

The Synthesis and Magnetic Properties of Nanosized Hematite (α -Fe₂O₃) Particles

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The synthesis of nanosized superparamagnetic hematite particles by dissolving ferric salts in hydrochloric acid and heating at 100°C is described. A hydrolysis reaction causes the formation of hematite particles. The influence of the sequence of additions on the resulting precipitates was studied using TEM and XRD. The magnetic behavior was characterized by magnetization measurements. It was found that small changes in the reaction conditions led to remarkable changes in final size and shape of the hematite crystallites. A well-defined subrounded morphology and an average diameter of 41 nm were obtained for superparamagnetic hematite particles. This is the largest size reported thus far for superparamagnetic hematite particles. © 2002 Elsevier Science (USA)

Key Words: hematite; precipitation; magnetization; superparamagnetic; crystallite size.

INTRODUCTION

Hematite (α -Fe₂O₃) has so-called parasitic or canted magnetism (1). This means that the magnetic moments of the two magnetic sublattices do not fully cancel each other, resulting in a small magnetic moment in the direction of the basal plane. When decreasing the size of magnetic particles, they change from multidomain to single domain (2). If the single-domain particles become small enough, the magnetic moment in the domain fluctuates in direction, due to thermal agitation which leads to superparamagnetism.

It is known that the coercive force opposing this effect is influenced by many factors, such as size and shape, packing density, and defects in the crystal structure. Usually, the coercive force decreases with the size of the crystallites (2). For spherical hematite it has been shown that there is a threshold diameter of about 8 nm below which the particles become superparamagnetic (3, 4). Other values for this threshold diameter have been reported as well, e.g., 14 nm (5).

This threshold diameter at which hematite becomes superparamagnetic was determined for particles synthesised accord-

ing to a precipitation developed by Matijevec and Scheiner (6), since this precipitation has been reported to produce well-defined monosized hematite crystals. This precipitation was further investigated, in order to prepare different batches of monosized hematite particles of varying particle sizes. Hematite particles of an average diameter of 41 nm were found to be superparamagnetic, which is the largest size reported thus far for superparamagnetic hematite particles.

MATERIALS AND METHODS

In the first method, as described earlier by Matijevec and Scheiner (6), doubly distilled water was heated to 100°C. The water was poured into a preheated Pyrex glass beaker. The temperature remained at 100°C. Concentrated (37 wt%) HCl was added to this system to make a 0.002 M HCl solution. The temperature was kept at 90–100°C. Finally FeCl₃ · 6H₂O (Fluka, Milwaukee, WI) was dissolved in this hot solution to make a 0.02 M Fe³⁺ solution. The beaker was closed and put into an oven that was preheated to 100°C, where it remained for 1 week. A sample was taken after 1, 2, 3, 5, and 6 days.

The second method deviated from the first in that the FeCl₃ · 6H₂O was dissolved in doubly distilled water at room temperature to make a 0.5 M Fe³⁺ solution, instead of dissolving directly into preheated water. Concentrated (37 wt%) HCl then was directly added to the 0.5 M ferric chloride solution to make the solution 0.025 M HCl. This solution was put into a large beaker and heated to 90–100°C, while stirring. This solution was diluted with heated doubly distilled water (90°C < T < 100°C) to a factor 25, to prepare a 0.02 M Fe³⁺ and 0.001 M HCl solution. The solution was stirred for a few minutes and then put into two Pyrex glass beakers. These beakers were closed and put into an oven that was preheated to 100°C, where it remained for 1 day and for 1 week, respectively. The difference here with the first method is that the solution of ferric chloride was not directly made at high temperature (90–100°C), but was first at room temperature in the form of a concentrated solution (0.5 M). Hydrolysis therefore might already start at temperatures below 90°C.

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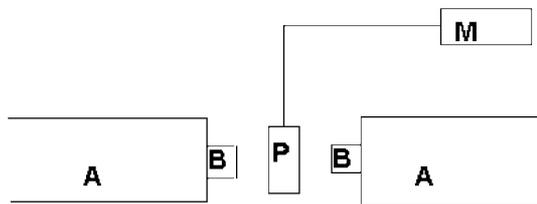


FIG. 1. Setup used for the magnetization measurements. B, a small fluctuating magnetic field is applied between these coils; P, adhesive tape with powder; M, meter that measures the movement of P.

For the third method the FeCl₃ · 6H₂O (Fluka) was first dissolved in doubly distilled water at room temperature to make a 0.5 M Fe³⁺ solution. Concentrated (37 wt%) HCl was added to the 0.5 M ferric chloride solution to make the solution 0.025 M in HCl. This solution was diluted with doubly distilled water by a factor 25, to make a 0.02 M Fe³⁺ and 0.001 M HCl solution. The mixture was stirred for a few minutes and then poured into a glass beaker. This beaker was closed and put into an oven that was preheated to 100°C, where it remained for 1 week. Thus, the difference with method two is that not only the concentrated solution (0.5 M), but also the diluted solution (0.02 M) was made at room temperature, before heating to 100°C, increasing the chance that precipitation would occur at a temperature below 90°C.

Dry powder was obtained by centrifuging the suspension until the supernatant was clear, washing the sediment with distilled water, resuspending the particles in distilled water and centrifuging again, and repeating these steps until a dry powder free of chloride was obtained.

Two transmission electron microscope (TEM) instruments were used to investigate the size and morphology of the precipitated particles. Either a Philips EM30 Twin/STEM TEM or a CM10H Philips TEM was used. In all cases, TEM samples were prepared by addition of alcohol to the dried powder and subsequent dispersion by ultrasonification for 10 min. One drop of the suspension was put on a copper grid that subsequently was dried in normal air prior to use in the TEM apparatus.

For determination of the phase composition and the average crystallite size of the dried powders X-ray diffraction (XRD) and X-ray line broadening (XRLB), respectively, were used. Measurements were performed with a Philips X'Pert-1 PW3710 diffractometer (Eindhoven, The Netherlands), using CuK α ($\lambda = 1.542$ Å) radiation and a Ni filter. The divergence slit was set to 1° and the receiving slit to 0.1. The same apparatus was used to measure the XRLB to determine the average crystallite size of the phases of the powders with the Scherrer formula (7).

The magnetization measurements were performed using a PMC Micro Mag Model 2900 magnetometer. A schematic representation of the apparatus is shown in Fig. 1. Between the two poles (A) a fixed magnetic field of 2 T is applied. Between the two coils (B) a small fluctuating magnetic field is applied. A small weighed amount of powder is put on adhesive tape (P) and put between the two coils B. The fluctuating magnetic field will cause the magnetic sample (P) to move back and forth according

to the change in the magnetic field. At meter (M) the movement of the sample P is registered. The magnetization for all samples was corrected for the used weight.

RESULTS

Hydrolysis of Ferric Chloride Solutions

The moment at which precipitation was first visible was different for the three used varieties of precipitations of a 0.02 M ferric chloride solution. In the second method, with the medium heating rate, precipitation occurred during addition of the concentrated ferric chloride solution. For the third method, with the slowest heating rate, precipitation occurred when heating up the 0.02 M ferric chloride solution from room temperature to 100°C. If the ferric salt was added directly (the first method), an orange-red colored suspension resulted after 1 week, while in the other two cases a purple brown suspension was produced.

These differences in observed precipitation behavior were reflected in the TEM pictures and XRD results. Figure 2 shows the particles that were produced if the ferric chloride salt was added directly into the preheated hydrochloric acid solution (method 1). The same particles were present after heating at 100°C for 1 day and for 1 week. Regularly shaped hematite crystals of 30 to 60 nm had been formed. The form was hexagonal to subrounded. XRD revealed the presence of hematite only. The average particle size determined from TEM pictures was 41 nm, while XRLB gave 46 nm as the average diameter. The size polydispersity of these particles was 15%. This precipitation reaction was repeated several times. The morphology of the precipitated particles was identical for each precipitation, but the average crystallite size, as determined by XRLB, varied from 47 to 71 nm.

If the ferric chloride was not added directly to the preheated hydrochloric acid solution, but first dissolved in cold water before heating to 100°C (methods 2 and 3), the results were very

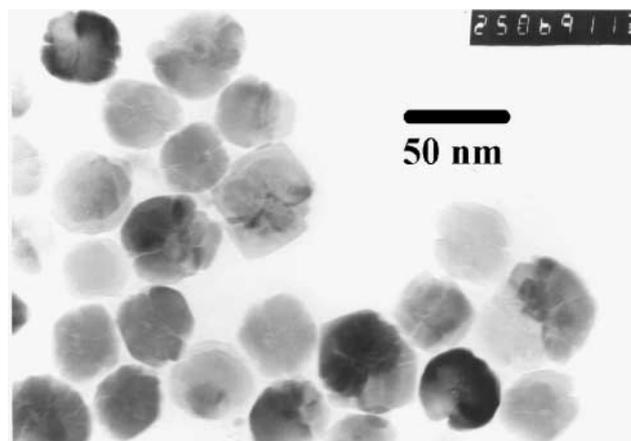


FIG. 2. TEM picture of hematite prepared by hydrolysis of 0.02 M FeCl₃ solution made by directly adding the salt at 100°C, after 1–7 days at 100°C.

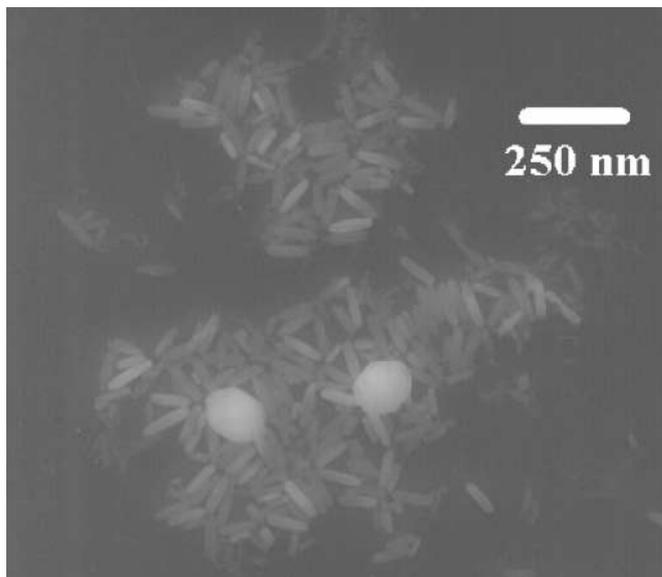


FIG. 3. TEM picture of akaganéite/hematite prepared by hydrolysis of 0.02 M FeCl_3 solution after adding 0.5 M FeCl_3 to diluted HCl solution at 100°C , after 1 day at 100°C .

different compared to method 1. The results of method 2 and 3 were similar. Therefore, only the results of method 2 are shown.

A mixture of two particle types was present after 1 day of heating at 100°C (method 2), as can be seen in Fig. 3. One type was a spindle of approximately 100 nm length and 20 nm width, while the other had an oval shape, with an average length of 150 nm and width of 100 nm. XRD showed the presence of two phases, hematite and akaganéite. After heating for 7 days at 100°C , only the oval-shaped particles were left (see Fig. 4),

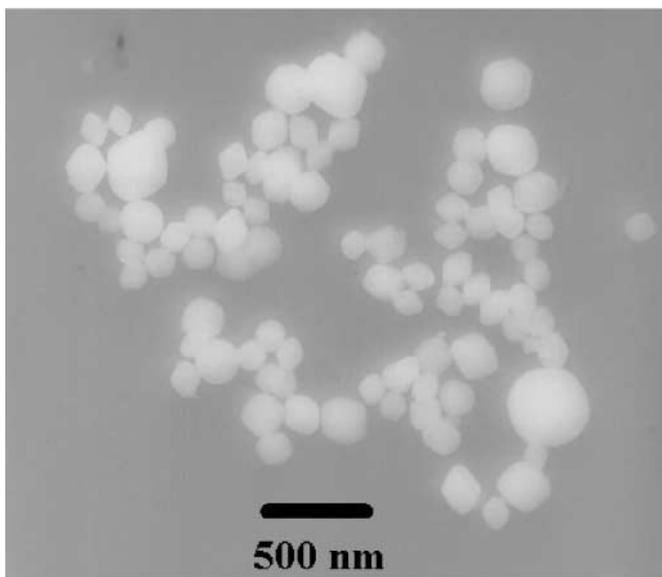


FIG. 4. TEM picture of hematite prepared by hydrolysis of 0.02 M FeCl_3 solution after adding 0.5 M FeCl_3 to diluted HCl solution at 100°C , after 7 days at 100°C .

TABLE 1
Results of Magnetization Measurements on Hematite Particles Prepared by Hydrolysis of 0.02 M FeCl_3 Solutions

Diameter, TEM (nm)	Polydispersity (%)	Diameter, XRLB (nm)	H_c (mT)	M_r (nAm)	M_s (nAm)	M_r/M_s
41	15	47	0.51	0.67	128	0.0053
59	13	71	3.91	23.6	454	0.0519
160	16		108	99	269	0.369

Note. H_c , coercive force; M_r , magnetization at $H = 0$ T; M_s , (maximum) magnetization reached at $H = 1.6$ T.

which were shown to be hematite by XRD. The majority of these hematite crystals had the same shape and size as after 1 day, but a minority of crystals had grown to larger particles of up to 500 nm diameter. Both methods 2 and 3 thus led to larger hematite crystals compared to method 1.

Magnetization of Subrounded Particles

The magnetization of the subrounded particles made by the hydrolysis of ferric chloride solution was measured as function of particle size. Three powders were used for this. The first two, with the smallest particle sizes, were two different batches of the first precipitation method, the third was a powder prepared by the second precipitation method. The values mentioned in Table 1 were calculated for 1 mg of material for each powder. H_c and M_r/M_s are both measures for the amount of ferromagnetic material present in the sample. The higher H_c and M_r/M_s , the more ferromagnetic the material. It is clear that the ferromagnetic nature decreases with particle size, because the anisotropic energy barrier for rotation of magnetic moments is proportional to the particle volume.

In Fig. 5, the magnetization curves of the largest particles of 160 nm are shown. It is clearly visible that these larger particles

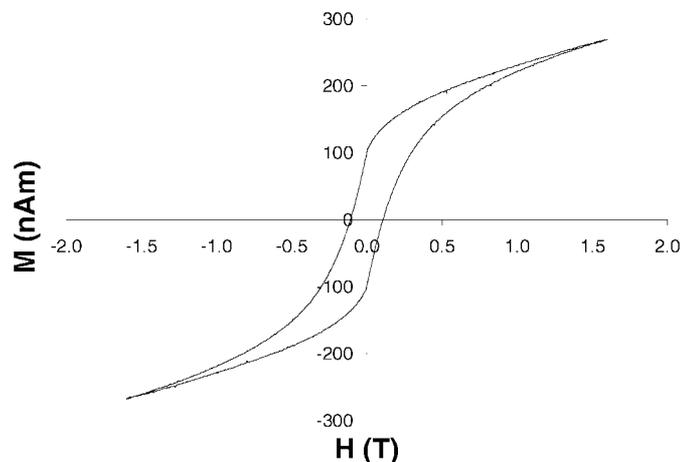


FIG. 5. Magnetization measurement of subrounded hematite particles with 160 nm average size.

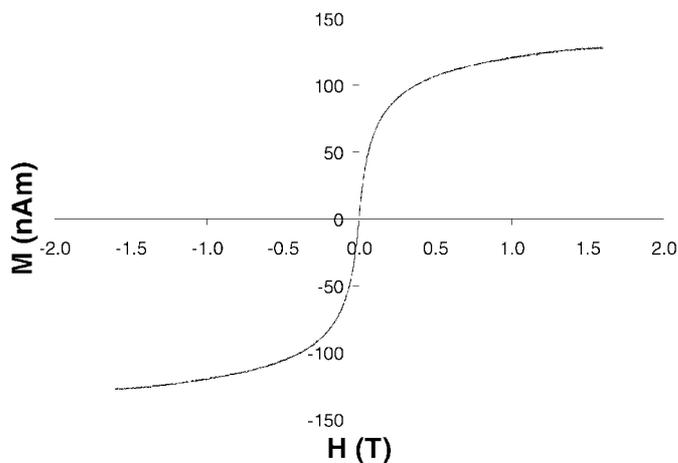


FIG. 6. Magnetization measurement of subrounded hematite particles with 41 nm average size.

exhibit hysteresis. The hematite particles with average size of 41 nm have almost no remnant magnetization at zero magnetic field strength, as can be seen in Fig. 6, which is an indication of superparamagnetism.

DISCUSSION

Hydrolysis of Ferric Chloride Solutions

The results of the precipitation experiments with ferric chloride show that very small changes in precipitation conditions may cause very large differences in the resulting crystal structure, size, and morphology. Matijevic and Scheiner were the first to report on the hydrolysis of a 0.02 M ferric chloride solution by heating at 100°C for 1 week (6). The hydrolysis resulted in subrounded particles with an average size of 46 nm. This hydrolysis was performed by addition of a concentrated (3.0 M) ferric chloride solution to a hydrochloric acid solution (6). In our study the aqueous ferric ion concentration could not be increased to above 0.5 M without the occurrence of precipitation reactions. Therefore, this 0.5 M solution was used to prepare a diluted (0.02 M) ferric chloride solution at 100°C (method 2). This seemingly small difference to the method of Matijevic and Scheiner (6) led to very different particles as reported by these authors (6). Much larger hematite particles were formed. This difference can probably be explained by the difference in pH between the two stock solutions. In the 0.5 M Fe³⁺-solution hydrolysis of the ferric ions may have occurred that did not occur in the more acidic 3.0 M Fe³⁺. The lower the ferric chloride solution, the higher the pH of the solution will be and the faster hydrolysis will occur.

If the prescription of Cornell and Schwertmann (8), who pointed out that the ferric chloride had to be added directly to the preheated HCl solution, was followed (method 1), the results of Matijevic and Scheiner were reproduced (6). Many investigators have reported on this precipitation reaction, following the

description of Matijevic and Scheiner (6). Most obtained the same morphology after heating at 100°C for 1 day, and reported average crystallite sizes varying from 46 nm (9) to 80 nm (10), just as was found in this study by repeating the same precipitation reaction several times. These deviations from the results of Matijevic and Scheiner (6) are probably caused by small differences in the hydrolysis rate. Bailey *et al.* (11) reported for the same hydrolysis reaction that only after 7 days spherical particles with an average size of 250 nm were formed.

Figures 3 and 4 and the XRD results show that before hematite was formed in the solution, akaganéite was formed as was reported before (6, 11). At a temperature >80°C a phase transformation to hematite takes place. Below this temperature, goethite is formed (12). The fact that neither method 2 nor method 3 led here to the formation of goethite indicates that any early formed akaganéite only started to transform after the temperature of the ferric chloride solutions (whether diluted or concentrated) was increased to above 80°C. Thus, the heating went faster than the transformation. Akaganéite is formed faster than hematite (or goethite) since it has a lower energy for nucleation. Hematite is a more thermodynamically stable crystal structure with a solubility in water lower than akaganéite (8).

Magnetic Properties

The smallest measured hematite particles (41 nm) are apparently single-domain particles, which also exhibit superparamagnetism. This implies that the magnetic domain size of these subrounded hematite particles is approximately or perhaps slightly larger than 40 nm.

As mentioned before, different values are given in literature for the critical particle size for transition of ferromagnetic to superparamagnetic behavior. These differences are related to differences in particle shapes and differences in the amount of strain and defects in the particles. Muench *et al.* (13) annealed hematite particles with sizes ranging from 30 to 326 nm at 500°C. In all cases the annealing led to an increase in T_M , the Morin transition temperature. This is the temperature at which hematite changes from canted antiferromagnetic to fully antiferromagnetic. This increase in T_M indicates that annealing makes the hematite less paramagnetic, since paramagnetic hematite would not have a T_M . The raising of T_M due to annealing can according to Muench *et al.* (13) be attributed to the decrease in the amount of lattice defects and strain. These observations are supported by Amin *et al.* (2). They showed that both H_c and M_r/M_s of ferromagnetic hematite particles increased due to annealing at 300°C (2). They reported a value of 0.1 for M_r/M_s for unannealed hematite particles with 40 nm average diameter (2), which is much higher compared to the here reported value of 0.005, although the particles were made by seemingly identical synthesis routes. Again, these differences can be explained only by small differences in the synthesis route, probably resulting in differences in the defect structure of the particles. Although annealing normally decreases the amount of lattice strain and defects in a powder, it can also cause coalescence of crystallites, increasing the average

crystal size. This last effect will certainly strengthen the ferromagnetic nature of nanosized hematite particles, which makes it difficult to separate the influence of the lattice strain and defects from the influence of the crystallite on the ferromagnetic nature.

Kündig *et al.* reported a critical size of 13.5 nm for hematite particles made by impregnation of silica with ferric salt solution and subsequent calcination at 500°C. The morphology of these particles was not described (5). For spherical hematite particles the critical size was reported to be 8 nm (3, 4). The largest critical particle size for the transition from ferromagnetic to superparamagnetic behavior for hematite particles reported so far is 32 nm (14), which is slightly lower than the here reported value of approximately 40 nm.

Strain in the hematite particles does not seem to be a likely cause for the large critical particle size reported here, since the crystallite size determined by XRLB was 46 nm for the smallest hematite particles, while TEM showed 41 nm. If the hematite particles would be strained, XRLB should indicate a lower particle size than TEM. The used synthesis methods seems to have produced particles with a well-ordered and unstrained lattice, since both the particles with average size 41 and 59 nm (as measured with TEM) have larger particle sizes if the XRD data would be taken as a measure.

SUMMARY AND CONCLUSIONS

Subrounded, uniform, and well-ordered crystalline hematite particles with unstrained lattice were made with an average diameter of 41 nm and a narrow particle size distribution within one day by hydrolysis of a 0.02 M ferric chloride solution. To obtain these particles it was important to add the ferric chloride directly into the preheated hydrochloric solution ($T > 90^\circ\text{C}$). The hydrolysis of ferric salt solutions is very sensitive to small changes in the reaction conditions, which result in large variations of average hematite particle size and shape. The magnetic

behavior of the produced subrounded hematite particles changed from canted antiferromagnetic, as normal for hematite, to paramagnetic when decreasing the particle size from 160 to 41 nm. This is the largest size reported thus far for superparamagnetic hematite particles.

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