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Effects of amines on the formation of β-ferric oxide hydroxide

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Colloidal particles of β-ferric oxide hydroxide (β-FeOOH) were prepared by ageing an $FeCl_3$ solution at 100 °C in the presence of various amines with different numbers of nitrogen atoms. The particle and crystallite sizes of the formed β-FeOOH decreased with increasing concentration of amines, but the particles produced contained no amine. The influence of triethanolamine on the growth of β-FeOOH particles was more marked than those of ethylenediamine, diethylenetriamine and triaminotriethylamine. The adsorption isotherms of nitrogen and water on the formed particles of different size were measured and surface fractal analysis was performed.

1. Introduction

The formation and properties of colloidal β-ferric oxide hydroxide (β-FeOOH) particles have been the subject of various investigations for a long time, because the monodispersed systems of these particles can be rather easily prepared and this phase has an interesting crystal structure [1–7]. The β-FeOOH crystal has the tunnels along the *c*-axis embracing chloride ions and water molecules, thus differing from α- and γ-FeOOH [4]. For this reason β-FeOOH particles show several interesting properties, i.e. complex thermal phase transformation [8], selective adsorption of small molecules such as water [9], etc. The morphology of β-FeOOH particles prepared by hydrolysing ferric salt solutions is known to depend on various conditions, such as the concentration of Fe^{3+} ions and anions, the temperature of hydrolysis and ageing, and the type of solvent [10–13]. Recently, we have studied the influence of various anions on the formation of β-FeOOH particles in aqueous solutions, and have found that phosphate ions interfere with particle growth while silicate ions do not affect it [14]. Furthermore, we have found that the chelating agents for Fe^{3+} ions, such as citrate salts, inhibit the formation of β-FeOOH, producing amorphous materials capable of the selective adsorption of water molecules [15]. However, these materials contained a considerable amount of the residual chelating agent. It is therefore desirable to discover a method of controlling the particle size without introducing many impurities.

In the present work, the structures and properties of β-FeOOH particles, obtained by hydrolysis of the ferric chloride solutions doped with various kinds of amines, were examined by various techniques. This paper describes the influence of amines on the growth of β-FeOOH particles.

2. Experimental procedure

2.1. Preparation of β-FeOOH particles

Hydrolysing a 0.1 $mol\,l^{-1}$ $FeCl_3$ aqueous solution containing different concentrations of amines in a capped container gave the dispersion of β-phase particles. The temperature and time of hydrolysis were 100 °C and 5 h, respectively. The pH of the suspension after hydrolysis was below unity at room temperature. The amines added to the solutions before hydrolysis were triethanolamine $N(CH_2CH_2OH)_3$ (TEA), ethylenediamine $H_2NCH_2CH_2NH_2$ (EDA), diethylenetriamine $HN(CH_2CH_2NH_2)_2$ (DETA), triaminotriethylamine $N(CH_2CH_2NH_2)_3$ (TTA), and the molar ratios of amine to Fe^{3+} ion in the solutions were from 0%–50%. The resulting particles were repeatedly washed in distilled water by centrifugation until no chloride ions were detected with a $AgNO_3$ solution, and finally dried in an air oven at 70 °C. Because the particles formed with more than 30% amine could not be sedimentated by centrifugation, they were washed successively with 1 $mol\,l^{-1}$ NH_4Cl solution, 1 $mol\,l^{-1}$ NH_4OH solution and distilled water.

2.2. Characterization of the particles formed

The morphology of the particles prepared was inspected with a transmission electron microscope (TEM). The crystallinity of the particles was determined by powder X-ray diffraction (XRD) using CuK_α radiation (15 mA, 30 kV). Simultaneous thermogravimetry and differential thermal analysis (TG–DTA) were done in air at a heating rate of 5 °C min^{-1}. Infrared spectra in KBr were taken in dry air by a FT–IR spectrometer with a scanning number of 20 and a resolution of 2 cm^{-1} and the sample concentration was 1 wt %. Elemental analysis and

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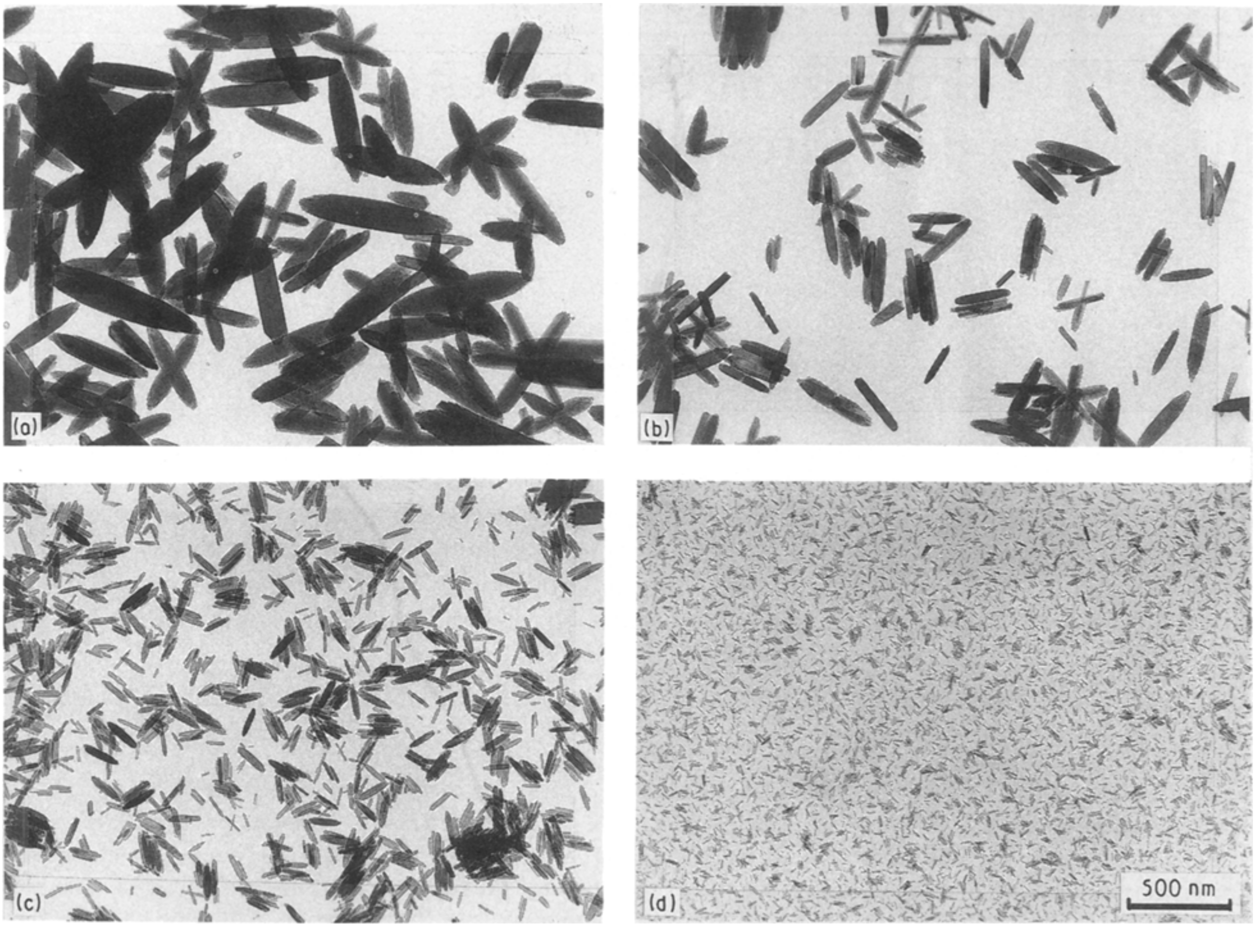

Figure 1 Transmission electron micrographs of the particles formed with different concentrations of TEA. (a) 0%, (b) 1.0%, (c) 10% (d) 30%.

fluorescence X-ray analysis assayed the residual amines and chloride ions in the particles, respectively. The specific surface areas of the particles were calculated by applying the BET equation to the adsorption isotherms of nitrogen measured at liquid nitrogen temperature with an automatic volumetric equipment. The adsorption isotherm of water was determined using an automatic adsorption balance. Prior to the adsorption of both the molecules the samples were treated *in vacuo* at 100 °C for 2 h.

3. Results and discussion

3.1. Morphology of the particles formed

Transmission electron micrographs of the particles made from the solutions doped with different amounts of TEA are shown in Fig. 1. The particles were rod-shaped and their modal sizes decreased with increasing TEA concentration of the starting solutions. The mean length, width and axial ratio of the particles are plotted against the concentration of TEA in Fig. 2. The length and width decreased as the concentration of TEA increased, but the axial ratio was almost constant with a low concentration below 0.3%, indicating that the particle shape was relatively less influenced by TEA while the modal size was much decreased. A minimum width and length appeared at a concentration of 0.3%. These results are different from the preparation using citrate ions, which yielded agglomerates of very fine less-crystalline particles above 5% [15]. The addition of other amines led to similar results to that of TEA, thus hereafter, this paper will describe mainly the results for TEA.

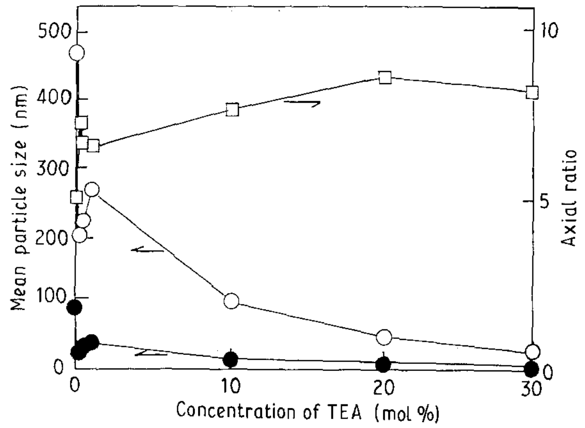

Figure 2 The mean length (○), width (●) and axial ratio (□) of the particles formed with different concentrations of TEA.

3.2. Structures of the particles formed

Fig. 3 shows the XRD patterns of the powders prepared in the presence of different amounts of TEA. All the patterns were characteristic of β-FeOOH and the peak intensities were lowered by increasing the concentration of TEA. The crystallite sizes, *L*, of the

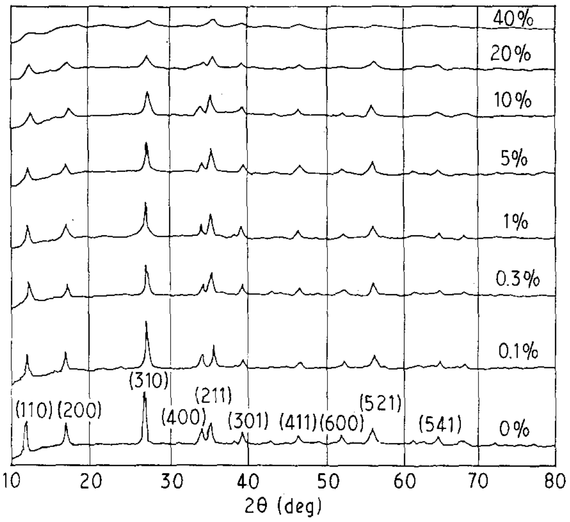

Figure 3 The XRD patterns of the particles formed with different concentrations of TEA.

particles, calculated using the Scherrer equation from the XRD peak due to the reflection from the (3 1 0) plane, are given as a function of the concentration of TEA in Fig. 4. The L value was reduced by adding TEA showing a minimum at a concentration of 0.3%, similar to the results for the particle size in Fig. 2 mentioned above. Such a minimum was noticed on adding TTA and DETA at ~ 0.5% and 1%, respectively, but less clear than for TEA. The decrease in L with DETA and TTA was more remarkable than that with TEA below 30%.

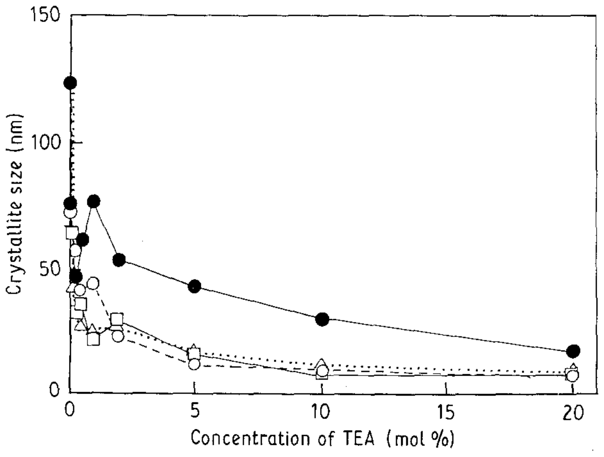

Figure 4 The relations between crystallite size and concentration of amines for the particles formed with different kinds of amines. (●) TEA, (△) EDA, (□) DETA, (○) TTA.

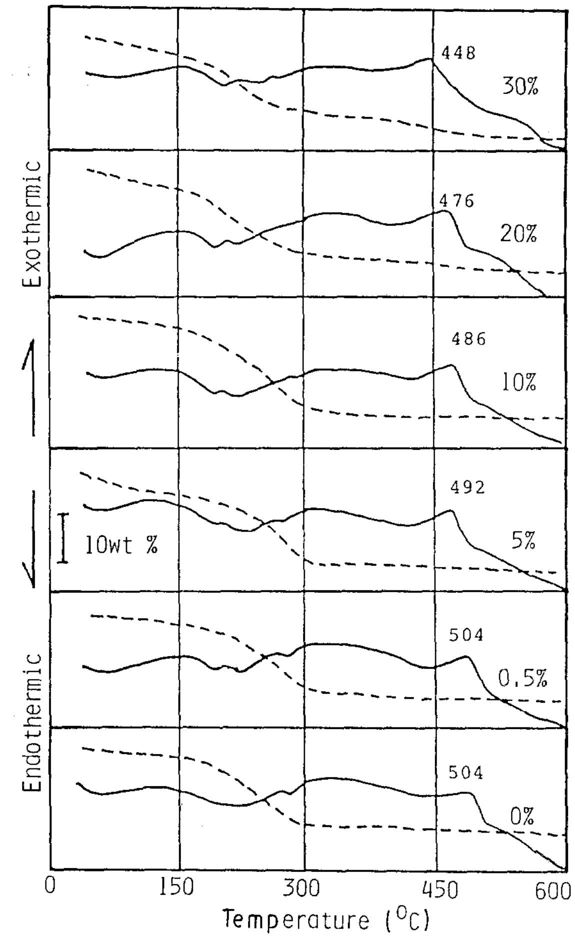

Figure 5 The TG–DTA curves of the particles formed with different concentrations of TEA. The solid and dashed lines are DTA and TG curves, respectively.

Fig. 5 illustrates the TG–DTA curves of the materials formed in the presence of different amounts of TEA. In the DTA curves depicted by the solid lines, a broad endothermic peak having several small peaks appeared at ~ 250 °C, and an exothermic peak appeared at 448–504 °C. The broad endothermic peak is assigned to the dehydration of the hydroxyl groups of β-FeOOH and the release of water molecules and chloride ions included in the tunnels of β-FeOOH crystals [9]. The exothermic peak is caused by the crystallization to α-Fe_2O_3 [16]. The intensity and position of the broad endothermic peak was not essentially affected by adding TEA below 20%. On the other hand, the position of the exothermic peaks shifted from 504 °C to 448 °C as the concentration of TEA increased. This may reflect the decrease in particle size on adding TEA. Similar TG–DTA results were obtained for the other amines.

The weight loss in the TG curves, shown by the dashed lines in Fig. 5, which was observed in the temperature range of the broad endothermic peaks from ~ 150–300 °C, was from 13–15 wt % for all samples. These weight loss values are larger than 10.1 wt % corresponding to the dehydroxylation reaction ($2FeOOH = Fe_2O_3 + H_2O$). Such a large weight loss might be due to the removal of water molecules and chloride ions in the tunnels, in addition to the dehydroxylation. The chloride ion contents, determined by fluorescence X-ray analysis, were 6.5 and 2.4 wt % for the samples prepared with 0% and 30% TEA, respectively. A considerable portion of these chloride ions remained in the particles after the transformation to α-Fe_2O_3.

The infrared spectra of the particles prepared with different amounts of TEA are shown in Fig. 6. The spectrum of the material obtained without TEA showed absorption bands at 3450, 3390, 840, 810, 690 and 640 cm^{-1}. The 840 and 690 cm^{-1} bands have been assigned to the deformation vibrations of Fe–OH groups [17], and the 3450 and 3390 cm^{-1} bands can be assigned to the stretching vibrations of these groups [18]. All these bands can be assigned to

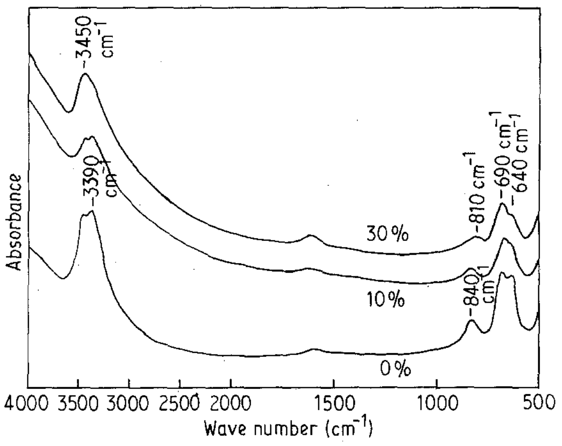

Figure 6 The FT–IR spectra of the particles formed with different concentrations of TEA.

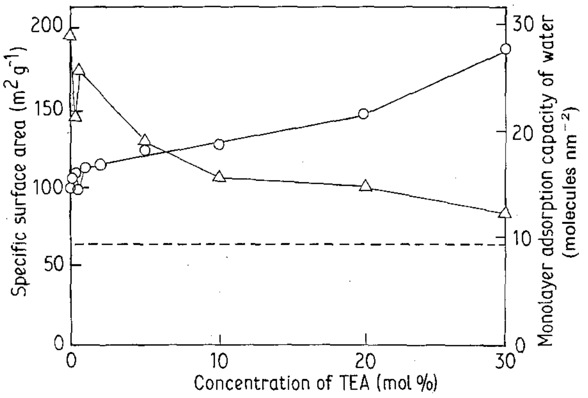

Figure 7 The nitrogen specific surface areas (○), and monolayer adsorption capacities of H_2O (△) of the particles formed with different concentrations of TEA. (- - -) The monolayer capacity of water of 9.3 molecules nm^{-2} evaluated from the cross-sectional area of the H_2O molecule.

the bulk Fe–OH groups, because the bands due to the surface Fe–OH groups have been found to appear at 3659, 3686 and 3723 cm^{-1} in the spectra taken *in vacuo* [18]. These surface Fe–OH bands did not properly appear in the spectra of Fig. 6, taken in air. It is noteworthy that the two strong Fe–OH bands around 3400 and 660 cm^{-1} in the spectra of Fig. 6 split into the 3450 and 3390 cm^{-1} bands and the 690 and 640 cm^{-1} bands, respectively. As can be seen from the crystal structure of β-FeOOH [4], the bulk Fe–OH groups exist in the wall of the tunnels in the crystal. Therefore, there seems to be two kinds of bulk Fe–OH groups, one of which interacts with water molecules and another which interacts with chloride ions. The smaller wave number bands at 3390 and 640 cm^{-1}, whose intensities decreased with the chloride ion content, can be assigned to the Fe–OH groups interacting with chloride ions. As seen in Fig. 6, all the bulk Fe–OH bands became small with increasing TEA concentration. This might be because of the rupture of the tunnel structure by the decrease in the particle size.

3.3. Adsorption of nitrogen and water molecules

The specific surface areas, S_n, of the powders prepared in the presence of TEA, calculated using the BET equation from the adsorption isotherms of nitrogen molecules, are plotted against the TEA concentration in Fig. 7. S_n increased with the concentration of TEA, coinciding with the decrease in the particle size on addition of TEA, as mentioned above.

To clarify the tunnel structures of the particles produced with TEA, the adsorption isotherms of water on these particles were measured at 25 °C. All the isotherms were of the BET type II showing a steep increase in the amount adsorbed at low equilibrium pressures, suggesting the existence of micropores. The monolayer adsorption capacity of water per unit mass of the adsorbent, calculated by applying the BET equation to these adsorption isotherms, somewhat decreased with increase in the concentration of TEA, despite a considerable increase in S_n. It has been reported that the tunnels of β-FeOOH crystals are so ultramicroporous as to be accessible to water but not to nitrogen molecules [19]. To verify the ultramicroporosity of the particles prepared in the present work, the monolayer adsorption capacity of water per unit surface area of the adsorbent was evaluated using S_n and is plotted against the concentration of TEA in Fig. 7. The monolayer adsorption capacity decreased from 29.5 to 12.4 molecules nm^{-2} with increasing TEA concentration. On the other hand, the monolayer capacity on the particle having no ultramicropores is 9.3 molecules nm^{-2} estimated from the cross-sectional area of the water molecule of 0.108 nm^2. As is seen in Fig. 7 the monolayer capacity per unit surface area comes close to 9.3 molecules nm^{-2} as the concentration of TEA increases, indicating that the number of tunnels accessible to only water molecules decreases with decreasing particle size.

Pfeifer and Avnir [20] proposed the fractal analysis of a solid surface using gas adsorption in order to estimate the surface roughness in molecular dimensions. According to their theory, S_n can be related to the diameter, d, of spherical particles as follows

$$\log S_n = -(D-3)\log d + C \qquad (1)$$

where C is a constant and D is a fractal dimension indicating surface roughness, the value of which is usually from 2–3. As described above, β-FeOOH particles of different size and similar axial ratio were obtained by adding amines, and therefore fractal analysis of these particles was performed. The mean particle length and width were used as the diameter, d, in Equation 1, because the β-FeOOH particles prepared in this work were not spheroids. Fig. 8 shows a linear relation between $\log S_n$ and $\log d$ for the particles prepared with TEA. This result suggests that Equation 1 can be applied to non-spherical particles of similar shape. The slopes of both the straight lines gave the same D value of 2.8, implying that these particles having similarly unlevel surfaces. According to the selected-area electron diffraction, the predominant crystal faces of β-FeOOH particle surfaces are ac and bc planes which are geometrically more heterogeneous compared with those of α- and γ-FeOOH particle surfaces [18].

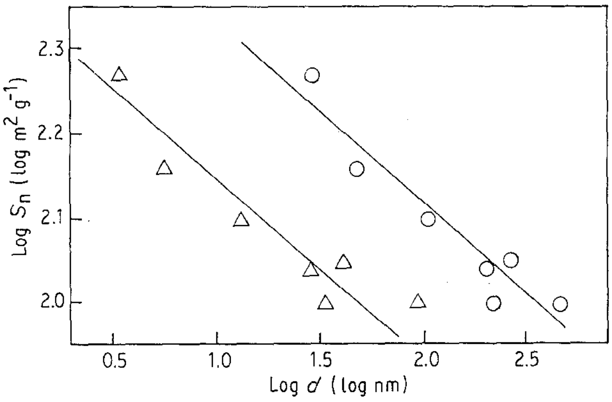

Figure 8 The fractal analysis of the particles of different size prepared with TEA. The mean length (○) and width (△) are used as the particle size.

3.4. Role of amines

All the β-FeOOH particles formed with the amines under investigation did not include nitrogen and carbon elements as indicated by element analysis. The FT–IR spectra (Fig. 7) of these particles also did not have absorption bands characteristic of the amines used. Furthermore, the TG–DTA curves showed no peaks and weight loss due to the release or decomposition of the amines. It is therefore clear that the amines added to the starting solutions were not involved in the resulting particles. This result is quite different from the case of adding citrate ions which were included in the particles formed [15]. To explain the mechanism whereby the citrate ions interfere with the growth of β-FeOOH particles, we have proposed the following two processes: (1) citrate ions strongly coordinate to Fe^{3+} ions to inhibit the hydrolysis of Fe^{3+} ions; (2) citrate ions are adsorbed on the nuclei formed by hydrolysis of Fe^{3+} ions interrupting the growth of the nuclei [15]. It is well known that citrate ions strongly coordinate to Fe^{3+} ions in an acidic medium of less than pH 1, but TEA has a low chelating ability with Fe^{3+} ions in such acidic solutions. Therefore, the interference by TEA might be attributed mainly to the adsorption process. The adsorption of the used amines on β-FeOOH particles is thought to be not so strong that the amines could be easily washed out with distilled water. As shown in Figs 2 and 4, the particle and crystallite sizes were minimum at a low concentration of amines. Although the detailed reason for this is not elucidated at present, it can be presumed that the adsorption state of the amines on the particles changes the concentration, thus giving a minimum. Because the adsorption of amines on β-FeOOH particles is under examination, the adsorption mechanism will be reported elsewhere.

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