuclei produced by hydrolysis inhibits the growth of the nuclei.

It is believed that the carboxylic group of acetate in the ammonium acetate could form a chemical bond between the metal ion and acetate ion [Sun et al., 1996]. The use of ammonium acetate as a precipitating agent greatly suppresses the formation of precipitates due to chelating effect. Therefore, no surfactants are necessary to stabilize the hydrosol after the formation of ferric hydroxide.

The stable $Fe_2(CH_3COO)_6$ sol was precipitated by the addition of acetone and centrifugation. Then, the $Fe_2(CH_3COO)_6$ particles were converted into iron oxide by the same procedure for $Fe_2(OH)_6$.

$$Fe_2(CH_3COO)_6 \rightarrow Fe_2O_3 + 3CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 \uparrow$$

2. Chemical Analysis

Chemical and structural changes which occurred during the combustion were monitored by a spectroscopic analysis. This may be helpful to understanding the combustion reaction mechanism. Figs. 1 and 2 show the FT-IR spectra of the simply dried powder and the heat-treated powder in the range 470-4,000 cm^{-1}. The dried powder of sample A showed the characteristic bands at about 3,300, 1,600 and 1,300 cm^{-1} corresponding to the O-H group, carboxyl group and NO_3^- ion, respectively. The disappearance of the charac-

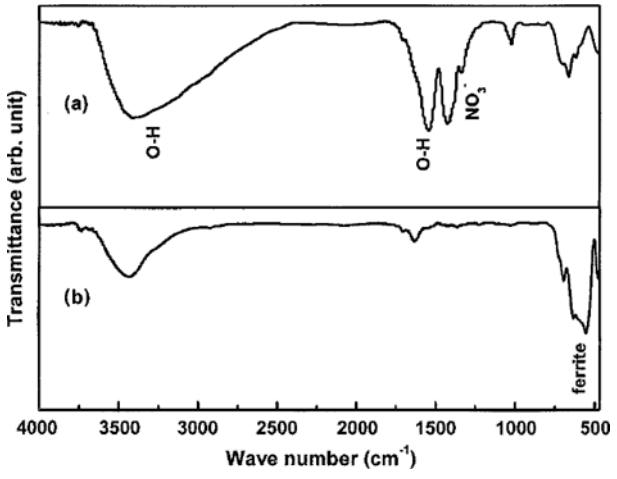

Fig. 1. FTIR spectra of particles prepared by ammonium acetate after (a) drying and (b) heat treatment at 250 °C.

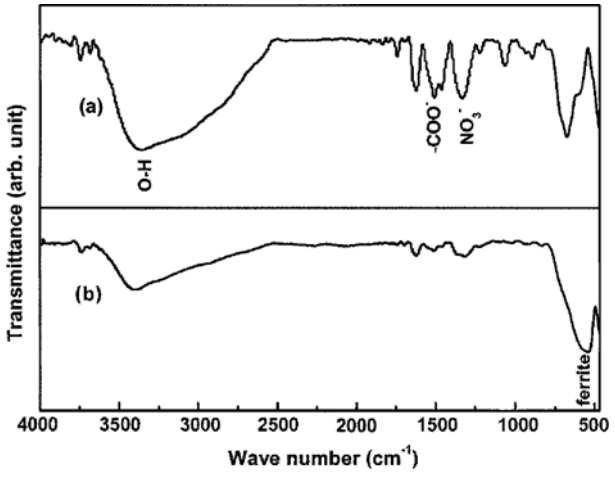

Fig. 2. FTIR spectra of particles prepared by NH_4OH after (a) drying and (b) heat treatment at 250 °C.

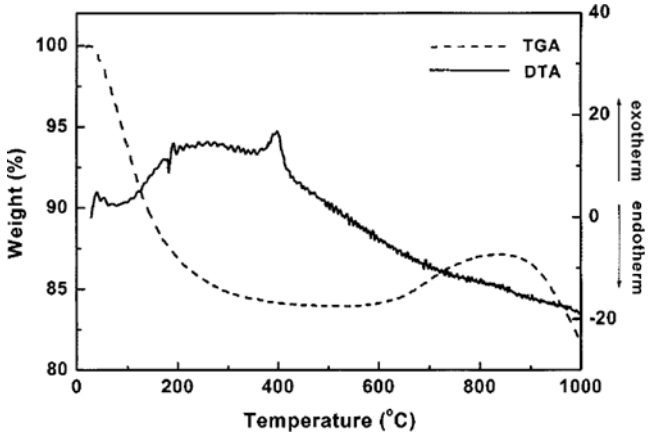

Fig. 3. TGA and DTA curves of precursor particles prepared by ammonium acetate.

teristic bands of carboxyl group and NO_3^- ion in the FT-IR spectra curve after heat treatment revealed that the carboxyl group and NO_3^- ion take part in the reaction during the combustion. Features that clearly correspond to the pure Fe_2O_3 product are shown. There are two characteristic peaks at 470 and 570 cm^{-1} which indicate the existence of the pure Fe_2O_3 particles. Further two bands at 3,440 and 1,620 cm^{-1} were due to characteristic FT-IR spectra of H_2O molecular adsorbed on the surface of Fe_2O_3.

Figs. 3 and 4 shows the TGA and DTA results of the precursor powders. The weight loss of sample A suddenly terminated at 250 °C while that of the sample B terminated 400 °C. Experimental observation showed that the precursor, formed from iron(III) nitrates and ammonium acetate with the molar ratio of 1:5, exhibited self-propagating combustion behavior. When the dried power was ignited at any point, the combustion rapidly propagated forward until all the powder was burnt out completely to form loose powder. This autocatalytic nature of the combustion process of nitrate-acetate powder was studied by thermal analysis (DTA and TG) of the dried power. Fig. 3 shows the DTA and TGA plots of the dried powders of sample A. The exothermic peak at about 250 °C is relatively sharp and intense. This indicates that the decomposition of the powder

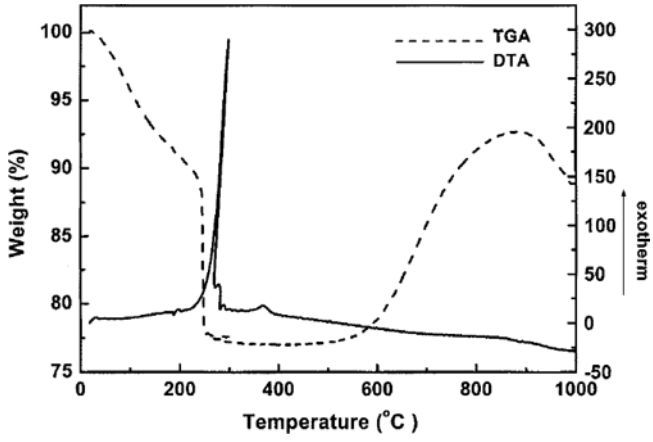

Fig. 4. TGA and DTA curves of precursor particles prepared by ammonium hydroxide.

occurs suddenly in a single step. As reported in other study, this peak stems from a thermally induced anionic redox reaction of the powder wherein the acetate ions act as reductant and nitrate ions act as oxidant [Roy et al., 1993]. This suggests that ammonium acetate not only works as a chelating agent but also provides the combustion heat required for synthesis of Fe_2O_3. Another experiment showed that sample B without acetate ion did not exhibit auto-combustion behavior in Fig. 4. Therefore, the lowering of the decomposition temperature may be attributed to the presence of nitrate-acetate ion on the particles. The exothermic peak in the DTA curve of nitrate-acetate powder corresponds to an autocatalytic anionic oxidation-reduction reaction between the nitrate and acetate system. Similar behavior was previously reported where nitrate decomposition in citrate nitrate gels took place above approximately 200 °C [Yue et al., 2000].

3. XRD, TEM and Particle Size Analysis

Fig. 5 shows the XRD pattern of a nanocrystalline (Fe_2O_3) sample with line broadening caused by the reduced size of the crystallites. In the case of the samples heated at 250 °C, the patterns of sample A show a broad band and narrow peaks of high intensity (Fig. 5 (d)). This indicates the formation of highly crystallized nanoparticles.

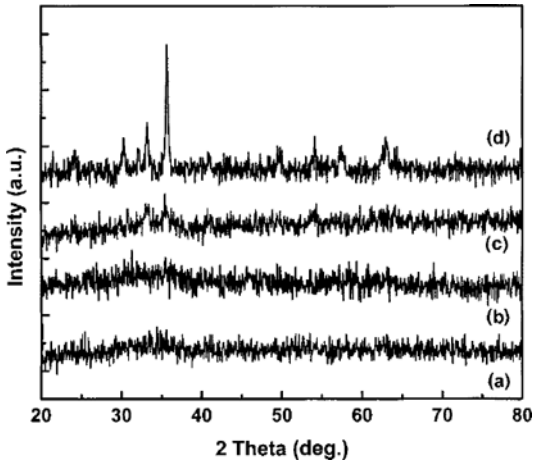

Fig. 5. XRD spectra of particles prepared before heat treatment of (a) sample B and (b) sample A, after heat treatment at 250 °C of (c) sample B and (d) sample A.

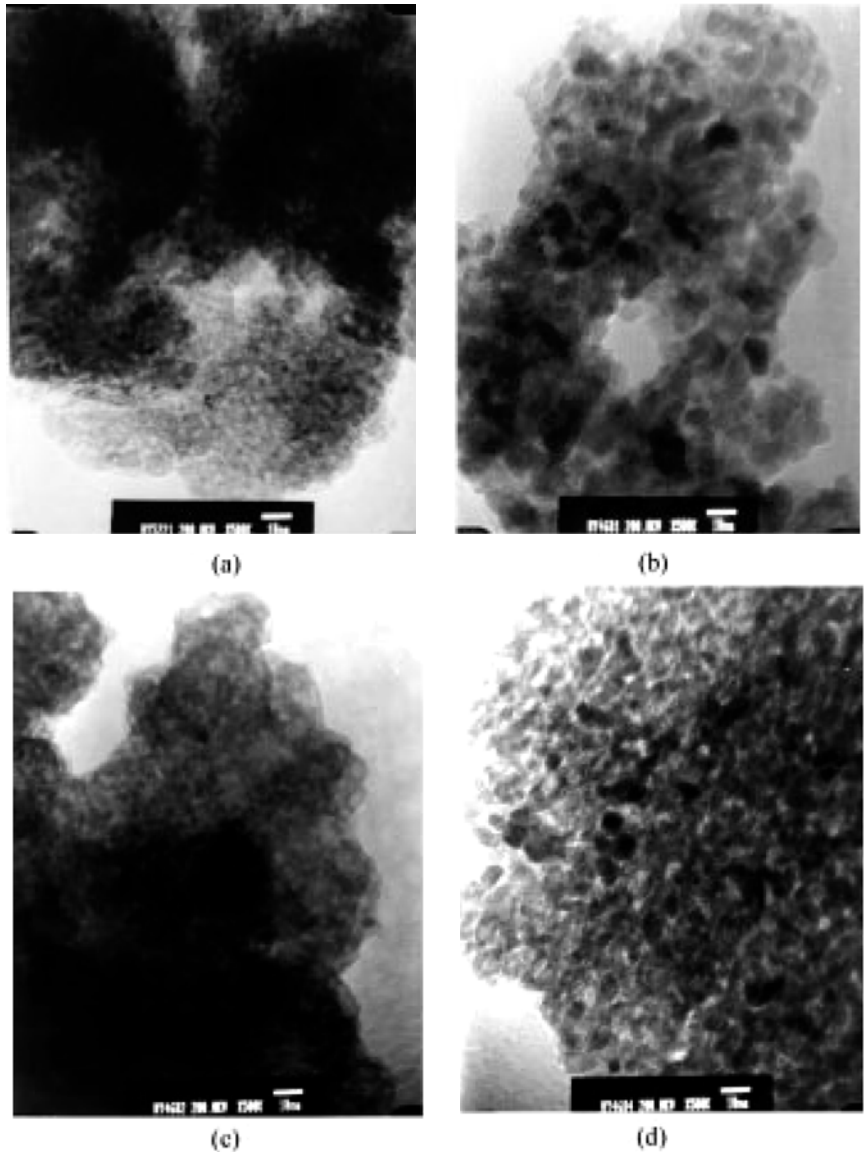

Fig. 6. TEM pictures of particles prepared by (a, b) ammonium acetate and (c, d) ammonium hydroxide.
(a, c): after drying
(b, d): after heat treatment at 250 °C

These peaks can be attributed to hematite (α-Fe_2O_3) or maghemite (γ-Fe_2O_3). The intermediate crystalline phase, such as α-Fe_2O_3 and γ-Fe_2O_3 which are often observed in the sol-gel, derive and co-precipitate precursors when they are calcined at a low temperature [Zhong et al., 1997]. Conversely, when the syntheses are performed with ammonium hydroxide, the patterns of sample B show a broad band of high intensity and broad peak of low intensity (Fig. 5(c)). This indicates the formation of particles with a low crystallinity, which suggests that the co-precipitation method by ammonium acetate requires a much lower calcination temperature and possesses a higher crystallinity than that by ammonium hydroxide. The XRD patterns of the precursor particles show a broad band (Fig. 5(a) and (b)). Therefore, dried powder is amorphous in nature.

Typical micrographs of the particles are shown in Fig. 6. In all the samples, particles are aggregated and exhibit indistinct boundary. The shape of particles in sample A is irregularly rounded while that of the sample B particles is approximately spherical. Heated

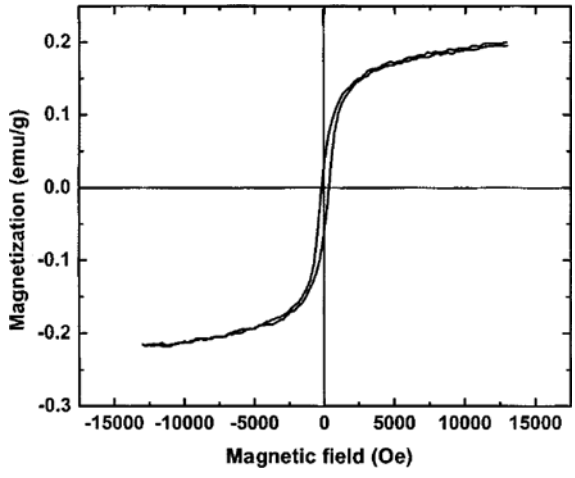

Fig. 7. Magnetic hysteresis loop for heat treated sample A at room temperature.

samples consisted of crystalline particles and precursor samples consisted of amorphous particles, which is in a good agreement with the XRD results. Sample A consists of 8-10 nm nanoparticle aggregates, while sample B is composed of 5-8 nm nanoparticles. Due to the aggregation of the particles and their indistinct boundary, it is not possible to obtain more accurate values. One can observe that the crystallinity and size of sample A increased more than that of sample B when the samples were heated at 250 °C. In all the cases, a narrow size distribution was obtained.

4. Magnetization Measurement

The magnetic properties depend on the particle size and synthesis mode. Saturation magnetization decreases with decreasing crystallite size. Superparamagnetism is often observed for particles below about 10 nm. The magnetization curves of only sample A were obtained at 300 K. The saturation magnetization, Ms, is reached for the sample A at 1.5 kOe. The magnetization curve (Fig. 7) yielded a coercivity (Hc) of 257 Oe, a saturation magnetization (Ms) of 0.2 emu/g, and a remanent magnetization (Mr) of 305 emu/g for sample A. In the case of sample B, the magnetization curve was broken, so that magnetic properties were not measured. This behavior seems to be related to the lack of crystallinity as has been previously observed in poorly crystalline iron(III) oxide particles prepared by ammonium hydroxide. All the amorphous nanosized materials show no hysteresis, and the magnetization was not saturated even at 1.5 kOe [Prozorov et al., 1999].

CONCLUSIONS

The quality of particles prepared with ammonium acetate is better than that of particles prepared with ammonium hydroxide. The particles have irregular round shape with nano size, narrow size distribution, fast crystalline formation rate at 250 °C and complete hysteresis loop at room temperature. It is quite different from particles prepared by other methods. On the other hand, particles synthesized with ammonium hydroxide have spherical shape with smaller nano size, low crystallinity and no hysteresis loop. Therefore, particles must be calcined at a higher temperature. This suggests that the coprecipitation method by ammonium acetate requires a much lower calcination temperature and can obtain higher crystallinity than that by ammonium hydroxide. We can conclude that this is a simple method to synthesize highly homogeneous iron oxide particle with nano-sized crystallites. The process is based on an aqueous system; therefore, it requires neither expensive chemicals nor special equipment in the synthesis. This result came from the chelating effect of carboxylate ion and self-propagating combustion behavior of nitrate-acetate ion. Therefore, it is expected that ultrafine particles at a low temperature could be prepared by using ammonium acetate without using surfactants.

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