The effect of phosphonate-based growth modifiers on the morphology of hematite nanoparticles formed *via* acid hydrolysis of ferric chloride solutions



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Paper

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The effect of organic phosphonate-based additives on α -Fe₂O₃ (hematite) crystallization *via* the forced hydrolysis of ferric chloride solutions has been studied using a range of additives containing 2, 3 or 4 pendant phosphonate groups. The hydrolysis reactions were carried out at pH 1.1 with an iron concentration of 0.01 mol L⁻¹, and with Fe : additive ratios ranging from > 8000 : 1 down to 200 : 1. In the absence of additive, the hematite particles are very uniform rhombic single crystals, with an average length of ≈ 100 nm. In the presence of phosphonates the particles become hexagonal, with the additives acting by inhibiting growth at (214) faces. At Fe : additive ratios lower than about 200 : 1, hematite formation is completely inhibited. Our results are consistent with a mechanism in which the akaganéite and hematite phases may both precipitate from the ferric chloride solution, with akaganéite apparently forming more rapidly than hematite. Inhibition of hematite formation by addition of the phosphonate additive can lead to β -FeOOH (akaganéite) being the dominant product phase, provided the concentration of Fe³⁺ in solution is above the equilibrium solubility of the akaganéite phase.

Introduction

Specific control of size and shape is one of the prime challenges in the synthesis of nanoparticles, since such characteristics at the individual particle level are known to play an important role in determining the properties of bulk dispersions and composites. Careful selection of reaction conditions, reagent concentrations and mixing regimes often provides a degree of size and shape control in nanoparticle precipitation reactions, and a considerable amount of recent research has been devoted to developing such methods.^{1,2} A more advanced goal in nanoparticle synthesis, however, is to exploit chemical additives, adsorbed species or template materials to control the crystal growth of nanoparticles and thus direct the formation of specific phases and crystal morphologies.

Iron oxide particles can be prepared in various morphologies via the forced hydrolysis of ferric chloride solutions, with careful control of reaction conditions providing highly uniform dispersions.^{3–5} Moderate concentrations of FeCl₃ have been shown to yield spherical, cubic or ellipsoidal hematite particles of micron dimensions, while rhombohedral single-crystals of α -Fe₂O₃ (hematite), of the order of tens of nanometers in diameter, are formed in solutions of low FeCl₃ concentration (<0.02 M) and pH of about 1.5.⁶ The presence of phosphate has been shown to have a strong influence on the morphology of hematite particles grown in these systems, with only small amounts of this anion directing an ellipsoidal habit on the hematite particles.^{7,8} This change in morphology has been shown to be caused by the binding of phosphate to crystal faces parallel to the hematite c-axis, thus limiting crystal growth to the c-direction. The crystal faces concerned have until now, not been precisely identified.

Given that the phosphate ion is known to adsorb strongly to iron oxide surfaces, and that it has been shown to affect the morphology of iron oxide particles, we have sought to investigate the potential for morphological control of iron oxide nanoparticles by employing a range of phosphonatebased molecules. The effect of organic phosphonate-based additives on the forced hydrolysis of ferric chloride solutions has been studied by Reeves and Mann,⁹ but these molecules have otherwise received little attention in regard to iron oxide precipitation, and the phosphonate additives used in this study have not previously been investigated as modifiers of hematite crystal growth. Our group has studied the effects of a range of phosphonate molecules on the crystal growth of calcite, and barium sulfate systems, using systematic variation of molecular structure of the phosphonate additives.^{10–12} In this paper, we describe the effects of phosphonate groups, on the precipitation of hematite *via* forced hydrolysis of FeCl₃ solutions.

Experimental

Phosphonate additives

The phosphonate-based additives, the structures of which are shown in Fig. 1, are for ease of reference designated by abbreviated names as follows: MNDP = methyl nitrilo dimethylenephosphonic acid; NTMP = nitrilo trimethylenephosphonic acid; EDTP = ethylenediamine tetraphosphonic acid; DOTP = tetraazocyclododecane tetramethylene phosphonic acid; EDTP was Aldrich AR Grade. Other phosphonate additives were synthesised in-house according to published methods.^{13,14}

Iron oxide nanoparticles

In a typical experiment, 50 ml of 0.2 mol L^{-1} FeCl₃ solution and 50 ml of 0.04 M HCl were mixed at room temperature, then 900 ml of hot deionized water (>90 °C) was added. The



Fig. 1 Phosphonate additives used in this study.

resulting solution $(1 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ in } \text{Fe}^{3+} \text{ and } 2 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ in HCl})$ was stirred for a few minutes, then divided into five parts of 200 ml each in 250 ml Pyrex bottles. 1.0 ml of 1000 ppm stock solution of the phosphonate additives was added to each bottle. The bottles were then sealed and placed in an oven at 98 °C and aged for 48 hours, during which time a fine orange-brown precipitate formed. After the bottles had been removed from the oven and the suspensions allowed to cool, the particles were washed in repeated centrifugation/ re-suspension cycles with deionized water, then ethanol, and stored as ethanol suspensions.

Particle characterization

Transmission electron micrographs (TEM) were recorded on a JEOL 2011 TEM operating at 200 kV. High resolution micrographs were obtained on a JEOL 3000FEG TEM operating at 300 kV. The samples were dispersed in ethanol with the aid of ultra-sonication, then cast and dried onto a conventional carbon-coated copper grid.

Powder X-ray diffraction patterns were recorded on a Phillips X'pert X-ray Analytical Powder Diffractometer using Co-K α radiation.

Results and discussion

In the precipitation of hematite from acidic ferric chloride solutions, it has been shown that phosphate adsorbs strongly on crystal planes parallel to the hematite *c*-axis, inhibiting growth on these faces and leading to the formation of particles with ellipsoidal morphology, elongated along the *c*-axis.^{4,9,15} The action of the phosphonate-based additives employed in this study appears to be more specific, with the phosphonates binding only to one of the crystal faces. Fig. 2a shows a TEM image of the well-defined rhombohedral particles obtained



Fig. 2 Hematite nanoparticles formed in the presence of increasing amounts of EDTP. a) No additive, b) [EDTP] = 0.5 ppm, c) [EDTP] = 5 ppm, d) [EDTP] = 10 ppm, e) [EDTP] = 20 ppm. Size bar in a) = 200 nm, all other size bars = 100 nm.

Table 1 Additive (EDTP) concentrations and molar ratios for the experiments shown in Fig. 1

Conc ⁿ (ppm)	Conc ⁿ /mmol L ⁻¹)	Molar ratio Fe : additive
0.5	0.0011	9090
5	0.011	909
10	0.023	434
20	0.046	217

from the acid hydrolysis of a solution of 0.01 mol L⁻¹ FeCl₃ in the absence of any additive. The particles are very uniform single crystals, with an average length of ≈ 100 nm. The most common orientation on the TEM grid shows a rhombic crystal face with angles of roughly 110–115° and 65–70° between the edges.

The TEM micrographs in Fig. 2 show the effects of an additive with four pendant phophonate groups: micrographs in Fig. 2 (b)-(e) correspond to increasing amounts of EDTP in the concentration range 0.0011 mmol L^{-1} to 0.046 mmol L^{-1} . The Fe^{3+} concentration in each case was 0.01 mol L⁻¹, and the concentrations and molar ratios of Fe : additive are presented in Table 1. The particles tend to become hexagonal in shape with the addition of moderate amounts of EDTP. Note that there are four smooth faces of the hexagonal crystals, while two opposite faces appear rough and irregular, suggesting that it is on these crystal planes that the phosphonates bind to promote the hexagonal morphology. The oblique angle between the smooth edges of the crystals is consistently about 112° in all samples, even though the aspect ratio of the particles changes with different additives or different concentrations of the same additive.

At the highest EDTP concentration, shown in Fig. 2(e) $(0.046 \text{ mmol } \text{L}^{-1})$ the particles are elongated and appear polycrystalline, seemingly comprising assemblies of small domains only a few nanometres in diameter. The phosphonate additives are relatively powerful growth modifiers as demonstrated by the fact that their effect on hematite crystallization is evident at very low additive concentrations. The series of experiments outlined in Fig. 2 show that the effect of EDTP is observed at concentrations as low as 5 $\mu mol \ L^{-1};$ a ratio of iron to additive of 9000 : 1. At EDTP concentrations above 0.046 mmol $L^{-1}\!,$ a ratio of iron to additive of about 200 : 1, complete inhibition of hematite precipitation is observed, with ferric chloride solutions remaining stable at 98 °C for a period of several weeks. So in addition to the morphological changes and growth inhibition resulting from additive binding to the crystal surface, the phosphonates also inhibit nucleation, possibly due to the formation of stable Fe(III)-phosphonate complexes, or via stabilization of the nucleating cluster below the critical nucleus size.

Site of additive binding

High resolution TEM images of the control particles indicate that the rhombic face of the crystals is the (104) face. Fig. 3 shows a high resolution image of a particle viewed at an orientation parallel to the basal plane. The spacing between lattice fringes visible in this image was measured from the Fourier transform of the image shown as an inset. The measured distance of 2.64 Å closely matches the expected *d* spacing of 2.69 Å for (104) planes in hematite.¹⁶ This morphology is also in agreement with that reported by Reeves and Mann.⁹

Fig. 4 shows a high resolution TEM image of a thin hematite crystal, formed in the presence of 0.5 ppm EDTP, viewed from an orientation orthogonal to the (104) face. Lattice fringes visible in the high resolution image shown in the inset reveal a pseudo-hexagonal symmetry that further confirms the identification of the (104) face. Through measurement of angles and

Fig. 3 High resolution image of the edge of a rhombic hematite particle formed in the absence of any additive, showing lattice fringes attributed to (104) lattice planes. Inset: Fourier transform of the section of the image shown by the white square.

Fig. 4 Hematite particle formed in the presence of 0.5 ppm EDTP. Inset top left: high resolution image of the region shown by the white box. Inset top right: Fourier transform of this high resolution image.

d-spacings obtained from the Fourier transform of the high resolution image shown in Fig. 4, the other faces of the rhombic crystals can be indexed as shown in Fig. 5. This morphology is consistent with the observed angles between the crystal faces, *i.e.* the expected angle between $(1\bar{2}0)$ and $(11\bar{4})$ planes is 113.8° . Our assignment of the $(2\bar{1}\bar{4})$ plane as the active site for phosphonate binding is more speculative however, since the particles formed with higher additive concentrations have

Fig. 5 Hematite morphologies. In the absence of any additive (left), and in the presence of phosphonate (right).

rather roughened surfaces on this face, making it difficult to accurately determine the angles relative to other crystal planes.

On the basis of reasonable estimates however, the (214) face seems the most likely candidate. Although the sites of phosphate (and phosphonate) binding on hematite have been described previously in more general terms, this is the first time a specific crystal face has been identified as the site of additive binding.

All of the phosphonates used in this study appear to act similarly in binding at the intersection of $(1\overline{2}0)$ and $(11\overline{4})$ faces, resulting in hexagonal particles with two opposite faces having roughened surfaces. The effects of MNDP, NTMP and DOTP can be seen in Fig. 6. MNDP is a di-phosphonate additive, while NTMP contains three pendant phosphonate groups, and DOTP four. In the particles precipitated in the presence of MNDP and NTMP, the roughened $(2\overline{14})$ face appears to be well developed and the particles have the form of "flattened" or elongated hexagons. When EDTP is employed at a similar concentration, (cf. Fig. 2) the particles have a more regular hexagonal shape and the $(2\overline{1}\overline{4})$ faces are smaller. This is also the case when DOTP is employed. These observations suggest that MNDP and NTMP may be more potent growth modifiers than EDTP and DOTP, although it must be conceded that the effect has not been quantified here, and further work will be needed to fully characterize the relative inhibitory effects of the four additives.

Mechanism of hematite precipitation

In samples precipitated in the presence of MNDP and DOTP, the hexagonal particles were associated with a considerable amount of much smaller, poorly-crystalline material, made up of approximately spherical particles only a few nanometres in diameter. The nature and particle size of this material suggests the hydrous ferric oxide, ferrihydrite. Ferrihydrite, which is given the approximate formula $Fe_2O_3 \cdot 9H_2O$, is generally the first product to form from ferric ion hydrolysis in acid media.^{16,17} Sugimoto and Muramatsu,⁴ in their study of the mechanism of hematite formation, did not observe evidence of ferrihydrite precursors, but Kan *et al.*⁶ reported the formation of nanometer-sized amorphous spheres in samples prepared under conditions very similar to those of our experiments.

It has been reported by a number of previous workers^{4–6,15} that β -FeOOH (akaganéite) is an intermediate phase in formation of hematite *via* acid hydrolysis of ferric chloride, with the conversion to α -Fe₂O₃ occurring *via* re-dissolution of the β -FeOOH particles and subsequent nucleation and growth of hematite from soluble iron hydroxide species. However, powder XRD spectra of the hydrolysis products obtained in this study showed no peaks attributable to akaganéite, but rather only hematite reflections were observed.† In fact we have seen no evidence of the akaganéite phase in any of our

[†] Due to its low crystallinity, 2-line ferrihydrite is difficult to detect in XRD spectra unless present in quantities greater than 10% by weight,¹⁷ so we can conclude that although there is certainly some ferrihydrite present in these samples it probably constitutes only a few weight percent of the material.

Fig. 6 Hematite nanoparticles formed in the presence of 5 ppm a) MNDP, b) NTMP and c) DOTP. Size bars = 100 nm.

experiments carried out at Fe^{3+} concentrations of 0.01 mol L^{-1} or less. This is problably due to the fact that at a concentration of 0.01 mol L^{-1} in Fe^{3+} , the system is below the solubility limit for akaganéite.¹ Thus we can conclude that at low Fe^{3+} concentrations, the pathway to hematite formation involves initial precipitation of ferrihydrite, followed by dissolution and reprecipitation to form hematite. In contrast, at higher concentrations of ferric chloride, the akaganéite phase forms as a side product in the pathway to hematite formation, and thus inhibition of hematite nucleation and/or growth can result in akaganéite being isolated as the major product of the hydrolysis reaction.

Most of the reported work on the ferric chloride system has been carried out at Fe³⁺ concentrations greater than 0.01 mol L^{-1,1,2} and in this concentration range, particles prepared in the absence of any additive are roughly cubic crystals of 1–2 µm in size. The particle morphology is, however, sensitive to the total chloride concentration and thus, at lower concentrations of FeCl₃, well-defined rhombohedral particles are obtained, with particle diameters typically in the range of 40–100 nm. The effect of the chloride ion on particle morphology is demonstrated in Fig. 7, which shows TEM images of the rounded cubic particles obtained when the chloride concentration is raised to 0.09 mol L⁻¹ by the addition of NaCl, while other reagents were maintained at the control conditions. The particles are also highly aggregated, and are

Fig. 7 Hematite particles formed in the absence of any additive, but with increased chloride ion concentration $([Fe^{3^+}] = 0.01 \text{ mol } L^{-1})$, $[Cl^-] = 0.09 \text{ mol } L^{-1})$. Inset: higher magnification image showing ferrihydrite particles surrounding larger hematite rhombs. Size bars main picture = 200 nm, inset = 50 nm.

associated with ferrihydrite, which to some extent appears to bind the aggregates together.

As mentioned earlier, a further effect of high chloride concentrations is to stabilise the β-FeOOH (akaganéite) phase.^{5,6,15} Reeves and Mann studied the effects of organic phosphonates on the acid hydrolysis of ferric chloride solutions at Fe^{3+} concentrations of 0.02 mol L⁻¹, and with Fe : additive ratios considerably lower than we have employed here; that is to say, relatively higher concentrations of additive were employed. They found that in most cases, the hydrolysis reaction was completely inhibited and no precipitate was formed, but in the case of 1,2-ethylenediphosphonic acid, the product was exclusively akaganéite. Our own experiments on the effects of EDTP at higher Fe³⁺ concentrations are consistent with these observations. Solutions of ferric chloride $(0.03 \text{ mol } \text{L}^{-1})$ aged for 48 hours in the absence of EDTP produced only hematite cubes, while the addition of EDTP led to the formation of inter-grown cubic particles associated with a considerable amount of rod-shaped akaganéite. With Fe : additive ratios lower than about 100 : 1, akaganéite was the only product observed after 48 hours at 98 °C.

Conclusions

The phosphonate additives examined in this study all show an inhibitory effect on the growth of hematite crystals formed via the acid hydrolysis of ferric chloride solutions. In the absence of the phosphonates, the hematite particles are uniform rhombic crystals with an average length of about 100 nm, and the basal plane of these rhombic particles is the (104) face. The addition of small amounts of phosphonate leads to a hexagonal morphology, probably caused by additive binding at $(2\overline{14})$ planes. In the case of EDTP, hematite formation is completely inhibited at concentrations greater than 20 ppm $(0.052 \text{ mmol } \text{L}^{-1})$. Thus, the morphological control provided by these additives seems to be quite specific, involving selective binding of the additive to a particular crystal face. In general terms, the location of phosphonates and phosphate ion binding on hematite has been described previously as "crystal faces parallel to the c-axis". This is the first time however, that a specific crystal face has been identified as the site of additive binding on hematite. Indexing of the crystal and identification of the additive binding site is important, since such information may provide clues as to the precise mode of interaction of the additive molecules with hematite surface groups. The underlying reasons for selectivity may arise from the geometry of pendant phosphonate groups relative to the orientation of atoms at the $(2\overline{14})$ surface, and molecular modelling of phosphonate interactions with hematite surfaces may provide further information to complement the results described here.

The comparison between experiments carried out at Fe³⁺ concentrations of 0.01 mol L^{-1} and those involving higher concentrations of ferric chloride provide an important insight into the mechanism of ferric ion hydrolysis in acid solutions. At higher Fe³⁺ concentrations, inhibition of hematite formation results in akaganéite precipitating as the dominant phase. This is consistent with a mechanism in which the akaganéite and hematite phases may both precipitate from the ferric chloride solution, with akaganéite apparently forming more rapidly than hematite. Given the greater solubility of akaganéite, however,16 the amount of this phase present in the mixture decreases with time as hematite forms and the overall Fe³⁻ concentration decreases below the equilibrium solubility of akaganéite. At low initial concentrations of Fe3+ (i.e. if the concentration is already below the limit for akaganéite precipitation) akaganéite is not observed, and hematite samples prepared in the presence of phosphonate additives can coprecipitate with ferrihydrite, which is a ubiquitous precursor to iron oxide formation.

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